<table>
<thead>
<tr>
<th>Title</th>
<th>Air to sea gas exchange of CO2 in the north-east Atlantic Ocean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Keane-Brennan, Jevon</td>
</tr>
<tr>
<td>Publication Date</td>
<td>2011-12-08</td>
</tr>
<tr>
<td>Item record</td>
<td><a href="http://hdl.handle.net/10379/2669">http://hdl.handle.net/10379/2669</a></td>
</tr>
</tbody>
</table>

Some rights reserved. For more information, please see the item record link above.
Air to Sea Gas Exchange of CO$_2$
in the north-east Atlantic Ocean

by

Jevon Keane-Brennan, B.Sc

A thesis submitted in partial fulfillment for the
degree of Doctor of Philosophy

in the
College of Science
School of Physics
CCAPS - Centre for Climate and Air Pollution Studies

Academic Supervisors:
Prof. Colin O’ Dowd
Dr. Brian Ward

December 2011
i)
Contents

Abstract vii

Acknowledgements viii

1 Introduction 1
  1.1 Earth’s Atmosphere ........................................... 1
  1.2 CO₂ in the Atmosphere ........................................ 3
  1.3 Carbon Cycle .................................................. 5
  1.4 CO₂ in the Ocean .............................................. 6
    1.4.1 Continental Shelf ....................................... 8

2 Background Information 10
  2.1 Boundary Layer ................................................ 10
  2.2 Eddy Covariance Technique ................................... 12
    2.2.1 Eddy Flux Equation Derivation ............................ 14
    2.2.2 Assumptions ............................................. 17
    2.2.3 Sources of Error ...................................... 17
  2.3 Micrometeorological Variables ................................. 18
  2.4 Air to Sea Gas Exchange of CO₂ ............................... 22
  2.5 Gas Transfer Velocity ........................................ 27
    2.5.1 Liss and Merlivat 1986 Relationship ..................... 29
    2.5.2 Wanninkhof 1992 Relationship ............................ 30
    2.5.3 Wanninkhof and McGillis 1999 Relationship ............. 31
    2.5.4 McGillis et al. 2001 Relationship ....................... 32
    2.5.5 Nightingale et al. 2000a and 2000b Relationships ...... 32
    2.5.6 McGillis et al. 2004 Relationship ....................... 33
    2.5.7 Ho et al. 2006 Relationship ............................. 34
  2.6 Other Micrometeorological Techniques ........................ 34
    2.6.1 Eddy Accumulation Technique ............................ 35
    2.6.2 Relaxed Eddy Accumulation (REA) Technique .............. 35
    2.6.3 Bowen Ratio Method ..................................... 35
    2.6.4 Aerodynamic Method .................................... 36
    2.6.5 Profile Method ......................................... 36
    2.6.6 Geochemical Tracers .................................. 36
    2.6.7 Purposefully Injected Tracers ........................... 37
3 Instrumentation

3.1 Celtic Explorer

3.1.1 Pro-Oceanus Systems Inc. (PSI) CO₂ Pro

3.1.1.1 Gas Transfer Interface

3.1.1.2 Infrared Gas Analyzer and Detector

3.1.1.3 Automatic Zero Point Calibration - AZPC

3.1.1.4 Instrument Start-Up and Data Output

3.1.1.5 Housing Information

3.1.1.6 Instrument Specifications

3.1.2 pCO₂ Instrument Tank

3.1.3 General Oceanics pCO₂ System

3.2 Mace Head Research Station

3.2.1 Eddy Covariance (EC) Instrumentation

3.2.1.1 Mace Head Tower

3.2.1.2 CO₂/H₂O NDIR Gas Analyzer

3.2.1.3 Sonic Anemometer

3.2.1.4 Calibration Routine

3.2.1.5 DLS - Data Logging System

3.2.1.6 System Limitations

3.2.2 Data Buoy

3.2.3 Other Instrumentation

3.2.3.1 LI-COR LI-6252

3.2.3.2 Wind Speed and Wind Direction

3.2.3.3 Relative Humidity and Atmospheric Pressure

3.2.3.4 Air Temperature

4 Analysis of Shipboard pCO₂ Data and PSI CO₂-Pro Performance

4.1 R.V. Celtic Explorer Surveys

4.1.1 CE0911 - Climate Change Survey

4.1.2 CE10001 - BSH Survey No.1

4.1.3 CE10002 - Climate Change, Oceanography, Biogeochemistry and Geology sections

4.1.4 CE10009 - Cetaceans on the Frontier 2010

4.1.5 CE10006 - Mackerel Egg Survey

4.1.6 CE10011 - Blue Whiting Acoustic Survey

4.1.7 CE10010 - Holland1 ROV/UL Sonar & MPPT/ Ring/Cathx Video Imaging Systems - Integration & Shakedown Cruise

4.1.8 CE10014 - Deep Water Coral and Fish Interaction off the west coast of Ireland

4.1.9 CE10003 - Climate and Ecosystem Sections on the Irish shelf

4.1.10 CE 10004 - Species at the Margins - Diversity Cruise

4.1.11 CE 10008 - Glacial and Non-Glacial Sediment Transport in the Rockall Trough and Porcupine Bank (North Atlantic)

4.1.12 CE10012 - Northwest Herring Acoustic Survey

4.1.13 CE10007 - Mackerel Egg Survey

4.1.14 CE10018 - Bathymetric Survey
6.1.2 Air Temperature and Atmospheric Pressure 144
6.1.3 Relative Humidity & Air CO$_2$ Concentration 145
6.2 Micro-Meteorology 148
  6.2.1 Friction velocity, $u^*$ 148
  6.2.2 Drag Coefficient, $C_D$ 149
  6.2.3 Roughness Length, $z_o$ 149
6.3 CO$_2$ Flux Data 150
  6.3.1 Data Collection 150
  6.3.2 Data Processing 151
    6.3.2.1 Despiking 151
    6.3.2.2 Rainfall Influences 152
    6.3.2.3 Wind Direction 154
    6.3.2.4 Atmospheric Stability, $\zeta$ 154
    6.3.2.5 Other Parameters 154
  6.3.3 Calculation of Flux Data 155
    6.3.3.1 Running Mean 155
    6.3.3.2 Cross Sensitivity of Water Vapour Correction 156
    6.3.3.3 Co-Ordinate Rotations 158
    6.3.3.4 Webb Correction 161
  6.3.4 Flux Analysis 164
    6.3.4.1 Filtering Statistics 164
    6.3.4.2 Application of Flux Corrections 166
    6.3.4.3 Wind Speed Relationship 167
    6.3.4.4 Seasonality 168
    6.3.4.5 Frequency Analysis 169
6.4 Gas Transfer Velocity 174
  6.4.1 Wind Speed Relationship 174

7 Conclusion 180
  7.1 Pro Oceanus CO$_2$ Pro Instrument 180
  7.2 Atmospheric and Sea-water pCO$_2$ Concentrations in Irish waters 181
  7.3 CO$_2$ Fluxes and CO$_2$ Transfer Velocity 183

A Gill Sonic Anemometer 185
B LI-COR 7500 Gas Analyzer 187
C Pro-Oceanus Systems Inc.(PSI) CO$_2$ Pro 189
D Equation Conversions 191
List of Figures 192
List of Tables 198
Abbreviations 199
Contents

Physical Constants 201
Bibliography 202
Abstract

Atmospheric carbon dioxide concentrations have been rising for the past 200 years, and started increasing at a faster rate during the last 60 years. The world’s oceans act as a reservoir for large amounts of CO\textsubscript{2}. How they will respond to increasing atmospheric concentrations of carbon dioxide is unknown. It is imperative that the movement of CO\textsubscript{2} between the air and the ocean is unequivocally understood.

Sea-water pCO\textsubscript{2} concentrations were measured in the north-east Atlantic Ocean off the island of Ireland, using a Pro-Oceanus CO\textsubscript{2} Pro pCO\textsubscript{2} instrument. The sensor was installed on the R.V. Celtic Explorer during 2010. The accuracy of the instrument was examined by bench-marking the sensor through a series of methods. Once completed, pCO\textsubscript{2} data collected by the instrument was analysed. CO\textsubscript{2} concentrations in the atmosphere remained stable throughout the year, while sea-water CO\textsubscript{2} concentrations varied on an seasonal basis. They were highest during the spring and winter months, whilst lowest during the summer months. This indicates that sea-waters off Ireland are most likely a sink for carbon dioxide during the summer months and are possibly a weak source in winter. Biological activity was the the main driving force behind the variation of carbon dioxide in the oceanic environment off Ireland.

Sea-water pCO\textsubscript{2} concentrations were also measured at Mace Head, Co. Galway, by installing a Pro Oceanus CO\textsubscript{2} Pro pCO\textsubscript{2} instrument on an all-weather buoy. During the winter of 2008/2009, sea-water pCO\textsubscript{2} concentrations were less than atmospheric concentrations and during the summer months of 2009, CO\textsubscript{2} concentrations in the ocean were highly variable, yet substantially higher than CO\textsubscript{2} concentrations in the over-lying air. CO\textsubscript{2} flux measurements were also conducted at Mace Head. Both of these data sets indicated that the coastal environment at Mace Head was a sink for carbon dioxide during the winter of 2008/2009 and a source of CO\textsubscript{2} during the summer months, in contrast to open ocean waters. CO\textsubscript{2} fluxes were corrected for cross-sensitivity and temperature effects. A negative correlation was calculated for the relationship between wind speed and CO\textsubscript{2} fluxes.

Gas transfer velocity values for CO\textsubscript{2} were also calculated at Mace Head. As wind speed increased, so did the CO\textsubscript{2} transfer velocity. This is in agreement with past experimental work. However, the dependence on wind speed was not as strong as calculated from past research. There was a lack of gas transfer velocity data at higher wind speeds, but this is a frequent issue when studying the wind speed/gas transfer velocity relationship.
Acknowledgements

Firstly and foremost, I would like to thank my supervisor Professor Colin O’ Dowd. If it were not for his academic and financial support, I would not be where I am today. When times were tough, he was able to provide the solutions and help me over the many obstacles that were encountered during my Ph.D. I would also like to thank Dr. Brian Ward for his help and advice during my research.

I would like to thank the Environmental Protection Agency (EPA) for funding my research, as without their help, none of this work would have been completed. Many thanks are sent to staff members at the Marine Institute (MI) and the crew and fellow scientists who were on-board the R.V. Celtic Explorer, many of them were amazing and very helpful during my research. I would like to thank my work colleagues at the School of Physics who helped me achieve the results in my experimental work. Many thanks are sent to the creators of Matlab, LaTex and Ocean Data View (ODV) software packages.

I would like to thank my fellow members of the Centre for Climate Change and Air Pollution Studies (CCAPS), especially Dr. Philip McVeigh and Mr. Brendan Kelly, all of ye were a major boost on the bad days and brilliant to be around on the good days. Thousands of thank yous are sent to “the lads” - Dan, Elaine, Fiona, Kevin\(^2\), Ronan and Séán. Each of us were there for each other through the lows and the highs of our Ph.D’s. I also would like to thank Emer and Elaine, for all the beautiful cooking. Ye are fantastic.

I would not be here today without my family in Kerry and abroad. Ye all contributed to my research and I will always be grateful. Finally, and by no means least, I would like to thank my girlfriend Sarah. You are truly amazing and were a rock of confidence throughout the trials and tribulations of my Ph.D. I will be forever indebted to you. Thank you and thank you all.
Chapter 1

Introduction

1.1 Earth’s Atmosphere

The planet Earth is surrounded by a protective blanket of air called the atmosphere. The atmosphere consists of a variety of gases, listed in Table 1.1, a number of which are known as “greenhouse gases” as they contribute to the warming of our atmosphere by trapping heat radiated from the earth. These greenhouse gases include water vapour (H$_2$O), methane (CH$_4$), nitrous oxide (N$_2$O), ozone (O$_3$) and carbon dioxide (CO$_2$).

\begin{table}
\centering
\caption{Composition of the atmosphere near the surface of the earth - Wallace and Hobbs (2006)}
\begin{tabular}{lll}
\hline
Gas (and Particles) & Symbol & Percent (by volume) \\
\hline
Nitrogen & N$_2$ & 78.08 \\
Oxygen & O$_2$ & 20.95 \\
Water Vapour & H$_2$O & 0 to 5 \\
Argon & Ar & 0.93 \\
Carbon Dioxide & CO$_2$ & 0.038 \\
Neon & Ne & 0.0018 \\
Helium & He & 0.0005 \\
Methane & CH$_4$ & 0.00017 \\
Hydrogen & H$_2$ & 0.00005 \\
Nitrous Oxide & N$_2$O & 0.00003 \\
Ozone & O$_3$ & 0 - 0.00001 \\
Xenon & Xe & 0.000009 \\
Particles (dust, soot, etc.) & & 0.000001 \\
Chlorofluorocarbons (CFC’s) & & 0.0000002 \\
\hline
\end{tabular}
\end{table}
Some of these gases have a considerable influence on the Earth’s climate. Incoming solar radiation travels through the atmosphere with relative ease. However, it encounters some resistance when trying to pass back through the atmosphere, after bouncing off the earth’s surface. Incident rays from the sun have wavelengths found in the short-wave part of the electromagnetic spectrum. At these short wavelengths (0.2 - 0.9 \( \mu m \)), radiation from the sun tends to not be absorbed by molecules in the atmosphere and is absorbed by the earth’s surface. This absorbed radiation is then released by the earth’s surface at wavelengths found in the long-wave part of the spectrum (5 - 20 \( \mu m \)). This terrestrial radiation is more likely to be trapped by greenhouse gases in the atmosphere, thus warming the earth’s lower atmosphere to a comfortable average temperature of 15 °C. This warming of the atmosphere is known as the greenhouse effect (Ahrens, 2000). Water vapour is the most abundant, followed by CO\(_2\), methane, nitrous oxide and ozone. The effectiveness of each greenhouse gas in influencing the Earth’s radiative budget is dependent on its atmospheric concentration and its ability to absorb outgoing long-wave terrestrial radiation (Watson et al., 1990). The contribution of each of these gases to the greenhouse effect differs: 60% from water vapour, 25% from CO\(_2\) and 8% from ozone, and the rest from trace gases including methane and nitrous oxide (Karl and Trenberth, 2003).

The earth’s atmosphere can be subdivided into four separate layers: troposphere, stratosphere, mesosphere and thermosphere. As height increases, air temperature decreases within the troposphere. Eventually, a point is reached when air temperature stops decreasing. This marks the tropopause, and the beginning of the stratosphere. The stratosphere contains the majority of ozone found in the atmosphere. Ozone absorbs incident UV radiation and, as a result, air temperature starts increasing with height. The mesosphere, which is the next layer, contains approximately 0.1% of the atmosphere’s mass (Ahrens, 2000). The top layer of the atmosphere, known as the thermosphere, is very warm, due to the absorption of solar radiation. A schematic of each of the layers and the height at which they are found is displayed in Figure 1.1. Although not shown, a fifth layer, known as the exosphere exists above the thermosphere. This layer is the upper most limit of our atmosphere.

The troposphere, the layer that is closest to the earth’s surface, is of most concern when studying the interaction between the surface and the overlying atmosphere.
1.2 CO\textsubscript{2} in the Atmosphere

Carbon dioxide (CO\textsubscript{2}) accounts for a small fraction of the total amount of gas in our atmosphere, approximately 0.04%. Although it occupies a small volume, it plays a very important role in the dynamics of our planet. CO\textsubscript{2} enters our atmosphere from several natural sources including: exhalations from both humans and animals, volcanic eruptions and the decay of vegetation and living creatures (Ahrens, 2000). However, since the industrial revolution in the 1800’s, the production of carbon dioxide from sources including the burning of fossils fuels (gas, coal and oil) and deforestation, have caused atmospheric CO\textsubscript{2} concentrations to move in an upward trend (Wallace and Hobbs, 2006). This gradual increase is believed to be as a result of anthropogenically produced carbon dioxide emissions for the following reasons

- Analysis of gas bubbles trapped in ice cores extracted from the Greenland and Antarctic ice sheets indicate that CO\textsubscript{2} concentrations in the atmosphere began to increase around the 1800’s - the beginning of the industrial revolution. CO\textsubscript{2} concentrations have been on the increase ever since (Ahrens, 2000).
• CO₂ concentrations are higher by several ppmv (parts per million by volume) in the northern hemisphere, compared to southern latitudes. The strongest man made carbon sources are located in the northern hemisphere (Ahrens, 2000).

• Atmospheric oxygen is observed to be decreasing at a rate of 3 ppmv per year, consistent with the hypothesis that CO₂ being added to the atmosphere is a product of combustion (Ahrens, 2000).

In 1958, a scientist by the name of Dave Keeling started making atmospheric CO₂ concentration measurements at Mauna Loa, Hawai’i, U.S.A.. These measurements, known as the *Keeling Curve*, are shown in Figure 1.2. They clearly show a steady increase of carbon dioxide in the atmosphere over the past fifty years. The pronounced annual cycle is due to large amounts of CO₂ being removed from the atmosphere during the spring and summer months, as a result of growth in plants and trees in the northern hemisphere.

![Atmospheric Carbon Dioxide Concentration Measurements at Mauna Loa, Hawai’i](image)

**Figure 1.2:** Atmospheric CO₂ concentration measurements at Mauna Loa, Hawai’i. From Woods Hole Oceanographic Institute (WHOI)

Anthropogenically produced CO₂ coupled with natural sources of carbon dioxide have resulted in an enhancement of the greenhouse effect, thus warming the atmosphere. This warming effect is mostly experienced in the troposphere (Santer et al., 2003). This additional rise in global temperature is worrying, as it could lead to a warming of the earth and increase in sea-water concentrations.
1.3 Carbon Cycle

Carbon transfers between several “natural reservoirs” on the planet by way of numerous processes and chemical transformations. There are four active reservoirs for carbon dioxide (CO$_2$): the atmosphere, the oceans, the terrestrial biosphere which includes all fresh water systems, trees, plants and soil carbon, and the earth’s crust (Duxbury and Duxbury, 1997). Through the processes of photosynthesis, respiration and decay, CO$_2$ moves between the atmospheric, oceanic, and biospheric reservoirs. Subduction and sea floor spreading allow carbon dioxide to transfer between the crust and mantle. Weathering and volcanism allow CO$_2$ to move from the crust and mantle into the atmosphere and oceans. This cycling of carbon dioxide, which is displayed in Figure 1.3 is important, as it regulates the concentration of CO$_2$ in the atmosphere (Wallace and Hobbs, 2006).

![Figure 1.3: Carbon Cycle. From Environmental Protection Agency (EPA)](image)

The earth’s natural reservoirs absorb and release CO$_2$. When one reservoir takes in carbon dioxide, that reservoir is known as a CO$_2$ sink. Whereas, if a reservoir releases CO$_2$, it is known as a source for carbon dioxide. A better understanding of the movement of CO$_2$ between each of these reservoirs is very important for future research in climate change.
1.4 CO$_2$ in the Ocean

Of all the natural reservoirs, the world’s oceans contain the greatest amount of carbon dioxide. It has been documented that they hold more than 50 times the total atmospheric content (Ahrens, 2000). The atmosphere is the link between the other reservoirs, and the ocean plays a major role in determining the atmosphere’s concentration by physical (mixing and circulation), chemical and biological means (Duxbury and Duxbury, 1997). CO$_2$ naturally moves across the air-sea interface, and as atmospheric concentrations of carbon dioxide have been reported to be on the increase due to man-made sources, it is estimated that almost half of all anthropogenically produced CO$_2$ has already entered the world’s oceans (Segar, 1998).

![Figure 1.4: Biological Pump of CO$_2$. From Woods Hole Oceanographic Institute (WHOI)](image)

Near the sea surface, plants and phytoplankton consume carbon dioxide by way of the process of photosynthesis. However, all marine organisms respire and carbon dioxide is produced and released into the surrounding water. When these marine creatures die, their remains can sink and accumulate along with other detritus on the sea floor. This natural settling process is known as the “biological pump”, a schematic of which is shown in Figure 1.4. This sinking of organic matter has the effect of
transporting carbon dioxide downward, reducing its concentration near the sea surface (Wallace and Hobbs, 2006). All of these important processes occur within the mixed-layer of the ocean. The spatial variability of the mixed layer is very large. It can range in depth from 20 m in the summer hemisphere to 500 m in the winter hemisphere in subpolar latitudes (Monterery and Levitus, 1997). Were it not for these processes, atmospheric CO$_2$ concentrations would be roughly 2.6 times greater than currently observed.

Increasing atmospheric CO$_2$ concentrations could lead to additional CO$_2$ entering the world’s oceans. Carbon dioxide dissolved in the world’s oceans can undergo a series of chemical reactions where bicarbonate and carbonate ions are created. These series of reactions allow CO$_2$ to play an important role in the ocean (Duxbury and Duxbury, 1997). Adding CO$_2$ to sea-water increases aqueous CO$_2$ and hydrogen ion concentrations; the latter lowers pH because pH = -log$_{10}$[H$^+$]. An increase in ocean acidity can lead to a lower calcium carbonate (CaCO$_3$) saturation in surface waters (Doney et al., 2009). CaCO$_3$ saturation states may influence both deposition and dissolution rates of mineralized skeletons in many marine organisms such as, corals, molluscs, tube-dwelling polychaetes, crustaceans, bryozoans and echinoderms (Milliman, 1974; Neinhuis et al., 2010). The rate of shell deposition may limit the maximum rate of body growth in some groups, which could impact upon growth rate and survival (Palmer, 1981). Across the planet, the average pH of the ocean’s surface layer has declined 0.12 unit, to approximately 8.1, since the beginning of the industrial revolution. Experimental work has been conducted on brittlestars and copepods, where the pH level was lowered by 0.2 - 0.4 unit, and results showed that these conditions were damaging for this marine species (Hardt and Safina, 2010). Ultimately, any fall in pH levels in the oceans could be hazardous for certain aquatic life. Ocean circulation is the large scale movement of waters throughout the world’s oceans. When warm waters reach polar latitudes, this water sinks due density variations. This sinking of water is known as downwelling. Carbon dioxide can then be transported downwards to great depths through the downwelling process. As a result of this, CO$_2$ can be stored deep in the world’s oceans, where it is locked away from contact with the atmosphere for hundreds or thousands of years (Segar, 1998). Eventually, some of this stored CO$_2$ can return to the sea surface through the process of upwelling. Upon reaching the air-sea interface, carbon dioxide can re-enter the atmosphere. It has been stated that “the role of the
oceans in absorbing and storing carbon dioxide is critical to carbon dioxide that has been, or will be, released by industrialised civilization, and to the severity of global climate change due to the enhanced greenhouse effect” (Segar, 1998). The oceans are huge storehouses for CO$_2$ and microscopic plants (phytoplankton) extract CO$_2$ from the surrounding sea-water during photosynthesis and store it below the ocean surface when they die. Would a warmer earth trigger a larger blooming of these tiny plants, in effect reducing CO$_2$ in the atmosphere? Or, would a gradual rise in ocean temperature increase the amount of CO$_2$ in the air due to the fact that warmer oceans can’t hold as much CO$_2$ as colder ones (Ahrens, 2000)? As the atmospheric concentration of CO$_2$ continues to rise, answers to these questions need to be urgently found.

The first step in trying to answer any of these questions is to collect CO$_2$ concentration data from both the ocean and the over-lying atmosphere. In order to do this, specialised and advanced instrumentation is necessary. New instrumentation is being manufactured to perform measurements of sea-water pCO$_2$ concentrations. One of these sensors is the Pro Oceanus Systems Inc. (PSI) pCO$_2$ instrument. A thorough evaluation of the workings and accuracy of this instrument was conducted, providing confidence in the sea-water pCO$_2$ data collected. Sea-water pCO$_2$ measurements were conducted in coastal regions, across the continental shelf and in open Atlantic waters off the coast of Ireland. These data provide a picture of the variability of carbon dioxide in Irish waters on an seasonal basis. When coupled with atmospheric CO$_2$ measurements, the possible direction of movement of CO$_2$ across the air-sea boundary can be examined.

1.4.1 Continental Shelf

The continental shelf is a relatively shallow part of the world’s oceans and is found along the edge of all continental landmasses. It varies in width, ranging from tens of metres to hundreds of kilometres (Duxbury and Duxbury, 1997). Although continental shelves occupy only 7% of the total ocean area, they play a very significant role with regard to the cycling of carbon dioxide between each of the natural reservoirs, most importantly the ocean and the atmosphere (Frankignoulle and Borges, 2001). The coastal ocean is one of the most biogeochemically active regions of the biosphere (Borges et al., 2006).
CO₂ enters continental shelf waters from sources, including rivers and from deeper waters through the upwelling process. More importantly, the overlying atmosphere is another source of CO₂ for continental marginal seas. However, there has been much doubt and discussion about whether continental shelves are sinks or sources for carbon dioxide. Out of all of the ocean basins, the largest coastal CO₂ sink is located in the Atlantic Ocean (8.4 x 10^{12} mol C yr^{-1}) (Chen and Borges, 2009). Studies in the Tasman continental shelf and coastal areas in the Beinline Sea and Okhotsk Sea concluded that these regions are also sinks for CO₂ (Borges et al., 2008; Takahashi et al., 2006). Yet, continental shelves off the coasts off the Arabian peninsula and California are sources of carbon dioxide for the atmosphere (Borges et al., 2006). Shelves located at higher latitudes tend to act as sinks of CO₂, whereas continental shelves nearer the equator act as sources of carbon dioxide (Chen and Borges, 2009). Evidence gathered indicates that overall, continental shelves are net sinks for atmospheric carbon dioxide. Yet, inner estuaries and salt marshes, which are part of the continental shelf system, release CO₂ into the atmosphere. This is as a result of the decay of terrestrial organic matter (Chen and Borges, 2009).

Sea-water pCO₂ measurements, plus other oceanic variables were collected over the continental shelf and at the Mace Head research station over the duration of a year. Upon analysis of these individual data sets, whether other oceanic parameters influenced the concentration of carbon dioxide in the surrounding sea-waters could be investigated. By measuring air and sea-water pCO₂ concentrations, plus CO₂ fluxes in the nearby atmosphere, the transfer velocity of CO₂ across the air-sea interface has been studied. Many meteorological variables influence the transfer velocity of CO₂, one of the most important parameters being wind speed. The relationship of wind speed and CO₂ transfer velocity was quantified during this experimental work.

Undoubtedly, there are many unanswered questions as to what role the oceans, including the continental shelves, of the earth will play with regard to carbon dioxide in our planet’s future. The ocean acts as both a sink and source for CO₂. As a result, better understanding the movement of CO₂ between the air and the ocean is vital for future studies into global climate dynamics.
Chapter 2

Background Information

2.1 Boundary Layer

As previously stated in Chapter 1.1, the atmosphere can be subdivided into further layers, one of these being the troposphere. It is within this layer of the atmosphere that the boundary layer, or atmospheric boundary layer can be found. An illustration of the boundary layer is displayed in Figure 2.1.

![Figure 2.1: Planetary Boundary Layer. From National Oceanographic and Atmospheric Administration (NOAA)](image)

The thickness of the boundary layer is variable in both time and space, ranging from hundreds of metres to a few kilometers. It is this part of the troposphere that
is directly influenced by the presence of the earth’s surface, and responds to surface forcings with a timescale of about an hour or less. Each of these forcings can cause the air in the boundary layer to be unstable or turbulent (Stull, 1988).

The turbulent motion of air in the boundary layer, which tends to occur in the horizontal direction, can be visualised as erratic swirls of air known as eddies. Shown in Figure 2.2, eddies can vary in both size and direction, and can occupy the same volume of air. Turbulence in the boundary layer can be generated either inertially, mechanically or thermally (Wallace and Hobbs, 2006). Mechanical turbulence can be caused by shear in the mean wind, which in turn is caused by frictional drag. Trees, mountains and houses can also lead to the creation of mechanical turbulence. Thermal turbulence is a result of the rising and sinking of warm and cold air respectively. Inertial turbulence is created due to the motion of larger eddies in the air (Wallace and Hobbs, 2006).

![Figure 2.2: Turbulent Eddies in the Atmosphere - (Burba and Anderson, 2007)](image)

Frequently, eddies differ in size and can be super-imposed on each other. Their relative strengths can be defined by the turbulence spectrum, pictured in Figure 2.3. This graph was first created by Issac Van der Hoven in 1957. The x-axis shows the size of the eddy in terms of the frequency of wind speed variation and time period. The y-axis is a measure of the portion of turbulence energy that correlates with an eddy of particular size.

The graph clearly shows two individual peaks in the turbulence spectrum. Both of these peaks are important, as they identify which size eddies contribute the most to
Chapter 2. Background Information

Figure 2.3: Schematic spectrum of wind speed near the ground estimated from a study by Van der Hoven (1957) - (Stull, 1988)

The turbulence kinetic energy (Stull, 1988). The peak on the left corresponds to wind speed variations contributed by weather systems and diurnal activity. The peak on the right side of the graph is associated with variations in wind speed that are due to micro-scale turbulence (Stull, 1988). It covers for a range of eddies that exist in a time frame ranging from 0.001 to 0.1 hours. The gap in the middle is known as the “spectral gap”, and distinguishes the separation of turbulent and non-turbulent motion (Stull, 1988).

The deterministic description of turbulence is very difficult, if not impossible. Therefore, the best method of describing turbulence is to use a statistical approach. The aim of using statistics is to describe the net effect of numerous eddies, instead of the specific behaviour of a specific eddy (Wallace and Hobbs, 2006). One statistical method used is known as the eddy covariance technique.

2.2 Eddy Covariance Technique

The eddy covariance technique (EC) is also known as the eddy correlation method or the eddy flux technique. It is a statistical method that analyzes high frequency wind and scalar atmospheric data sets. The method is regarded as a key atmospheric flux technique to measure and calculate vertical turbulent fluxes within atmospheric boundary
layers. Flux measurements are popularly used to estimate water and heat fluxes in the atmosphere. They are also used to measure the exchange of CO$_2$, methane and other trace gases between some of the natural reservoirs. It has been stated that the EC technique is one of the most direct, and defensible ways to measure such fluxes (Burba and Anderson, 2007). The EC technique is regarded as being mathematically complicated and significant care is required when setting up and analyzing data.

The word “flux” comes from the Latin word meaning “to flow”, and is defined as the rate of transfer of a quantity across a unit area (Stull, 1988). Flux is dependent on: (1) number of things which cross the area, (2) the size of the area that is being crossed, and (3) the time which it takes to cross this area (Burba and Anderson, 2007).

In Figure 2.2, we show that the flow of air in the atmosphere can consist of numerous eddies. However, by examining the eddies, one at a time, a better understanding can be grasped about the movement of air in the vertical direction. Figure 2.4 aids with this purpose.

![Figure 2.4: Two particular eddies at a given point in time and space - (Burba and Anderson, 2007)](image)

At a moment in time, $t_1$, eddy number 1 moves an air parcel, $c_1$ in the downward direction with a speed $w_1$. At the next moment in time, $t_2$, at the same point, eddy number 2 moves air parcel, $c_2$ upwards with speed $w_2$. Each of the air parcels can have characteristics such as temperature, humidity, gas concentration and gas density. If each of these characteristics are measured in conjunction with the speed of air in the vertical direction, then the vertical upward or downward fluxes of temperature, gas
density, etc. can be calculated. It is this analysis that is the general principle of the eddy covariance technique: covariance between a particular concentration of interest and the vertical wind speed of the eddies (Burba and Anderson, 2007).

Turbulent fluctuations occur rapidly, ranging from milliseconds to seconds, as displayed on the right side of Figure 2.3. In order to make measurements of turbulent fluctuations, sophisticated instrumentation is necessary (Burba and Anderson, 2007). Instrumentation used during this experimental work is described in more detail in Chapter 3. Turbulent fluctuations of any micro-meteorological variable can be thought of as the fluctuations superimposed on the mean of that value. This idea is known as Reynolds decomposition. For example, wind speeds in the u, v and w directions can be written in the following format

\[
\begin{align*}
    u &= \bar{u} + u' \\
    v &= \bar{v} + v' \\
    w &= \bar{w} + w'
\end{align*}
\]  

(2.1)

where the prime denotes the fluctuating part or the departure from the mean of the variable in question. u, v and w are variables measured by the sonic anemometer, see Section 3.2.1.3. They each correspond to the orthogonal components of the wind vector (GillInstruments, 2004).

### 2.2.1 Eddy Flux Equation Derivation

There exists one important equation when applying the eddy covariance technique. This equation and its derivation are explained below.

Firstly, the vertical flux of a particular quantity can be presented by Equation 2.2.

\[
F = \rho_a w s
\]  

(2.2)

Here the flux is equal to the mean product of air density, vertical wind speed and the mixing ratio of the gas of particular interest (CO\textsubscript{2} in our case), where \( s = \rho_c / \rho_a \). \( \rho_c \) is the density of CO\textsubscript{2} and \( \rho_a \) is the density of dry air. By using Reynolds decomposition, Equation 2.2 can be separated into means and deviations. This new equation is displayed in Equation 2.3.
Chapter 2. Background Information

\[ F = (\bar{\rho}_a + \rho'_a)(\bar{w} + w')(\bar{s} + s') \]  \hspace{1cm} (2.3)

The density of the air is now represented as an average of a period of time i.e a half an hour, and an instantaneous deviation from this mean for every unit of time i.e 0.1 seconds. These values are suggested values and vary between experimental research and are dependent on which instruments are used.

The question of choosing an appropriate averaging interval is dependent on the nature, structure and time scales of the fluctuations over which the average is taken (Malhi et al., 2004). It is very important to ensure that the averaging period for flux calculations is appropriate for all eddy scales contributing to the vertical flux in question. The averaging time frame should not be too long so that non-turbulent mesoscale variability is included. Very low frequency perturbations can be caused by non-stationarity of the local flow. Non-stationarity can occur during frontal passages, sudden boundary layer growth or decay or other short-term boundary layer disturbances such as the passage of clouds. They can be identified as periods when the time series varies in a systematic and non-turbulent way (Norris et al., 2008). An average time frame of about 30 minutes is generally regarded a reasonable compromise (Massman and Lee, 2002). ChinaFLUX adopted a 30 minute averaging period during their experimental work, as this average is widely used in many surface-air exchange investigations (Sun et al., 2006). Also, sea-water pCO\textsubscript{2} concentrations were collected every half hour. This data is discussed further in Chapter 5. As a result, It was felt appropriate that a 30 minute block average be used during the application of the eddy covariance technique during this experimental work.

In Equation 2.3, the vertical wind speed and the mixing ratio of the quantity of interest are displayed in a similar manner as that of the density of air. Equation 2.3 can be developed further

\[ F = (\bar{\rho}_a \bar{w} \bar{s} + \bar{\rho}_a \bar{w}' \bar{s}' + \bar{\rho}_a \bar{w} \bar{s}' + \bar{\rho}_a w' \bar{w} s' + \bar{\rho}_a w' \bar{s} s' + \rho'_a \bar{w} \bar{s} + \rho'_a \bar{w} \bar{s}' + \rho'_a w' \bar{w}' s' + \rho'_a w' \bar{s}' s') \]  \hspace{1cm} (2.4)
In Equation 2.4, the averaged deviation from the average is zero, hence the above terms can be removed. By removing these terms, we arrive at Equation 2.5

\[ F = (\bar{\rho}_a \bar{w} \bar{s} + \bar{\rho}_a \bar{w}' \bar{s}' + \bar{w} \bar{\rho}'_a \bar{s}' + \bar{s} \bar{\rho}'_a \bar{w}') + (\bar{\rho}'_a \bar{w}' \bar{s}') \] (2.5)

Next, an important assumption is made: density fluctuations are assumed to be negligible. Sometimes, this is not the case in certain situations. For example, strong winds that flow over the ridge of a mountain could create large density fluctuations, causing \((\rho'w')\) to be large. If so, they should not be ignored. However, when the EC technique is used over reasonably flat and open spaces, which include the sea surface, fields and open plains, the density fluctuations can be safely assumed inconsequential.

After this assumption is applied, the following terms can be removed from Equation 2.5.

\[ F = (\bar{\rho}_a \bar{w} \bar{s} + \bar{\rho}_a \bar{w}' \bar{s}' + \bar{w} \bar{\rho}'_a \bar{s}' + \bar{s} \bar{\rho}'_a \bar{w}') \] (2.6)

creating Equation 2.7

\[ F = (\bar{\rho}_a \bar{w} \bar{s}) \] (2.7)

Another assumption is made where the mean vertical flow is assumed negligible for horizontal homogeneous terrain (no divergence/convergence). As a result of this assumption, the first term in Equation 2.7 can be removed, creating Equation 2.8, which is the “eddy flux equation”.

\[ F = (\bar{\rho}_a \bar{w} \bar{s}) \] (2.8)

Some instruments usually do not measure the mixing ratio, \(s\), of a given gas. So there is another assumption to be taken into consideration. It being, that the product of mean air density and mean covariance between deviations in the instantaneous vertical wind speed and mixing ratio is equal to the mean covariance between deviations in
instantaneous vertical wind speed and gas density. As a result, Equation 2.8 can be rewritten as Equation 2.9.

$$F = (w'\rho'_c)$$ (2.9)

### 2.2.2 Assumptions

Three assumptions have already been made when using the eddy covariance technique. However, there are some more assumptions that must be satisfied. Some of these assumptions depend on selecting a proper experimental set-up site, whilst others depend on atmospheric conditions and weather. These other assumptions include:

- Measurements at a point can represent an upwind area
- Measurements are done inside the boundary layer of interest
- Fetch/footprint is adequate - fluxes are measured only at area of interest
- Flux is fully turbulent - most of the net vertical transfer is done by eddies
- Terrain is horizontal and uniform: average of fluctuations is zero; density fluctuations negligible; flow convergence & divergence negligible
- Instrumentation used to measure the CO$_2$ gas concentration and vertical wind velocity are able to detect very small changes in eddy size at very fast sampling rate

### 2.2.3 Sources of Error

When making scientific measurements in the outdoor environment, there will always be a degree of error. Errors can arise because of assumptions, problems with instrumentation and specifics of surrounding terrain. As a result there are some potential flux errors. Clearly it is advantageous to try and remove or correct as much of these errors as possible. There exists a group of errors called frequency response errors which include
Instrument time response: This error arises due to the fact that some instrumentation may not be fast enough to record all of the rapid changes that result from the rotating eddies.

Sensor separation: Due to the physical separation between the places where wind speed and scalar concentration are measured, the covariance is computed for parameters that were not measured at the exact same point. Measuring these parameters at the exact same point is physically impossible.

Scalar path averaging: This error is due to the fact that the sensor path is not a point measurement, but rather an integration over some distance. As a result of this, it could average out some of the changes caused by the eddy transport.

Tube attenuation: If a closed path analyzer is used as part of the experimental set-up, tube attenuation can occur. This is caused by the attenuation of the instantaneous fluctuation of the concentration in the sampling tube.

Other frequency response errors may arise due to high pass filtering, low pass filtering, sensor response mismatch and digital sampling. Although noted, frequency response errors were not corrected for during this experimental work, as they were deemed negligible. McVeigh and O’Dowd (private communication) calculated that the total of all of these correction factors were on average approximately 6% of the total flux calculated for a half hour time frame.

Aside from frequency response errors, other sources of errors exist. These include sensor time delay, spikes and noise in the measurements, unleveled instrumentation, the Webb-Pearman-Leuning density term, sonic heat flux errors, band-broadening, oxygen sensitivity, and data filling errors. Attempts were made to correct for some of these errors during this experimental work.

Note: Sections 2.2.1 to 2.2.3 is sourced from Burba and Anderson (2007).

2.3 Micrometeorological Variables

In Equation 2.1, we showed how any micro-meteorological variable can be separated into a fluctuating part and a mean part. The mean part of Equation 2.1 is calculated
by applying a running mean across the data set. A running average or moving average is calculated for a given set of numbers $X_1, X_2, X_3, ...$ by Equation 2.10.

\[
\frac{X_1 + X_2 + \cdots + X_N}{N}, \quad \frac{X_2 + X_3 + \cdots + X_{N+1}}{N}, \quad \frac{X_3 + X_4 + \cdots + X_{N+2}}{N}, \ldots
\]  

(2.10)

where the data set has a moving average of order $N$.

One requirement of the eddy covariance technique is that the mean particle number concentration (in our case - $\text{CO}_2$ concentration), does not vary dramatically over the averaging time frame (in our case - 30 minutes) used to calculate the mean value. If the calculated mean remained constant throughout the time period, the time series is said to be stationary. However, this seldom occurs when making measurements of atmospheric variables. For example, if the particle number concentration was increasing overall during the time period, deviations from the mean will only be correct when an instantaneous measurement is equal to the calculated mean, and will be incorrect elsewhere during the time frame. A similar situation could occur if the particle number concentration was decreasing. These increasing and decreasing trends need to be removed from the data series. This is achieved by applying a moving average or running mean to the data series. By using a running mean, the data is detrended.

Fluctuations at any particular point are calculated by subtracting the running mean from the original data set. These deviations from the mean are represented by $'$, and are used to calculate the variances and covariances in the data set.

The variance is defined as the average square of the departure of the variable from its mean. It is expressed through Equation 2.11.

\[
\sigma^2 = \frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2 = \frac{1}{n} \sum_{i=1}^{n} x_i^2 - \bar{x}^2 \quad \text{or} \quad \sigma^2 = \bar{x'}x'
\]  

(2.11)

where $x'$ is the departure of the variable from its mean. The overbar denotes the time period over which the block averaging occurs. During this experimental work, a time period of 30 minutes was chosen. The variances of the orthogonal components of wind speed, $u$, $v$ and $w$, are
\[ \sigma_u^2 = \overline{u'u'} \quad \sigma_v^2 = \overline{v'v'} \quad \sigma_w^2 = \overline{w'w'} \quad (2.12) \]

The covariance of two variables, with n data points, is the average product of the departures of the two variables from their means and is shown in Equation 2.13. Again, the overbar is the time period over which the block averaging occurs.

\[ \sigma_{xy} = \frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) = \frac{1}{n} \sum_{i=1}^{n} x_i y_i - \bar{x}\bar{y} \text{ or } \sigma_{xy} = \overline{x'y'} \quad (2.13) \]

All turbulent fluxes are calculated from the covariances of any two meteorological variables. These fluxes are explained in further detail below.

**Carbon Dioxide Flux, \( F_c \):** The vertical flux of CO$_2$ in the atmosphere is represented by Equation 2.14. It is the covariance of the vertical wind speed component and the atmospheric concentration of carbon dioxide.

\[ F_c = \overline{w'c'} \quad (2.14) \]

**Water Vapour Flux, \( F_q \):** Similarly, the equation for the vertical flux of water vapour is calculated by the covariance of the vertical wind speed component and the concentration of water vapour in the atmosphere. It is shown in Equation 2.15.

\[ F_q = \overline{w'q'} \quad (2.15) \]

**Temperature Flux, \( F_T \):** This flux is calculated by using Equation 2.16: the covariance of the vertical wind speed component and the temperature of the surrounding air.

\[ F_T = \overline{w'T'} \quad (2.16) \]

**Momentum Flux, \( \tau \):** This flux is the covariance of the streamwise horizontal wind speed and vertical wind speed components. It is a measure of the horizontal wind shear and is expressed through Equation 2.17. It has the units m$^2$/s$^2$.

\[ -20- \]
Friction Velocity, \( u^* \): Also known as shear velocity, it represents the magnitude of the velocity fluctuations in the boundary layer and has the units m/s.

\[
\begin{align*}
\tau &= u'w' \\
\Rightarrow \quad u^* &= \sqrt{-u'w'} \quad \text{or} \quad \sqrt{-\tau}
\end{align*}
\]  

Drag Coefficient, \( C_D \): This parameter is a dimensionless measure of the effect of the surface on wind flowing over it. It is associated with the production of wind shear.

\[
C_D = \frac{u^*}{U^2}
\]  

• \( u^* \) is the friction velocity
• \( U \) is the macroscopic wind speed, \( U = \sqrt{\bar{u}^2 + \bar{v}^2 + \bar{w}^2} \)

Roughness Length, \( z_o \): This is the height when wind speeds reach 0 m/s. It is dependent on roughness elements on the surface and is calculated by Equation 2.20.

\[
\begin{align*}
 z_o &= z e\frac{\kappa}{C_D} \\
\end{align*}
\]  

• \( z \) is the measurement height, 22 m in this case. This is the height of the Mace Head tower where the eddy covariance instrumentation was installed. This is discussed further in Chapter 3.
• \( \kappa \) is the von Karman constant \( \approx 0.4 \)
• \( C_D \) is the drag coefficient

Monin-Obukhov Length, \( L \): Also known as the Obukhov length, it is a scaling parameter useful in the surface layer. It can be interpreted as being proportional to the height at which buoyancy forces begin to dominate over mechanical forces in the production of turbulence (Stull, 1988). It can be calculated by Equation 2.21.
Chapter 2. Background Information

\[ L = \frac{-c_{p} \bar{\rho} \bar{T} u^*}{\kappa g H_s} \]  \hspace{1cm} (2.21)

- \(c_{p}\) is the specific heat capacity of air at a constant pressure
- \(\bar{\rho}\) is the average air density
- \(\bar{T}\) is the average air temperature
- \(u^*\) is the friction velocity
- \(\kappa\) is the von Karman constant \(\approx 0.4\)
- \(g\) is acceleration due to gravity
- \(H_s\) is the sensible heat flux

**Atmospheric Stability, \(\zeta\):** The Monin-Obukhov length can be used to define a very important scaling parameter, \(\zeta\). It is sometimes referred to as a stability parameter and is dimensionless. This scaling parameter is used to determine when the boundary layer is stable or unstable. A positive value of \(\zeta\) implies that the surface layer is statically stable. Whereas a negative value implies that it is unstable (Stull, 1988). It can be calculated by Equation 2.22.

\[ \zeta = \frac{z}{L} \]  \hspace{1cm} (2.22)

- \(z\) is the height of measurement - 22 m. This is the height of the Mace Head tower where the eddy covariance instrumentation was installed. This is discussed further in Chapter 3.
- \(L\) is the Monin-Obukhov length

### 2.4 Air to Sea Gas Exchange of CO\(_2\)

The concentration of carbon dioxide, often called xCO\(_2\) can be expressed in terms of its partial pressure, pCO\(_2\). The partial pressure of a gas is defined as the pressure that a gas would have if it occupied a volume by itself.
Atmospheric pCO$_2$ concentrations (pCO$_{2a}$) vary slightly throughout the world. However, pCO$_2$ concentrations in the world’s oceans, (pCO$_{2s}$), dramatically vary both seasonally and geographically. If the partial pressure of carbon dioxide in the air (pCO$_{2a}$) is greater than the partial pressure of carbon dioxide in the sea water (pCO$_{2s}$), then CO$_2$ will flow from the air into the sea. The opposite would occur if pCO$_{2a}$ < pCO$_{2s}$. This transfer of carbon dioxide across the air-sea boundary is known as the air-sea flux of CO$_2$. This difference in pCO$_2$ concentrations between the air and sea (∆pCO$_2$) is regarded as the main driving force behind the air-sea flux of carbon dioxide (Schuster and Watson, 2007). However, because pCO$_{2s}$ concentrations vary on greater scale in comparison to atmospheric concentrations, the air-sea flux is mainly determined by sea water concentrations of CO$_2$ (Takahashi et al., 2002). Research has been conducted into the spatial and temporal variability of the uptake and release of CO$_2$ by the world’s oceans (Feely et al., 2001). Using data collected from field work, air-sea fluxes throughout the world were plotted on a single map. This map is displayed in Figure 2.5.

![Figure 2.5: Distribution of the climatological mean annual sea-air CO$_2$ flux (moles CO$_2$ m$^{-2}$ yr$^{-1}$) for the reference year 1995 representing non El-Niño conditions. This has been computed using the mean monthly distribution of sea-air pCO$_2$ difference, the climatological NCEP 41-year mean wind speed and the wind speed dependence of the CO$_2$ gas transfer velocity of (Wanninkhof, 1992). This map yields an annual oceanic uptake flux for CO$_2$ of 2.2 ± 0.4 Pg C yr$^{-1}$ (Takahashi et al., 2002)](image)

In a global context, the world’s oceans are regarded as a sink for CO$_2$. However, as Figure 2.5 shows, regionally the ocean has sources and sinks of carbon dioxide. Red, orange and yellow areas on the map are regions that are sources of carbon dioxide for the atmosphere. These areas include the Eastern Equatorial Pacific Ocean and the
Chapter 2. Background Information

Arabian Sea. Areas that are deep blue and purple are sink regions for carbon dioxide, which mostly include any temperate sea areas, where warm tropical water meets cold currents flowing from polar regions. It has been estimated that the global uptake of CO$_2$ by the world’s oceans is 0.8 Pg C yr$^{-1}$ (Tans et al., 1990). However, as years passed, and research and techniques were improved, CO$_2$ uptake flux by the global oceans was revised to 2.2 Pg C yr$^{-1}$ (Takahashi et al., 2002). However, it has also been stated that the global oceanic uptake of CO$_2$ is in the region of 1.3 ± 0.3 Pg C yr$^{-1}$ (Ho et al., 2006).

It is assumed that CO$_2$ moves across the air-sea interface by diffusional transfer between the two reservoirs. This direct transfer of CO$_2$ is a combination of molecular and turbulent diffusion across the sea surface microlayer (Woolf, 1997). The sea surface microlayer is one millimetre in thickness at the top of the ocean nearest the sea surface. The exchange rate of carbon dioxide between the atmosphere is dependent on local meteorological and environmental conditions (McGillis et al., 2004). The amount of carbon dioxide in the sea surface varies with temperature, salinity, and bioproductivity. Whereas, gas transfer can vary with wind speed, atmospheric stability, sea state and surfactants. The creation and entrainment of bubbles at the sea surface is another important factor in gas exchange at the air-sea boundary (McGillis et al., 2001a).

As wind speed increases over the ocean surface, turbulent conditions and breaking waves usually occur. Air from the atmosphere becomes trapped in breaking waves, leading to the formation of bubbles which can play a significant role in gas exchange (Liss and Merlivat, 1986). Part of the atmosphere becomes encapsulated inside the bubble, and when the bubble is submerged, gases diffuse into the surrounding water (Woolf, 1997). By bypassing the molecular sublayer bottleneck, bubbles can travel to greater depths/pressures, allowing the enhancement of the dissolving processes of gases and also reach the surface, break, and release gases (Fairall et al., 2000). Whitecaps are also created in the presence of high wind speeds. It has been mentioned that the presence of whitecaps on the sea surface can increase the gas flux by generating intense patches of turbulence and by creating bubble plumes (Asher et al., 1995). It has been hypothesized that as a result, whitecaps are a low resistance vent through the sea surface (Monahan and Spillane, 1984).

Sea water temperature influences the concentration of carbon dioxide, which in
turn affects the exchange of CO\(_2\) across the air-sea interface. The water temperature in the upper few metres of the ocean, is mainly regulated by physical processes (i.e., solar energy input, sea-air heat exchanges, and mixed layer thickness) (Takahashi et al., 2002). Middle to high latitudes tend to act as a sink for CO\(_2\). Cooler water temperatures, which occur in these regions, have a larger capacity to dissolve carbon dioxide than warmer waters (Rutgersson et al., 2007). Whereas, in tropical regions, where water temperatures tend to be higher, carbon dioxide source regions are found. Liss and Merlivat (1986) state that water temperature is an important parameter, not only because of its influence on solubility, but also because of its effect on transfer velocities. It was shown that heating effects in the upper few metres of the water were the primary source of the variability in sea water pCO\(_2\) concentrations (DeGrandpre et al., 2004).

The ocean contains organic materials or surfactants which can affect the surface viscoelasticity and surface tension at the sea surface. These variables influence air-sea gas exchange (Fairall et al., 2000). Past research conducted in wind-wave tank experiments found that surfactants can have a large inhibitory effect on gas transfer (Jahne et al., 1984; Broecker et al., 1978). Also, it was shown that surfactant concentrations equaling less than is necessary to form a mono-molecular microlayer can significantly retard gas exchange at low to intermediate wind speeds (Frew, 1997; Wanninkhof and Mc Gillis, 1999). It was mentioned that there was a possibility that the gas transfer velocity of gases could be fetch dependent and also that the chemical enhancement of CO\(_2\) exchange could occur at low wind speeds (Wanninkhof, 1992). The enhancement occurs when CO\(_2\) reacts with water or hydroxide ions at the water surface.

Gases will dissolve into liquids to an extent that is determined by the equilibrium between any undissolved gas and the gas that is dissolved in the liquid. The transfer of gases across the air-sea boundary follows this principle. Henry’s Law states that when a gas (CO\(_2\)) comes into contact with the surface of a liquid (sea-water), the amount of gas which will go into the solution is proportional to the partial pressure of that gas in question. Henry’s Law states that

\[
c_e \cong c_a / K_H
\]  

(2.23)

where \(c_e\) is the concentration of the CO\(_2\) at the water surface that would be in
equilibrium with the atmosphere, \( c_a \) is the concentration of carbon dioxide in the atmosphere, and \( K_H \) is the dimensionless Henry’s coefficient (Fogg and Sangster, 2003). The movement of carbon dioxide across the air-sea interface will occur as long as the actual concentration of CO\(_2\) in the sea-water \((c_w)\) differs from \(c_e\) (Jacobs et al., 1999). Fits that have been proposed in past research result in \( K_H \approx 1 \) for CO\(_2\) in the case of sea water at a temperature of 12\(^\circ\)C with a salinity of 31% (Jacobs et al., 1999; Weiss, 1974).

The partial pressure of CO\(_2\) in the atmosphere can be calculated by the equation
\[
p_{CO_2a} = x_{CO_2a}(P - P_{H_2O}),
\]
where \(P\) is the ambient pressure and \(P_{H_2O}\) is the water vapour pressure (McGillis et al., 2004). However, during this experimental work, air pCO\(_2\) concentrations were calculated in a similar way to sea-water pCO\(_2\) concentrations. pCO\(_2s\) were calculated by the equation
\[
p_{CO_2s} = x_{CO_2s}(P/1013.25),
\]
where \(P\) is the ambient pressure. 1013.25 is a conversion factor as there are 1013.25 millibars in 1 atmosphere.

The bulk method to determine the flux of a gas relies on the assumption that the transfer across the air-sea boundary is governed by the concentration difference between the ocean and the atmosphere (McGillis et al., 2001b). This transfer or flux of CO\(_2\) between the sea-water and the overlying atmosphere is commonly parameterized by the following equation:

\[
F_{CO_2} = (k_{CO_2})(K_0)(\Delta p_{CO_2})
\]

- \(F_{CO_2}\) is the air-sea flux of carbon dioxide
- \(k_{CO_2}\) is the gas transfer velocity of carbon dioxide
- \(K_0\) is the solubility of carbon dioxide in sea water
- \(\Delta p_{CO_2}\) is the difference between the partial pressure of carbon dioxide in the sea-water \((p_{CO_2s})\) and the overlying air \((p_{CO_2a})\)

The air-sea flux can be measured by using the eddy covariance technique, as discussed in Section 2.2. This technique measures gas fluxes at the scale of turbulent transport, circumventing many problems associated with indirect methods (McGillis
et al., 2001a). The gas transfer velocity is discussed further in Section 2.5. If the flux of gas across the air-sea interface is to be calculated, then the solubility of that gas needs to known (Wanninkhof, 1992). Solubility of CO\(_2\) in sea-water is well documented and is a function of sea water temperature and salinity (Weiss, 1974). Solubility values for CO\(_2\) are calculated using the empirical formulation

\[
K_0 = \exp(-60.2409 + 93.4517(100/T) + 23.3585\ln(T/100) + \\
S[0.0223517 + (-0.023656(T/100)) + 0.0047036(T/100)^2]) 
\]  

(2.25)

- \(S\) is the salinity of the water in %
- \(T\) is the water temperature in K.
- \(K_0\) is solubility expressed in mol/L/atm

This equation is derived from the integrated van’t Hoff equation and the logarithmic Setchenow salinity dependence (Weiss, 1974).

Also, Henry’s coefficient, \(K_H\) can be related to the solubility of CO\(_2\) in sea water by the equation \(K_H = 1/(K_0 \text{ R } T)\), where \(K_0\) is solubility, \(R = 8.314 \text{ J/mol K}\), is the universal gas constant and \(T\) is temperature in K (Jacobs et al., 1999).

### 2.5 Gas Transfer Velocity

The gas transfer velocity, \(k_w\), is a parameter that describes the kinetics of the air-sea gas exchange of various gases, and is often parameterized with wind speed (Nightingale et al., 2000a). The relationship between wind speed and gas transfer velocity has been documented and researched, based on laboratory tank experiments and field studies while taking into account numerous physical variables and parameters (Liss and Merlivat, 1986; Wanninkhof, 1992; Jacobs et al., 1999; Wanninkhof and McGillis, 1999; Nightingale et al., 2000a; McGillis et al., 2001a, 2004). Large differences and a wide range of solutions exist between each, as a result of uncertainty in field results and poorly constrained forcing functions (Wanninkhof and McGillis, 1999). One of the main and unanimous conclusions is that as wind speed increases, the transfer velocity
also increases. However, if the relationship between wind speed and transfer velocity is nonlinear, large uncertainties are obtained for moderate to high wind speeds (McGillis et al., 2001b).

Figure 2.6, is a plot of parameterizations and relationships developed between wind speed and transfer velocity from past experimental work, all of which are discussed in further detail in Sections 2.5.1 through 2.5.7.

\[ k_{660} = k_w \left( \frac{660}{Sc} \right)^{-n} \]  

\[ (2.26) \]

The gas transfer velocity for CO\textsubscript{2} can be normalised for salt water at a temperature of 20\degree C by means of the *Schmidt number* dependence proposed by Wanninkhof (1992).
which is discussed in Wanninkhof (1992). $n$ is the hydrodynamic variable adjusted for flow condition. It is usually, $n = 0.5$.

$$Sc = 2073.1 - 125.62 \ T + 3.6276 \ T^2 - 0.043219 \ T^3$$  \hspace{1cm} (2.27)

where $T$ is the water temperature in $^\circ$C.

Air side values of $Sc$ tend to be near 1, and gases with solubilities less than 33, like CO$_2$ will encounter a greater transfer resistance in the sea water (Fairall et al., 2000). The gas transfer velocity is often displayed as $k_w$, where the $w$ signifies greater influence from the water-side molecular sublayer.

Much experimental work has been conducted, trying to resolve the relationship between $k$ and wind speed. Such work is discussed in further detail below.

### 2.5.1 Liss and Merlivat 1986 Relationship

Liss and Merlivat (1986) examined gas transfer rates across the air-sea boundary. Transfer velocities were investigated using experimental work that was conducted in a laboratory using a wind tunnel (Broecker and Siems, 1984) and data that were obtained in the field. Field data were collected during the study (Wanninkhof et al., 1985), where the tracer sulphur hexafluoride (SF$_6$) was intentionally added to a lake. From these studies, Liss and Merlivat (1986) showed that the relationship between wind speed and gas transfer velocity could be divided into three separate regimes, where different physical processes appeared to be controlling gas exchange. These regimes were: (1) Smooth Surface Regime, (2) Rough Surface Regime and (3) Breaking Wave (Bubble) Regime.

During the smooth surface regime, the water surface was generally smooth with very few waves. Wind speeds were in the region of 0 - 5 m/s (±3 m/s) and gas transfer velocity increases very gradually. Between 5 and 10 - 12 m/s, the rough surface regime was observed. Here the water surface was covered with waves, but not rough enough for the breaking of waves to be common. During this regime, the gas transfer velocity increased at a higher rate. This was as a result of the presence of waves. During the wave breaking regime, where wind speeds were greater than 10 m/s, the creation of bubbles became common due to wave breaking, which enhanced the gas transfer rate.
The following three relationships were proposed and are shown in Equations 2.28, 2.29 and 2.30 for the variation of gas transfer velocity with wind speed.

\[ k_w = 0.17(u), \text{ for } u \leq 3.6 \]  
\[ k_w = 2.85(u) - 9.65, \text{ for } 3.6 < u \leq 13 \]  
\[ k_w = 5.9(u) - 49.3, \text{ for } u > 13 \]

where \( k_w \) is the gas transfer velocity and \( u \) is the wind speed measured at a height of 10 m. It has been stated that the Liss and Merlivat relationship could be closely approximated by a quadratic dependence in the range from 0 - 15 m/s, of the form \( k = 0.177u^2 \) (Wanninkhof, 1992).

### 2.5.2 Wanninkhof 1992 Relationship

Wanninkhof (1992) also investigated the relationship between gas transfer velocity and wind speed, using a quadratic dependence. A “proportionality factor, \( f' \)”, where \( k_{av} = f(u_{av10}^2) \), in the relationship between the two parameters was determined using the bomb- and natural- gas exchange data (Broecker et al., 1985, 1986), and the Red Sea bomb- \(^{14}C\) data (Cember, 1989). One resulting equation was Equation 2.31 \(^{14}C\)

\[ k_{av} = 0.39(u_{av}^2)(Sc/660)^{-0.5} \]  

where \( k_{av} \) is the gas transfer velocity, \( u_{av} \) is the long-term averaged wind speed. This equation is only applicable when the wind speed measurements are “long-term averaged”. The variance of wind speed during the measurement interval can be of significant influence on the gas transfer velocity (Wanninkhof, 1992). As a result, gas transfer velocities measured over long time periods with variable winds will be higher than those transfer velocities which are measured instantaneously. For instantaneous measurements under steady wind speeds, the resultant equation was Equation 2.32:
\[ k = 0.31(u^2)(Sc/660)^{-0.5} \]  

(2.32)

where \( k \) is the gas transfer velocity and \( u \) is the steady wind speed. The relationship for long-term averaged wind speed and steady wind speed yielded gas transfer velocities that differ by 30\%, for the same average wind speed (Wanninkhof, 1992). This quadratic relationship satisfied the global \(^{14}\)C constraint.

### 2.5.3 Wanninkhof and McGillis 1999 Relationship

Results from the GasEx-98 survey were studied and the possibility of a cubic relationship between wind speed and gas transfer velocity was explored. The theoretical basis for the dependency was based on the idea that at low wind speeds, the gas transfer velocity was impaired by surfactants on the sea surface (Wanninkhof and McGillis, 1999). Also, at high wind speeds the gas transfer velocity was enhanced due to bubbles. The derived equation for short-term/steady winds was Equation 2.33:

\[ k = 0.0283 u_{10}^3 (Sc/660)^{-1/2} \]  

(2.33)

where \( k \) is the normalised gas transfer velocity for CO\(_2\), \( u_{10}^3 \) is the wind speed measured at a height of 10 m and \( Sc \) is the Schmidt number. For long term averaged wind speeds, Equation 2.34 was applicable:

\[ k_{av} = [1.09 u_{10av} - 0.333 u_{10av}^2 + 0.078 u_{10av}^3](Sc/660)^{-1/2} \]  

(2.34)

The long term relationship was strongly dependent on the assumption of a Weibull wind distribution at high winds. Both relationships satisfied the global isotopic constraints (Wanninkhof and McGillis, 1999). These constraints are gas transfer velocity values that have been calculated from isotopic tracers that exist in both the ocean and the atmosphere, which are discussed further in Section 2.6.6.

However, in order to validate this cubic dependency, more covariance studies are necessary (Wanninkhof and McGillis, 1999).
2.5.4 McGillis et al. 2001 Relationship

Data collected during the GasEx-98 survey were analyzed, in order to try and establish a relationship between wind speed and gas transfer velocity. The GasEx survey was conducted during June 1998 in the North Atlantic within a strong CO₂ sink region (McGillis et al., 2001a). The eddy covariance technique was used to directly measure CO₂ fluxes. Other techniques including the profile and dual tracer techniques were also implemented. The cruise provided an opportunity to compare each of the methods against each other. These other techniques will be discussed further in Section 2.6.

Using the calculated flux data, the carbon dioxide concentration difference and solubility data in Equation 2.23, gas transfer velocity data were calculated. When the transfer data was plotted against wind speed, the best fit for the plotted data was Equation 2.35:

\[ k_{660} = 3.3 + 0.026 \ u_{10}^3 \]  \hspace{1cm} (2.35)

where \( k_{660} \) is the normalised gas transfer velocity and \( u_{10} \) is the wind speed measured at a height of 10 m. This relationship was in general agreement with isotopic and indirect method results.

2.5.5 Nightingale et al. 2000a and 2000b Relationships

Data were collected during a study in the Pacific Ocean called IronEx2. The dual tracer technique, discussed further in Section 2.6.7, was used to analyze air-sea gas exchange. Gas transfer velocity values were derived from the change in the ratio of both tracers. Wind speed and gas transfer velocity were parameterized by equation 2.36

\[ k_{600} = 0.24 \ U_{10}^2 + 0.061 \ U_{10} \]  \hspace{1cm} (2.36)

where \( k_{600} \) is the transfer velocity normalised to a Schmidt number of 600 and \( U_{10} \) is the wind speed at a height of 10 m. It was mentioned that some scatter was observed in the data set. However, this scatter was put down to a combination of uncertainty in \( k_w \) and \( U_{10} \), variability in the wind speed data during the period of measurement
and influences from other parameters, aside from wind speed. It was noted that the possibility of algal blooms and natural surfactants impacting on transfer velocities was not observed.

Research was also conducted into air-sea gas exchange using the dual tracer technique (Nightingale et al., 2000b). Experimental work was carried out in the North Sea during February 1992 and 1993. Applying a best fit to the dual tracer data, the relationship between wind speed and gas transfer velocity was parameterized by Equation 2.37

\[ k_{000} = 0.222 \ U_{10n}^2 + 0.333 \ U_{10n} \]

2.5.6 McGillis et al. 2004 Relationship

Data were collected during the GasEx2001 survey investigating CO\(_2\) fluxes and trying and quantify the relationship between the transfer velocity and wind speed (McGillis et al., 2004). The GasEx2001 survey was a 15 day cruise conducted in the equatorial Pacific near 125°W and 3°S. A combination of ships, buoys and drifters, which were equipped with various instrumentation capable of measuring oceanic and atmospheric parameters, were used during the survey.

\( \text{CO}_2 \) concentrations in the ocean were higher than those in the atmosphere: the region was a carbon dioxide source for the atmosphere. The area experienced low-intermediate wind speeds, the average wind speed over the course of the survey was 6.1 \( \pm \) 1.3 m s\(^{-1}\). Other physical processes, including wind speed were observed to influence the rate of transfer of CO\(_2\) between the ocean and the atmosphere. Diurnal influences were taken into account when studying the exchange of carbon dioxide across the air/sea interface. Overall, results from the GasEx2001 survey showed that air-sea CO\(_2\) exchange was slightly higher than other experimental studies at low wind speeds.

A parameterisation between wind speed and gas transfer velocity was calculated from data collected during the survey, displayed in Equation 2.38

\[ k_{660} = 8.2 + 0.014 \ u_{10N}^3 \]
where $k_{660}$ is the normalised gas transfer velocity and $u_{10,N}$ is the wind speed measured at a height of 10 m.

### 2.5.7 Ho et al. 2006 Relationship

Ho et al. (2006) conducted the SAGE (SOLAS Air-Sea Gas Exchange) Experiment in the south western Pacific Ocean, off the eastern coast of New Zealand at roughly 46.5°S and 172.5°E. Gas transfer velocities were measured using the $^3$He/SF$_6$ dual tracer technique. Past experiments that have tried to quantify the relationship between wind speed and gas transfer velocity have been unable to consistently measure data at high wind speeds ($>$11.3 m s$^{-1}$). The SAGE Experiment was able to circumvent this issue, as portions of the experimental work were conducted during periods of high wind speeds ($>$15 m s$^{-1}$).

Results from the experimental work revealed a quadratic relationship between wind speed and transfer velocity. The parameterization developed is shown in Equation 2.39:

$$k_{600} = (0.266 \pm 0.019)u_{10}^2$$

(2.39)

where $k_{600}$ is the normalised transfer velocity and $u_{10}$ is the wind speed at a height of 10 m. Overall, the relationship between wind speed and gas transfer velocity derived from data recorded during SAGE was in good agreement with previous experimental work conducted in both the open ocean and coastal seas, as displayed in Figure 2.6.

### 2.6 Other Micrometeorological Techniques

Aside from the eddy covariance technique, as sometimes environmental conditions may prevent its application, there exist other possible methods that can be used for measuring and studying CO$_2$ fluxes and air-sea gas exchange. These include:

- Eddy Accumulation Technique
- Relaxed Eddy Accumulation (REA) Technique
- Bowen Ratio Method
• Aerodynamic Method
• Profile Method
• Tracer Techniques - Geochemical and Deliberate

2.6.1 Eddy Accumulation Technique

The eddy accumulation technique is similar to the EC technique. It is based on the concept of measuring the turbulent transportation of gases. However, it samples updrafts and downdrafts separately, where the sampling is proportional to the strength of the updraft and downdraft. The updraft average concentration is then subtracted from the downdraft average concentration and the net flux is obtained. Some of the main challenges for the eddy accumulation technique is to make sure that the sampling is done proportionally to the strength of the updraft and downdraft (Burba and Anderson, 2007). Also, that any small changes in concentration need to be measured accurately.

2.6.2 Relaxed Eddy Accumulation (REA) Technique

This method is a modification of the previous technique. It is described as a conditional sampling method where air is pumped into reservoirs depending on the vertical velocity. Reservoirs are selected based on a vertical velocity threshold, \( w_0 \), but the filling rate is constant. The flux is computed from the difference in concentration difference between “up” and “down” reservoirs (Fairall et al., 2000). One of the main challenges of the REA technique is to make sure that empirical coefficients are evaluated correctly, that corrections are properly applied and that small changes are sampled appropriately (Burba and Anderson, 2007).

2.6.3 Bowen Ratio Method

This technique is a relatively old and well-established technique. Fluxes are calculated from surface energy budget components and are assumed to be proportional to the ratio of temperature and humidity gradients between two different heights. When using the Bowen Ratio method, the assumption that turbulent exchange coefficients
for heat, water and gases are similar is required. One of the main challenges to this technique is related to the fact that the exchange coefficients are often not similar between temperature, water vapour and other gases, but rather gas-specific and may change dramatically (Burba and Anderson, 2007).

2.6.4 Aerodynamic Method

Using this method, the flux is computed from the vertical profiles of wind speed and gas concentration. Turbulent exchange coefficients for momentum and any gas of interest are either assumed to be similar, are measured or are modeled. One of the main difficulties associated with the aerodynamic method is that difficulties exist in determining the turbulent exchange coefficient for momentum. Also, the fact that the turbulent exchange coefficient between momentum and gases is not always similar. Atmospheric stability is also an issue, as it can significantly affect the calculated flux (Burba and Anderson, 2007).

2.6.5 Profile Method

The flux profile method involves measuring the gas of interest in the atmosphere as a function of height above the surface. It has been mentioned that the profile method is normally not used for measuring air-sea gas transfer (Liss and Merlivat, 1986). It was also stated that it was a poor method because there is very little gradient to measure in the overlying air of the ocean (Deacon, 1977). For CO$_2$ transfer between the air and ocean, a typical gradient of concentration in the air would be around 0.05 ppm between 1 and 10 m above the sea. This is a tiny percentage of the atmospheric concentration and quite difficult to measure precisely. However, with advances in technology, the flux profile method offers several advantages in determining air-water fluxes, as it averages over small spatial and temporal scales (McGillis et al., 2004).

2.6.6 Geochemical Tracers

Isotopic tracers can be used to quantify the movement of gases across the air-sea interface. These tracers include $^{14}$C, $^3$He/$^4$He or $^{222}$Rn/$^{226}$Ra (Jahne and Haußecker, 1998). It has been summarised how $^{14}$CO$_2$ from both natural and bomb sources can be used
to obtain global-average values for the gas transfer velocity of carbon dioxide (Broecker and Peng, 1974, 1984). These values average globally to about 20 cm hour\(^{-1}\). One obvious disadvantage of this method is that this figure is averaged globally and does not take into account seasonality changes or meteorological variables such as wind speed, thus making this indirect measuring technique unsuitable for the study of air-sea gas transfers.

### 2.6.7 Purposefully Injected Tracers

By injecting certain tracers on purpose, air-sea gas exchange can be studied. This technique is known as the “dual tracer technique” (Watson et al., 1991). This method was based on the release of quantities of sulphur hexafluoride (SF\(_6\)) and 3-helium (\(^3\)He) into the mixed layer. The inert gases are injected into the body of water at a constant ratio. These specific tracers were used because they could be measured at very low concentrations and their diffusivities are dissimilar, \(^3\)He diffuses at a faster rate than SF\(_6\) (McGillis et al., 2001b). Gas transfer velocities across the air-sea interface could then be calculated from the ratio change in the two tracers over time. Transfer velocities could be calculated using the equation:

\[
k_{3\text{He}} - k_{\text{SF}_6} = \ln\left(\frac{r_1}{r_2}\right) \frac{h}{(t_2 - t_1)}
\]  

(2.40)

where \(r_i\) is \(^3\)He/SF\(_6\) at a time \(t_i\) (after background concentrations have been deducted). \(h\) is the mean depth of the water column. The gas transfer velocity for each tracer is related to power law dependence (\(n\)) on the Schmidt number, displayed through the equation

\[
k_{3\text{He}}/k_{\text{SF}_6} = S_{c3\text{He}}/S_{c\text{SF}_6}
\]  

(2.41)

Previous studies have used the dual-tracer technique (Watson et al., 1991; Wanninkhof et al., 1993, 1997; Nightingale et al., 2000a; McGillis et al., 2001a; Wanninkhof et al., 2004; Ho et al., 2006).
Chapter 3

Instrumentation

During the course of this research, a variety of instrumentation was used to measure various parameters, both on land and at sea, necessary for the work undertaken. Information on each of these instruments, both on the R.V. Celtic Explorer and at the Mace Head Research station, are outlined in the following sections.

3.1 Celtic Explorer

The R.V. Celtic Explorer is a ship at the cutting edge of marine research in Ireland. The vessel is excellently designed, fitted with the latest electronics and scientific equipment, making the ship ideal for conducting research into carbon dioxide concentrations in Irish waters. Numerous research surveys are conducted each year by various institutions covering a variety of topics including: fisheries, oceanography, buoy handling, acoustics and environmental sampling. Waters surveyed include the Irish continental shelf, Porcupine Bank, Celtic Sea, Irish Sea, North Sea, English Channel and Atlantic Ocean.

The ship is 65.5 m in length and 15 m in width. A dry laboratory at a size of 75 m², containing various electronic equipment can be found on board. For any sea-water orientated work, there is a wet/fish lab, chemistry lab and water lab, totalling a size of 70 m². A picture of the vessel is displayed in Figure 3.1.
3.1.1 Pro-Oceanus Systems Inc. (PSI) CO$_2$ Pro

This particular instrument was one of the core pieces of instrumentation used during the course of this research Figure (3.2). It is designed to measure the amount of carbon dioxide in sea-water.

The device is manufactured by Pro-Oceanus Systems Inc., located in Bridgewater, Nova Scotia, Canada. It is a compact, light-weight pCO$_2$ sensor that is designed for use on moorings, in underway mode, in the laboratory or on a research vessel.
A schematic of the flow paths inside the pCO$_2$ instrument are shown in Figure 3.3. The pCO$_2$ instrument operates under the idea that as the gas transfer interface of the instrument is surrounded by sea-water, gas from the surrounding water exchanges across the interface. Gas that travels through the interface passes through a humidity sensor, solenoid valve (AZPC), circulation pump and flows into an IR (infra red) optical detector, where the amount of carbon dioxide in the gas sample is measured. The sample of gas leaves the detector, passing through a second solenoid valve (AZPC) and re-enters the gas transfer interface, where it can be further equilibrated. The path of the gas flow is outlined by the red arrows in Figure 3.3.

**Figure 3.3: Schematic of the pCO$_2$ instrument**

### 3.1.1.1 Gas Transfer Interface

When the Pro Oceanus pCO$_2$ instruments are manufactured, the gas transfer interface is normally located inside the instrument, in a small space completely separate from the chamber that houses all of the instrument electronics. This space is on the left side of the instrument as shown in Figure 3.5. Water is pumped into and out of the chamber via an inlet and outlet, pictured in Figure 3.2, with the aid of a Seabird pump.
The pCO$_2$ sensors installed on board the R.V. Celtic Explorer had the gas transfer interface installed externally, thus removing the need for a pump. The support structure for the gas transfer interface has copper wiring inter-weaved through itself and around the interface. The actual interface is a gas permeable tubular membrane made from silicone, which has a very high permeability for gases. This high permeability is important as it helps with the flow of CO$_2$ from the sea-water to the infra-red optical cell. A picture of the support structure and gas transfer interface is displayed in Figure 3.4.

Figure 3.4: Support structure for the gas transfer interface (on right side of instrument)

The copper wiring serves two purposes. First, it holds the silicone tube away from surfaces so that the water and dissolved gas can access the whole tubing area. Second, copper inhibits biofilm formation on or around the interface. Gas passes through the the silicone membrane by a combination of gas solubility and diffusion though the membrane. The difference in CO$_2$ concentration between the sea-water and the air inside the membrane is the main reason for the transfer of CO$_2$ across the interface.

If the instrument is manufactured with the interface internally, the use of the pump serves some additional purposes. The flow of water through the chamber shear thins the mass transfer boundary layer next to the interface. The resistance to gas transfer through the interface is roughly half due to solution and diffusion through the silicone...
membrane and half due to the diffusion boundary layer in the water next to the interface surface. By shear thinning the boundary layer, the equilibration of gases occurs more quickly. Also, use of the pump reduces biofilm build up as it would separate any biofilm on the surface of the membrane. Whether the gas transfer interface is internally or externally fitted to the instrument, the end equilibration result would not change, only the response time and potential for biofouling differs.

3.1.1.2 Infrared Gas Analyzer and Detector

The instrument is factory calibrated from 0 - 600 ppm CO$_2$ as standard, unless otherwise specified. The PSI CO$_2$ Pro is fitted with a non dispersive, infrared gas analyzer and features onboard sensors that allow automatic pressure, temperature and humidity compensation via code in the sensor board EPROM.

During fabrication the detector is calibrated against known mixtures of carbon dioxide in dry air in order to get the important non-liner relationship between sensor readings and CO$_2$ ppm. The calibration is performed at a known cell pressure and temperature. The company uses a three segment least-square fit to quadratic equations for this linearization. This equation then provides an uncorrected CO$_2$ ppm for each raw sensor output.

During operation, (1) a temperature correction is applied to the uncorrected CO$_2$ ppm. Normally the cell is thermostatically controlled to 40 °C, so this factor is really only important if the thermostat is not controlling properly. Next, (2) a pressure correction is applied to account for the pressure present in the sample cell, and the difference between the current pressure and the pressure present in the cell during calibration. Since higher pressure puts more CO$_2$ molecules between the IR source and the detector, the pressure correction is quite important. This correction for pressure is empirically derived so that it includes both ideal gas law effect and the gas pressure broadening effect on infrared absorption.

Next, (3) the measurement is corrected for the presence of water vapour. There is no overlap between the CO$_2$ and H$_2$O absorption lines at the wavelengths used by the sensor, so there is no direct effect of water vapour on carbon dioxide readings. However, there are effects that do change the output of the optical detector in the presence or
absence of water vapour. There is a dilution effect when adding water vapour to a given concentration of CO₂ in dry air that would reduce the apparent CO₂ reading and there is a foreign gas broadening effect when adding water vapour to a given concentration of CO₂ in dry air that increases the apparent CO₂ reading.

These two effects somewhat offset each other - the residual effect on apparent CO₂ is about 1.5% of the CO₂ reading from dry to saturated at room temperature. The water vapor corrections are applied to the uncorrected CO₂ reading to account for the foreign gas broadening effect and the CO₂-free air offset. The dilution effect is not corrected for, so that the output of the detector is given in moles of CO₂/total moles of gas.

Averaging is applied to the outputted values from the detector in order to improve resolution and reduce fluctuations. The instrument uses an exponential running average algorithm with a time response to a step change of 5.6 seconds to 66% of the final value and 26.4 seconds to 99% of the final value. If a new CO₂ reading differs from the current running average by more than the AVLIMIT value, a new running average is begun. Thus, when the CO₂ concentration is changing rapidly, the averaging is eliminated and the instrument can track changes at the basic instrument data rate of 1.6 seconds. The default AVLIMIT is 0.3% of full scale or 1.8 ppm for a 600 ppm instrument.

3.1.1.3 Automatic Zero Point Calibration - AZPC

In order for the instrument to make measurements accurately, it can automatically zero itself. The Automatic Zero Point Calibration (AZPC) procedure is initiated when the detector board inside the instrument has a power interruption and the solenoid valves are opened. During the AZPC, the gas stream is routed through a chamber which contains the chemical ascarite (HNaO). Ascarite strips the air sample of carbon dioxide, providing a 0 ppm CO₂ measurement.

The CO₂ AZPC measurement compensates for changes in optical cell performance and significant changes in environmental parameters such as gas stream temperature. It also minimizes the effects of sample cell contamination, changes in detector sensitivity and pre-amplifier gain. The AZPC is used in determinations of carbon dioxide readings until a new AZPC is performed. It was recommended that the AZPC be performed
at least once a day, more often when conditions such as water temperature varied significantly. During this experimental work, an AZPC measurement was conducted every three hours. At the beginning/end of each survey, the ascarite was inspected, to make sure that it did not need to be replaced. As the ascarite was exhausted, it changed colour. A picture of the absorbent chamber inside the instrument is displayed in Figure 3.5.

![Chamber containing ascarite inside the instrument](image.png)

**Figure 3.5:** Chamber containing ascarite inside the instrument

### 3.1.1.4 Instrument Start-Up and Data Output

When power is applied to the instrument, it must first go through an initialization process. During the first 40 seconds, the sensor carries out an internal calibration of the electronics. Once this is completed, the optical cell temperature is checked. The instrument warms the optical cell until it reaches 40°C. This temperature is selected because it is approximately 15°C above the average expected water temperature. If the temperature difference between the detector and sea-water was too high, the sensor would take longer to warm up and consume more power. Then the instrument performs an AZPC, as described in Section 3.1.1.3. Once all of these steps are completed, the sensor starts outputting data. It makes a measurement every 1.6 seconds. An example of the data output string by the instrument is displayed in Table 3.1.
Table 3.1: Sample data string output from the PSI CO$_2$ Pro

<table>
<thead>
<tr>
<th>MT</th>
<th>Zero</th>
<th>CO2M</th>
<th>CO2AV</th>
<th>ANLT</th>
<th>MB</th>
<th>HT</th>
<th>ATMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>47380</td>
<td>44766</td>
<td>306.29</td>
<td>39.7</td>
<td>18.8</td>
<td>21.5</td>
<td>1050</td>
</tr>
</tbody>
</table>

- **MT (Measurement Time Stamp)** - The date, month, hour, minute and second are displayed. However, during this research, the pCO$_2$ instruments did not display a timestamp. There was no particular reason for this set-up. The timestamp was created manually, which is explained below.

- **Zero** - This reading is the result from the most recent AZPC (Automatic Zero Point Calibration). PSI recommend that the AZPC reading should be above 44000.

- **CO2M** - This is the raw output of the optical detector. It is exponentially proportional to the number CO2AV, the number of CO$_2$ molecules between the infrared source and detector.

- **CO2AV** - CO$_2$ concentration (xCO$_2$) in ppm. Corrected for temperature, pressure and humidity.

- **ANLT** - Optical cell temperature. Should be around 40 °C.

- **MB** - Humidity sensor reading in millibars.

- **HT** - Humidity sensor temperature.

- **ATMP** - Gas stream pressure in millibars.

A computer program was installed on the PC where the sea-water pCO$_2$ concentration data was logged. This program operated automatically and split the data into hourly files at the top of each hour. As a result, the timestamp could be easily created for each hourly file.

The output of the detector, xCO$_2$ is the number of molecules of carbon dioxide divided by the total number of gas molecules in the sample cell. Therefore, the output is in ppm. pCO$_2$ concentrations, which have the units µatm are obtained by using Equation 3.1.
3.1.1.5 Housing Information

The housing of the instrument is protected with zinc anodes which help in reducing corrosion. The CO$_2$ Pro has a unique omni-position ACME thread mason jar closing mechanism. All of the instruments electronics are located on the inside of the instruments housing. These electronics can be accessed by screwing off the mason jar ring, and sliding the endcap out of the housing. The endcap is attached to the electronics drawer, which supports all of the instrument’s electronics. The mason jar ring and endcap are made from Delrin, whereas the housing is made from aluminium. The mason jar ring is visible in Figure 3.2, on the left side of the instrument. The handles that can be used to slide the endcap and electronics drawer are also displayed in Figure 3.2.

3.1.1.6 Instrument Specifications

The specifications and characteristics of the instrument, according to the manufacturer, are displayed in Tables C.1, C.2 and C.3 in the appendices.

Note: Large portions of 3.1.1 were obtained from Johnson and Scholefield (2010) or from direct contact with Pro-Oceanus Systems Inc. (PSI).

3.1.2 pCO$_2$ Instrument Tank

For this research, two (PSI) CO$_2$ Pro instruments were installed on board the R.V. Celtic Explorer (CE). Both instruments were housed inside a stainless steel tank in the wet laboratory inside the vessel. The tank had the dimensions 80 cm in length, 50 cm in width and 75 cm in height. Pictures of the tank with the pCO$_2$ sensors inside are displayed in Figures 3.6 and 3.7.

As the ship departed port for each survey, the non-toxic sea-water supply system would be switched on. This system allows sea-water to be pumped on board and sampled for various purposes. The inlet for the non-toxic system was located at the bow of the vessel at a depth of approximately 5 m. Sea-water would flow into the tank.
through tubing connected to a valve on the wall in the water lab. The sea water would flow through a filter and a flowmeter, both are shown in Figure 3.6. The filter ensured that no large items such as shells, rocks, fish etc. were brought into the tank, that could possibly damage the instruments. The flowmeter allows water flowing into the tank to be set to between 5 and 10 litres/min. A valve on the wall allows the flow to be controlled as required. There are two outlets on the tank, displayed in Figure 3.6, which allow the sea-water to leave the tank and be emptied back overboard. The tank is fitted with a stainless steel cover, which is firmly attached before each survey. The cover reduces the possibility of CO$_2$ from the surrounding air entering water inside the tank and altering the concentration of carbon dioxide in the sea-water surrounding the sensors.

Both instruments were secured inside the tank by two separate black brackets, pictured in Figure 3.7. These brackets clamped onto the sensors and held them in place in the vertical axis. Both sets of black brackets, were held in position inside the tank by bolts attached to a small stainless steel ledge. This ledge was welded onto the wall of the tank. When the tank would fill with sea-water, the height of the water would reach above the black brackets, thus ensuring that the gas transfer interfaces of both pCO$_2$ sensors were submerged at all times. A Seabird SBE39 temperature instrument was also installed inside the tank, pictured in Figure 3.7. This sensor provides the temperature of the sea-water flowing through the tank.

Power was supplied to all of the instruments from an electronics box that was
attached to the wall inside the wet laboratory. Voltages were appropriately converted
inside the electronics box, before power was sent to the instruments. As the pCO₂
sensors had no internal data loggers, recorded data was logged on a PC in the dry lab
onboard the vessel.

Each time the Celtic Explorer returned to port, the tank was opened, cleaned and
filled with fresh water, so the instruments were ready for the next survey. Some silt
and fine particulate would enter the tank during the previous survey and was removed.
During every alternate port call, the ascarite inside the instruments was inspected, to
visually ensure it was not exhausted.

3.1.3 General Oceanics pCO₂ System

Another pCO₂ system was also installed on the R.V. Celtic Explorer from General
Oceanics Inc. in Miami, FL, U.S.A. The instrumentation was called the UW (Under-
Way) pCO₂ system. The pCO₂ system consisted of two core components: a dry-box
and a wet-box. A third component, a deck-box could also be installed. Both the
dry-box and wet-box are pictured in Figure 3.8 and Figure 3.9.

![Figure 3.8: General Oceanics pCO₂ system drybox](image1)

![Figure 3.9: General Oceanics pCO₂ system wetbox](image2)

The dry-box, so called because no water passes through it, housed all of the neces-
sary electronics needed in order to operate the system. These included a laptop: used
to start the system and alter various settings and a LI-COR CO₂ gas analyzer: used
to calculate the concentration of carbon dioxide in the air samples passing through it.
Sea-water passed through the wet-box of the pCO$_2$ system. More specifically, the sea-water flowed through an equilibrator, which was closed off from the surrounding air, at a rate of around 2 L/min. Water entered the equilibrator through a conical nozzle, which created a spray, enhancing the transfer of CO$_2$ from the sea-water into the headspace of the equilibrator. Headspace gas is then circulated through the system to the gas analyzer, before returning to the equilibrator. The gas is dried before it is sent to the LI-COR gas analyzer, where the xCO$_2$ calculations are made. Atmospheric CO$_2$ concentration measurements are also conducted by the system. A long piece of tubing, connected to the dry-box, allowed air to be sampled at the bow of the ship.

The pCO$_2$ system was also connected to a set of gas standards. The system is programmed to take measurements from the tanks at certain intervals, ensuring high levels of accuracy in all measurements made by the LI-COR gas analyzer.

### 3.2 Mace Head Research Station

The Mace Head research station is located near the village of Carna, Co. Galway (53° 20’N and 9° 54’W). It is perched on the extreme west coast of Ireland, making it an ideal place for conducting atmospheric and oceanographic research.

![Figure 3.10: Location of the Mace Head Research Station](image-url)
3.2.1 Eddy Covariance (EC) Instrumentation

As already mentioned, sophisticated instrumentation is absolutely necessary in order to attempt and successfully measure vertical fluctuations in the atmosphere. Instrumentation normally used when using the EC technique include a sonic anemometer and a gas analyzer. During this research, a LI-COR-7500 IRGA and a Gill Anemometer were used for these purposes respectively.

These instruments need to make measurements rapidly, so that they cover all frequency ranges. However, they also need to be very sensitive to the small changes in the quantity of interest. They should not distort larger eddies with a large support structure, which allows them to record data at great heights. The tower which supports these instruments should not obstruct the flow or shadow the sensors from the wind. They should be aerodynamic enough to reduce the possibility of the creation of smaller eddies, so that they can measure carefully at heights close to the ground (Burba and Anderson, 2007). The required support structure and instrumentation is described in detail in the following sections.

3.2.1.1 Mace Head Tower

The majority of experimental work was conducted at the Mace Head Research Facility, mentioned above. The support structure (tower) used to support the eddy covariance instrumentation was located at Mace Head, approximately 90 m from the shoreline (50 m at high tide). It was manufactured from aluminium, and had a height of approximately 22 m. It is supported by a series of guy-wires to maintain stability. A picture of the tower can be seen in Figure 3.11.

The sonic anemometer and the infra-red gas analyzer (IRGA) were installed on the tower at the end of an aluminium boom, approximately 2.5 m from the edge of the tower, in order to minimize flow distortion. The boom was pointing outwards from the tower in the prevailing wind direction. Additionally, a secondary support boom was used and attached to the main boom. This reduced the influence of movement and vibrations on the instrumentation.
3.2.1.2 \textbf{CO}_2/\text{H}_2\text{O} \text{ NDIR Gas Analyzer}

The \text{CO}_2/\text{H}_2\text{O} \text{ NDIR Gas Analyzer} used in this experimental work was a LI-COR LI-7500 manufactured by LI-COR Biosciences based in Nebraska, U.S.A.. The LI-7500 is a high performance, non-dispersive, open path infrared \text{CO}_2/\text{H}_2\text{O} analyzer designed for use in eddy covariance flux measurement systems (Licor, 2000). It can measure the concentration of carbon dioxide and water vapour in the atmosphere. An image of the LI-7500 as part of the eddy covariance system at Mace Head is displayed in Figure 3.12. Some of its important features include:

- Simultaneous measurements of \text{CO}_2 and \text{H}_2\text{O} in the free atmosphere.
- High speed measurements. Internal 150 Hz measurements are digitally filtered to provide a true 5, 10, or 20 Hz bandwidth.
- Withstands exposure to rain or snow without damage to calibration shift.
- Versatile output options: DAC’s, SDM, and RS-232
- Software provides for easy user calibration and configuration

A beam of infrared radiation travels between two sapphire windows on the instrument. The beam is modulated at 152 Hz by a chopper wheel so that it alternates...
Figure 3.12: A picture of the sonic anemometer and the CO$_2$ and H$_2$O gas analyzer

continuously between absorbing and non-absorbing wavelengths for each gas. CO$_2$ and water vapour absorb infrared radiation at different and specific wavelengths. These wavelengths are 2.59 $\mu$m and 4.26 $\mu$m for H$_2$O and CO$_2$ respectively. The absorbance of either quantity is calculated by Equation 3.2. Digital signal processing techniques demodulate the signal and convert the raw values into number density, after making a correction for cross-sensitivity.

\[
\alpha_i = \left(1 - \frac{A_i}{A_{io}}\right)
\]

(3.2)

- $\alpha_i$ - absorbance
- $A_i$ - power received from the source in an absorbing wavelength for gas $i$
- $A_{io}$ - power received from the source in a reference wavelength that does not absorb gas $i$
There is a small pressure dependency for both gases, and a small temperature
dependency for CO\textsubscript{2} (discussed further in Section 6.3.3.4) when converting absorbances
to mass density that is accounted for using a pressure and temperature sensor inbuilt
into the electronics of the control box. The LI-7500 is mounted at an angle of 15\degree,
as shown in Figure 3.12, so that the possibility of precipitation accumulating on the
sapphire windows is reduced.

Another part of the LI-7500 instrumentation, is the control box which houses
the unit’s high speed Digital Signal Processor (DSP). The DSP has linearised, user-
configurable 16-bit Digital to Analogue Converters (DAC), with an output signal that
is user scalable from 0 - 5 V DC, updated around 300 times per second. Each DAC can
be configured by specifying the source channel that drives the analogue signal, in our
case that would be carbon dioxide. Then values from the channel would correspond to
values between 0 V and 5 V. Over the course of this research, 0 V corresponded to 0
mmol/m\textsuperscript{3} for both CO\textsubscript{2} and H\textsubscript{2}O. 5 V corresponded to 25 mmol/m\textsuperscript{3} for CO\textsubscript{2} and 1000
mmol/m\textsuperscript{3} for H\textsubscript{2}O. The equation for converting between mmol/m\textsuperscript{3} and µmol/mol is
in Appendix D. These values were selected because all expected measurement ranges
would be included in observed data sets. Ranges were also chosen to start from 0 due
to the fact that the instrument was calibrated using a zero gas as well as a span gas.
The calibration procedure is explained in further detail in Section 3.2.1.4.

The DAC output of the LI-7500 has a fixed throughput delay of 240 ms. This can
be increased in steps of 6.5 ms to minimize the offset with other instruments and allow
for easier synchronisation, i.e. sonic anemometer. The delay was increased to 298.5 ms
(3 execution intervals at 10 Hz) by setting the delay count to 9 (9 x 6.5 ms = 58.5 ms),
giving a smaller unaccounted lag of 0.0015 s.

Selectable output bandwidths of 5, 10 or 20 Hz (with response times of 0.1 s, 0.05
s and 0.025 s) were available, and determined the signal averaging done by the digital
filter. The LI-7500 manual recommends that the analyzer should sample at a frequency
greater than or equal to twice the bandwidth. As the eddy covariance system was set
to a sampling frequency of 10 Hz, the bandwidth was set to 5 Hz. The gas-analyzer
analogue outputs were low-pass filtered to remove high frequency electronic noise.

Note: Section 3.2.1.2 was mostly sourced from Licor (2000) and Licor (2004).
3.2.1.3 Sonic Anemometer

The sonic anemometer, used as part of this experimental work, was manufactured by Gill Instruments Ltd, Hampshire, United Kingdom. The complete name for the instrument is the Omnidirectional (R3) Research Ultrasonic Anemometer. A picture of the instrument is displayed in Figure 3.12. During all experimental work, it was endeavored to have the sonic anemometer as level as possible to ensure accuracy.

The sonic anemometer measures three orthogonal wind velocity components in the u-direction, v-direction and w-direction. It also measures the speed of sound (SOS) in air. It is capable of making measurements at rapid frequencies, up to, and including 100 Hz. The instrument has a high resolution, range, accuracy and specifications. These are all listed in Appendix A.

The anemometer is fitted with three pairs of ultrasonic transducers, orientated differently so that they each act as a couple of transmitters and receivers. High frequency ultrasound pulses are sent between each pair during operation. The wind speed along each axis, which is the path between each transducer pair, is calculated from the length of time it takes for an ultrasound to travel in both directions between the transducers. A pair of measurements are made along each axis at a rate of 100 Hz, which is then averaged to give 10 readings per second (10 Hz).

The speed of sound measurement from the sonic anemometer uses the time of flight from all three axes, helping to reduce noise and errors, as well as giving better correlation with velocity measurements. Measuring on all three axes leads to simpler implementation because crosswind corrections can be performed within the internal software of the instrument without the need for difficult vector algebra. The sonic temperature can be calculated from the speed of sound measurements.

The sonic anemometer was positioned, as shown in Figure 3.12, so that the u-axis of the instrument was aligned in the westerly direction. The v-axis was pointed in the southerly direction. The w-axis represented the upward vertical wind direction.

Note: Section 3.2.1.3 is mostly referenced from GillInstruments (2004).
3.2.1.4 Calibration Routine

The Gill sonic anemometer did not require any calibration over the course of this experimental work. This was a considerable advantage, making it ideal for eddy covariance measurements. The instrument was factory calibrated when purchased. However, the LI-7500 needed some additional attention and calibration.

There are two types of calibration for the LI-7500: factory calibration and user calibration. The factory calibration consists of determining the values of the calibration coefficients. The user calibration (which was performed at Mace Head), consists of setting the analyzer zero and span. The accuracy of the instrument is dependent on both the factory and user calibrations.

Factory Calibration:

The calibration coefficients determined at the factory are valid for several years. The factory uses a series of thirteen working calibration gases ranging in concentration from 0 - 3000 ppm. The thirteen working standards are verified against a set of primary WMO (World Meteorological Organisation) standards known to an absolute accuracy of 0.06% or better. These calibration coefficients are obtained from a 5th order polynomial fit to the entire range of concentration from 0 - 3000 ppm.

The calibration procedure for water vapour is similar to that of carbon dioxide, except that water vapour mole fractions are generated using the LI-610 Portable Dew Point Generator. Fifteen data points between 0°C and 40°C dewpoint are used during the calibration procedure, and a 3rd order polynomial is fit to the data. These calibration coefficients determined at the factory should also be valid for several years.

User Calibration:

LI-COR Biosciences recommends that the LI-7500 analyzer be calibrated every few months, so that the instrument’s accuracy can be maintained. The sensor was calibrated on the following dates:

- May 1st 2009 - It was noted that the instrument had drifted by approximately 5 $\mu$mol/mol since the previous calibration.
- September 30th 2009 - It was noted that the instrument had drifted by approximately 1 µmol/mol since the previous calibration.

- February 17th 2010 - It was noted that the instrument had drifted by approximately 3 µmol/mol since the previous calibration.

These drifts were deemed negligible as they were extremely small and were not corrected for during this experimental work. The calibration procedure is outlined as follows:

1. The LI-7500 analyzer and control box were removed from the tower at Mace Head, and brought down to the lab at ground level. All necessary wiring and cables were also removed.

2. Power was supplied to the LI-7500 analyzer and control box via a voltage converter, which reduced the voltage from 230 V at the mains to 12 V. Red and green LED’s light up signifying that the instrument is fully powered.

3. The LI-7500 was connected to a laptop, where it could be accessed using specific software. Using this software, settings for the instrument could be inspected and changed if needed. The AGC (Automatic Gain Control) was inspected. This value should always be between 55 and 60%. If the AGC value were at 100%, the infrared beam in the optical path would be fully impeded.

4. A metal cylinder is fitted to the LI-7500 head, fully enclosing the optical path from the surrounding air. Tubing is connected between the metal cylinder and a flow meter. The flow rate of gas during the calibration was kept to around 1 litre per minute.

5. The zero was performed by attaching tubing between the flow meter and an air tank supplied from Air Products Ireland. The air had a H₂O concentration of <3ppm and a CO₂ concentration of <1ppm. The tank was opened and air was allowed to flow through the metal cylinder at a rate of roughly 1 litre/min. Then the sensor was zeroed accordingly, by clicking on the “zero” button on the software.

6. The span of the CO₂ channel was calibrated using a tank containing air of a known CO₂ concentration. This tank had a CO₂ concentration of 382.36 ppm.
The gas concentration was of the highest accuracy standards (filled by NOAA (National Oceanic and Atmospheric Association) in Boulder, Colorado). Once again air was allowed flow from the tank through to the metal cylinder at a rate of 1 litre/min. Once the readings stabilized, the “span” button was selected on the laptop. It was important to zero the instrument first and then span, not visa versa.

7. The LI-7500 head and control box were re-installed at the top of the tower and the logging program was re-started.

A picture of the calibration procedure is displayed in Figure 3.13.

![Figure 3.13: Calibration procedure of the LI-7500 analyzer](image)

The analyzer’s zero is mostly affected by temperature, and the state of the internal chemicals. The zero’s response to temperature is relatively small (typically 0.1 or 0.2 ppm per °C and 0.01 mmol/mol/°C for H₂O). Also, this drift is measured at the factory, and subsequently compensated for in software. As a result, the zero should be quite stable over several months.

The analyzer’s span is affected by both temperature and pressure as well as the state of the internal chemicals. For carbon dioxide at ambient concentrations, the span is very insensitive to temperature. Large pressure changes (40 kPa) will affect the
CO₂ and H₂O spans by <1%, for ambient CO₂ concentrations (≈ 400 ppm) and high humidities (20 mmol/mol). So, diurnal pressure variations should not be a concern.

There are two small plastic bottles located inside the LI-7500 head. These bottles contain soda lime and magnesium perchlorate. They keep the analyzer housing free from CO₂ and water vapour. These chemicals were changed on an annual basis, as per the manufacturers instructions.

Note: Some portions of Section 3.2.1.4 were sourced from Licor (2000).

3.2.1.5 DLS - Data Logging System

As both the sonic anemometer and the LI-7500 were installed in a tough and enduring environment making measurements, a reliable and sturdy data logging system (DLS) was required. The instrumentation was installed on top of the Mace Head tower at a height of 22 m and was set logging data at a rate of 10 Hz. In order to log, transmit and store the data recorded, a black weatherproof box was permanently placed at the top of the tower, shielding the DLS from the natural elements. A picture of the black box is shown in Figure 3.14, and a schematic of the DLS is displayed in Figure 3.15.

![Figure 3.14: Black Weatherproof Box](image)

Located inside the box was a pc/104 logging computer, also known as the Prometheus, and power supply for all of the electronics necessary for the operation of the eddy covariance instrumentation. The pc/104 logging computer was manufactured by a company
called Diamond Systems Inc. An RS422 cable connected the sonic anemometer to an RS422/RS232 converter. This converter was then connected to the Prometheus device. Power was supplied to the converter in such a manner that power to and data from the anemometer travelled along the same cable. The head of the LI-7500 was connected to the control box by a particular cable that was manufactured by LI-COR Biosciences. This cable provided power to the LI-7500 head, while also transmitting data back to the control box. The control box outputted an analogue data signal, which was transmitted to one of the analogue data acquisition inputs of the Prometheus device.

Data was logged by a ANSI C program, which was written and tested by Dr. Michael Geever. The script was stored inside the pc/104 logging computer. This program set up the serial port for acquisition, initialised features such as drivers, boards, baud rate settings, A/D settings and the destination file to which data was written. An ethernet cable connected the Prometheus device to a PC inside the lab at ground level. This PC was used to access the Prometheus device, to stop and start the data logging program and to offload any recorded data. Once the program was running, recorded data could be inspected on the screen of the PC.

The sonic anemometer controlled the logging frequency for both instruments as input data strings from the anemometer were parsed to extract the relevant information upon arrival. Analogue channels were then scanned for voltages from the gas analyzer.
These voltage readings were converted to concentration values dependent upon the measurement range selected. Voltages were converted using Equation 3.3.

$$X = \frac{V_X R_X}{5}$$  \hspace{1cm} (3.3)

- $X$ - CO$_2$ or H$_2$O
- $V$ - Measured voltages
- $R$ - Upper limit of CO$_2$ and H$_2$O measurement ranges

### 3.2.1.6 System Limitations

Naturally enough, the elements can influence the operation of both instruments. If rain, dew, frost or snow accumulates on the sonic transducers, thus altering the path length, slight errors can occur in measurements being made at the time (GillInstruments, 2004). Also, precipitation can affect the LI-7500. If water droplets coalesce on the sapphire windows of the instrument, the path of the infrared beam can be influenced or even blocked, thus causing poor data measurements. Even precipitation passing through the path of the beam can cause recorded data to be unreliable.

The LI-7500 head is sensitive to vibrations of around 152 Hz ± the bandwidth (and upper harmonics) (Burba and Anderson, 2007). However, the instrument is completely insensitive to vibrations which are slower than this and slightly sensitive to vibrations higher than this. Guy wires used to support the tower reduce the possibility of vibrations influencing the instrumentation. Also, evidence exists where energy dissipated from the LI-7500 head can heat part of the air in the optical path, thus causing a bias in CO$_2$ transport estimates to and from the atmosphere. However, this effect is most pronounced in colder climates (below -10°C). Fortunately, these temperatures seldom occurred at the Mace Head research station.

### 3.2.2 Data Buoy

An all weather data buoy was moored offshore from Mace Head at a distance of approximately 3 km from the research station (53° 19.86’ N and 9° 55.95’ W). The buoy was deployed by the Marine Institute (MI) during July 2008. (Figure 3.16).
A variety of instrumentation was installed on the buoy, measuring numerous atmospheric and oceanographic variables. However, only data from certain sensors were of particular interest for this research. These instruments included the

**WXT510 - Weather Station** This instrument measured atmospheric pressure, relative humidity, air temperature, rainfall, wind direction and wind speed.

**WQM - Water Quality Monitor** This sensor measured chlorophyll fluorescence, dissolved oxygen and salinity.

**Pro Oceanus $\text{pCO}_2$ Sensor** This instrument measured the concentration of carbon dioxide in the sea-water.

Every half hour, sensors on the buoy would switch on automatically at different times and make a measurement. Measurements from each instrument were then sent and stored on a data acquisition system known as the **TMBB**. The TMBB (TechWorks Marine Black Box) was located above the water surface on the inside of the buoy. Once all data was collected from the instrumentation and stored on the TMBB, the data was then sent via GPRS (General Packet Radio Service) to the Marine Institute, where it was processed and placed on a FTP (Field Training Preparation) site.

---

**Figure 3.16: Offshore Data Buoy at Mace Head**
Chapter 3. Instrumentation

The most important instrument on the Mace Head Buoy was the Pro Oceanus pCO$_2$ sensor, as it was this data that was used, in conjunction with atmospheric CO$_2$ measurements from the LI-COR LI-6252 on the tower, described in Section 3.2.3.1, and the eddy covariance instrumentation discussed in Section 3.2.1, to calculate the gas transfer velocity data.

The pCO$_2$ sensor was installed on the buoy using a stainless steel cartridge frame and clamps. During maintenance visits, the frame could be raised and lowered via a pulley system. When the frame and pCO$_2$ sensor was in position under the water surface, it was placed inside a large nylon tube of 1 m internal diameter. The nylon tube had several holes in its side, to allow sea-water to flow through and circulate around the pCO$_2$ sensor. The sensor was kept at a depth of approximately 2 m beneath the water surface when in final position. A SBE submersible pump was attached to the instrument so that an equilibrated water sample flowed through the inner chamber and around the gas transfer interface. Pictures of the frame, pulley system and nylon tube are shown in Figures 3.17 and 3.18.

3.2.3 Other Instrumentation

As Mace Head is an internationally acknowledged research station, numerous other sets of instrumentation were installed and operational at the time of this research. These instruments could be used as alternative sources for certain data sets including wind speed, wind direction, relative humidity and air CO$_2$ concentration. thus allowing data
sets to be compared, ensuring higher levels of confidence and accuracy. Some of these instruments are described in the following sections.

### 3.2.3.1 LI-COR LI-6252

The LI-COR 6252 is a closed path, differential, non-dispersive infrared gas analyzer. It was installed in the other shore lab at the base of the 22 m tower. The lab is located on the right side in Figure 3.11. Data recorded by this system was processed as part of the RAMCES/LSCE monitoring network. Air CO$_2$ concentrations were measured each hour and were of a very high standard and accuracy. Air was sampled from up the tower, close to the LI-7500. The instrument was calibrated frequently each day. This data could be used to investigate whether the CO$_2$ concentration measured by the LI-7500 was accurate. The LI-6252 data were used to calculate the $\Delta p$CO$_2$ values for Equation 2.23. A picture of an LI-6252 is displayed in Figure 3.19. The main contact at RAMCES was Michel Ramonet.

![LI-6252 Infrared Gas Analyzer](image)

**Figure 3.19:** LI-6252 Infrared Gas Analyzer

### 3.2.3.2 Wind Speed and Wind Direction

Wind speed and wind direction measurements were collected at Mace Head at another location, aside from the sonic anemometer at the top of the tower. The instrument used to measure the wind direction was a Vector Instruments W200P potentiometer wind vane. This instrument is pictured in Figure 3.20.
Also used, was a Vector Instruments A100L cup anemometer, which was used to measure wind speed. A picture of this instrument is located in Figure 3.21. Both of these instruments were installed near “The Cottage” laboratory at Mace Head.

### 3.2.3.3 Relative Humidity and Atmospheric Pressure

Relative humidity measurements were collected by a Vaisala Model HMP45D sensor, which was installed beside “The Cottage” laboratory. A picture of this instrument is displayed in Figure 3.22. While atmospheric measurements were conducted by a Vaisala PTB220 barometer, which is pictured in Figure 3.23.

### 3.2.3.4 Air Temperature

A Sensing Devices Ltd Platinum Resistance Thermometer RT Series was used to collect air temperature data at Mace Head. This sensor was also installed near “The Cottage” laboratory.
Chapter 4

Analysis of Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

The PSI CO$_2$-Pro instruments were installed on the R.V. Celtic Explorer (CE) briefly during June 2009 and permanently from December 2009. In order to distinguish between each pCO$_2$ instrument, they were referred to as “PO1” and “PO2”. Data that was recorded from cruises conducted during 2009 and 2010 were studied and analyzed for this experimental work. The pCO$_2$ instruments operated during one survey in 2009 and nineteen separate surveys for the duration of 2010. At the end of each survey, when the CE returned to port, the recorded data were collected from the onboard computer. Data were filtered for various factors - fresh water influences, times when the non toxic water supply was switched off and zeroing effects: all of which are discussed in Sections 4.2.1 to 4.2.3. The sea-water pCO$_2$ data were binned into half-hour average segments before analysis was started. In total, over 5000 hours of usable data was gathered over the course of 2009 and 2010.

4.1 R.V. Celtic Explorer Surveys

A description of each of the twenty surveys is outlined in Section 4.1.1 to Section 4.1.20. Cruise paths are displayed according to the CE’s position at a given time, recorded in Julian Day. The map used to display the survey path shows the island of Ireland and two different shades of grey depicting 500 metre and 1000 metre depths. A summary
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

of all important surveys conducted in 2009 and 2010 are displayed in Tables 4.1, 4.2 and 4.3.

<table>
<thead>
<tr>
<th>Survey</th>
<th>Name</th>
<th>Start Date</th>
<th>End Date</th>
<th>Chief Scientist</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE0911</td>
<td>Climate Change Survey</td>
<td>14/06/09</td>
<td>22/06/09</td>
<td>Christian Mohn</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of CE cruises between June 14th and 22nd 2009

<table>
<thead>
<tr>
<th>Survey</th>
<th>Name</th>
<th>Start Date</th>
<th>End Date</th>
<th>Chief Scientist</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE10001</td>
<td>B.S.H Survey No.1</td>
<td>15/01/10</td>
<td>02/02/10</td>
<td>Stefan Schmolke</td>
</tr>
<tr>
<td>CE10002</td>
<td>Climate Change, Oceanography, Biogeochemistry and Geology Sections</td>
<td>05/02/10</td>
<td>17/05/10</td>
<td>Glenn Nolan</td>
</tr>
<tr>
<td>CE10009</td>
<td>Cetaceans on the Frontier 2010</td>
<td>18/02/10</td>
<td>04/03/10</td>
<td>Dave Wall</td>
</tr>
<tr>
<td>CE10006</td>
<td>Mackerel Egg Survey</td>
<td>05/03/10</td>
<td>17/03/10</td>
<td>Helen McCormick</td>
</tr>
<tr>
<td>CE10011</td>
<td>Blue Whiting Acoustic Survey</td>
<td>19/03/10</td>
<td>06/04/10</td>
<td>Ciaran O’Donnell</td>
</tr>
<tr>
<td>CE10010</td>
<td>Holland1 ROV/UL Sonar &amp; MPPT Ring/-Cathx Video Imaging Systems - Integrations and Shakedown Cruise</td>
<td>10/04/10</td>
<td>16/04/10</td>
<td>Daniel Toal</td>
</tr>
<tr>
<td>CE10014</td>
<td>Deep Water Coral and Fish Interaction off the west coast of Ireland</td>
<td>19/04/10</td>
<td>11/05/10</td>
<td>Anthony Grehan</td>
</tr>
<tr>
<td>CE10003</td>
<td>Climate and Ecosystem Sections on the Irish Shelf</td>
<td>16/05/10</td>
<td>22/05/10</td>
<td>Glen Nolan</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of CE cruises between January 15th and May 22nd 2010
<table>
<thead>
<tr>
<th>Survey</th>
<th>Name</th>
<th>Start Date</th>
<th>End Date</th>
<th>Chief Scientist</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE10004</td>
<td>Species at the Margins - Diversity Cruise</td>
<td>23/05/10</td>
<td>01/06/10</td>
<td>Louise Alcock</td>
</tr>
<tr>
<td>CE10008</td>
<td>Glacial and Non-Glacial Sediment Transport in The Rockall Trough and Porcupine Bank (North Atlantic)</td>
<td>03/06/10</td>
<td>17/06/10</td>
<td>Aggeliki Georgiopoulo</td>
</tr>
<tr>
<td>CE10012</td>
<td>Northwest Herring Acoustic Survey</td>
<td>18/06/10</td>
<td>06/07/10</td>
<td>Ciaran O’Donnell</td>
</tr>
<tr>
<td>CE10007</td>
<td>Mackerel Egg Survey</td>
<td>08/07/10</td>
<td>28/07/10</td>
<td>Brendan O’Hea</td>
</tr>
<tr>
<td>CE10018</td>
<td>Bathymetric Survey</td>
<td>28/07/10</td>
<td>22/08/10</td>
<td>Jon Rothwell</td>
</tr>
<tr>
<td>CE10005</td>
<td>MODOO - MOdular Deep Ocean Observatory and its application in the Porcupine Abyssal Plain area</td>
<td>16/09/10</td>
<td>22/09/10</td>
<td>Jon Campbell</td>
</tr>
<tr>
<td>CE10015</td>
<td>Irish Groundfish Survey 2010</td>
<td>25/09/10</td>
<td>06/10/10</td>
<td>Dave Stokes</td>
</tr>
<tr>
<td>CE10013</td>
<td>Celtic Sea Herring Acoustic Survey</td>
<td>08/10/10</td>
<td>26/10/10</td>
<td>Ryan Saunders</td>
</tr>
<tr>
<td>CE10017</td>
<td>CBSH Survey No.4</td>
<td>28/10/10</td>
<td>14/11/10</td>
<td>Achim Schulz</td>
</tr>
<tr>
<td>CE10016</td>
<td>Irish Groundfish Survey - Leg 2</td>
<td>15/11/10</td>
<td>02/12/10</td>
<td>Hans Gerritsen</td>
</tr>
<tr>
<td>CE10016</td>
<td>Irish Groundfish Survey - Leg 3</td>
<td>04/12/10</td>
<td>19/12/10</td>
<td>Hans Gerritsen</td>
</tr>
</tbody>
</table>

**Table 4.3:** Summary of CE cruises between May 23rd and December 19th 2010

### 4.1.1 CE0911 - Climate Change Survey

*Cruise Length:* 9 days. The CE departed Horgans Quay, Cork, Co. Cork on the afternoon of June 14th (JD165) and returned to port in Killybegs, Co. Donegal on
Chapter 4. Analysis of the Shipboard pCO₂ Data and PSI CO₂-Pro Performance

June 22nd (JD173) - Figure 4.1. This was the only survey, where I was on board.

*Chief Scientist:* Christian Mohn - NUI Galway.

*Survey Route:* Upon leaving Cork Harbour, the CE cruised in a south-westerly direction towards the continental shelf edge. The ship moved off the shelf at approximately 49.8°N and then headed north-east, travelling back across the shelf edge. The CE continued north and then headed due west across the Porcupine Trough and Porcupine Seabight, and then cruised north off the continental shelf. The vessel surveyed waters over the shelf edge and continental shelf off the west coast of Ireland. Around June 21st (JD172), the CE made for port. The entire cruise was relatively calm with the average atmospheric pressure of approximately 1020 mb observed.

![Cruise Track - CE0911 - June 14th (JD165) - June 22nd (JD173)](image)

**Figure 4.1:** Cruise Track - CE0911 - June 14th (JD165) - June 22nd (JD173)

### 4.1.2 CE10001 - BSH Survey No.1

*Cruise Length:* 19 days. The R.V. Celtic Explorer departed Galway, Ireland on the evening of January 15th (JD015) and arrived into Hamburg, Germany on January 19th (JD019). The vessel departed Hamburg port on January 21st (JD021) and returned on
January 27th (JD027). The CE departed on January 29th (JD029), docking in Cobh, Ireland on February 2nd (JD033) - Figure 4.2.

*Chief Scientist:* Stefan Schmolke - BSH.

*Survey Route:* Upon departing Galway Bay, the ship headed north along the coast of Ireland towards the Outer Hebrides Islands. After passing John O’ Groats, the CE headed south-east, in the direction of the Elbe estuary. The research survey was conducted in the North Sea, near the Dutch, German and Danish coastlines. After the cruise was completed, the ship returned to Hamburg. On its return to Ireland, the R.V. Celtic Explorer departed Germany and headed south-west towards the English Channel. After passing Land’s End and entering the Celtic Sea, the ship headed for Cork Harbour. At the beginning of the survey, a maximum wind speed of 21.36 m/s was recorded. Overall, the survey observed an average wind speed of approximately 9 m/s.

![Cruise Track - CE10001 - January 15th (JD015) - February 2nd (JD033)](image)

*Figure 4.2: Cruise Track - CE10001 - January 15th (JD015) - February 2nd (JD033)*

4.1.3 **CE10002 - Climate Change, Oceanography, Biogeochemistry and Geology sections**

*Cruise Length:* 13 days. The ship departed from Cobh, Co. Cork on February 5th (JD036) and returned to Galway, Co. Galway on February 17th (JD048) - Figure 4.3.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

Chief Scientist: Glenn Nolan - Marine Institute.

Survey Route: After leaving Cobh, the ship turned east heading towards St. Georges Channel. Eventually, the ship moved north through the Irish Sea and over the north coast of Ireland, staying close to the mainland. Upon arrival at Erris Head, Co. Mayo, the CE headed away from land, in a north-westerly direction across the Rockall Trough. The ship then moved in a south-westerly direction, remaining on the boundary between the Rockall Trough and Rockall Plateau. The CE travelled back across the Rockall Trough towards the Porcupine Seabight and stayed there for approximately two days. Then the vessel headed due west over the continental shelf and returned to port. The majority of the survey measured wind speeds between 5 and 10 m/s. However, between JD046 and JD048, wind speeds increased to between 10 - 14 m/s.

Figure 4.3: Cruise Track - CE10002 - February 5th (JD036) - February 17th (JD048)

4.1.4 CE10009 - Cetaceans on the Frontier 2010

Cruise Length: 15 days. The CE left Galway, Co. Galway on February 18th (JD049) and docked in Cork, Co. Cork on March 1st (JD060) for a few hours. The ship then
departed and returned to Galway, Co. Galway on March 4th (JD063) - Figure 4.4.

Chief Scientist: Dave Wall - Irish Whale and Dolphin Group.

Survey Route: The vessel departed port and headed WSW towards the Porcupine Bank and the edge of the continental shelf. The CE travelled waters off the shelf edge, close to the Porcupine Seabight. The ship then headed in a southerly direction, surveying close to the shelf edge. For approximately two days, the vessel remained close to 48.8°N and 10.0°W. During JD058, the CE left the area and travelled northeast over the continental shelf and returned to port in Cork, Co. Cork. Parts of the ship track could not be displayed, as there was no latitude or longitude data available.

![Cruise Track - CE10009 - February 18th (JD049) - March 4th (JD063)](image)

Figure 4.4: Cruise Track - CE10009 - February 18th (JD049) - March 4th (JD063)

### 4.1.5 CE10006 - Mackerel Egg Survey

Cruise Length: 13 days. The CE departed from Galway, Co. Galway on March 5th (JD064) and docked in Rushbrooke, Co. Cork for a few hours during March 7th
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

(JD066). The vessel soon departed Rushbrooke and the survey continued until the CE returned to Galway, Co. Galway on March 17th (JD076) - Figure 4.5.

*Chief Scientist:* Helen McCormick - Marine Institute.

*Survey Route:* After departing Galway Bay, the ship headed WSW towards the Porcupine Plateau and then changed direction travelling back across the Porcupine Seabight. The CE headed for the Irish coast and returned to Cork Harbour. After leaving port the vessel headed south into the Celtic Sea and then travelled due west at 47.8°N. The survey continued south of Ireland in the Celtic Sea, travelling back and forth over the continental shelf and off the shelf edge. Around JD075, the CE headed in a north-easterly direction towards Galway Bay. Some parts of the ship track were not plotted due to no latitude or longitude data being available.

![Figure 4.5: Cruise Track - CE10006 - March 5th (JD064) - 17th (JD076)](image)

**4.1.6 CE10011 - Blue Whiting Acoustic Survey**

*Cruise Length:* 18 days. The ship departed Galway, Co. Galway on March 19th (JD078) and returned to the same port on April 6th (JD096) - Figure 4.6.

*Chief Scientist:* Ciaran O’Donnell from the Marine Institute.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

Survey Route: Upon leaving Galway Bay, the ship headed north and entered Killary Harbour, Co. Mayo for a period of time on the evening of its departure. Soon after, the CE headed in a NNE direction along the Irish coast as far north as 56.4°N. It then travelled due west across the continental shelf, Rockall Trough and Rockall Plateau. At 17.5°W, the ship headed north and then back east to the continental shelf. The majority of the cruise was conducted as the ship travelled back and forth across the Rockall Trough, whilst overall moving north. Soon after reaching 59.0°N, the R.V. Celtic Explorer headed SSW and returned to port in Galway, Co. Galway.

![Cruise Track - CE10011 - March 18th (JD077) - April 6th (JD096)](image)

Figure 4.6: Cruise Track - CE10011 - March 18th (JD077) - April 6th (JD096)

4.1.7 CE10010 - Holland1 ROV/UL Sonar & MPPTRing/Cathx Video Imaging Systems - Integration & Shakedown Cruise

Cruise Length: 7 days. The R.V. Celtic Explorer departed Galway, Co. Galway on April 10th (JD100) and returned to Galway Bay on April 16th (JD106) - Figure 4.7.

Chief Scientist: Daniel Toal - University of Limerick.
Survey Route: After departing Galway Harbour, the ship travelled in a westerly direction, parallel to the Galway coast. Upon clearing the Aran Islands, the CE headed south and performed a triangular circuit, before returning close to the mainland near Rossaveel Harbour, Co. Galway. During JD102, the ship headed northwest towards the shelf edge, staying there for approximately two days. The ship travelled in a south-east direction, back towards the Irish coast, after leaving the shelf edge. The CE spent sometime in Rossaveel Harbour before returning to the open ocean. The ship started heading for port sometime during JD105. The whole survey was relatively calm. The average wind speed was approximately 6 m/s.

Figure 4.7: Cruise Track - CE10010 - April 10th (JD100) - 16th (JD106)

4.1.8 CE10014 - Deep Water Coral and Fish Interaction off the west coast of Ireland

Cruise Length: 23 days. The R.V. Celtic Explorer departed Galway, Co. Galway on April 19th (JD109) before returning to port in Galway on May 11th (JD131) - Figure 4.8.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

*Chief Scientist:* Anthony Grehan from the National University of Ireland Galway.

*Survey Route:* The CE travelled north-west across the continental shelf and Rockall Trough to the Rockall Bank during the beginning of the survey. The ship cruised back and forth along the edge of the Rockall Bank for a few days, before continuing south towards an area of ocean on the edge of the Porcupine Bank, but mostly off the shelf edge. The ship then travelled over the Porcupine Trough and surveyed an area of ocean close to the shelf edge off the south west coast of Ireland: near 51.4°N, 11.7°W. During this time, the CE moved from this area to Dingle Bay for a period of time. After returning to the area, the CE headed north-east and returned to shore. The survey had a average wind speed of 5.8 m/s, inferring mostly calm conditions that were experienced.

![Cruise Track - CE10014 - April 19th (JD109) - May 11th (JD131)](image)

*Figure 4.8:* Cruise Track - CE10014 - April 19th (JD109) - May 11th (JD131)

4.1.9 CE10003 - Climate and Ecosystem Sections on the Irish shelf

*Cruise Length:* 7 days. The R.V. Celtic Explorer departed Galway, Co. Galway on May 16th (JD136) and docked in Killybegs, Co. Donegal on May 22nd (JD142) -
Figure 4.9.

*Chief Scientist:* Glenn Nolan from the Marine Institute.

*Survey Route:* After departing Galway Harbour, the vessel headed south along the south-west coast of Ireland until the ship was offshore from Mizen Head, Co. Cork. The CE headed due south and then turned in a WNW direction towards the continental shelf edge. Upon leaving the shelf edge, the ship headed into Bantry Bay and then back out to sea, travelling north as far as 53.0°N. The vessel then travelled due east until it reached the mainland, where it then proceeded north along the coast to the shelf edge. Upon leaving the shelf edge, the CE returned close to the north-west coast of Ireland. On JD141, the ship returned once more to the shelf edge, before entering Donegal Bay and returning to port. At the beginning of the cruise, wind speeds peaked at approximately 11.5 m/s. However, towards the end of the survey, wind speeds were observed to be mostly between 1 and 4 m/s.

4.1.10 **CE 10004 - Species at the Margins - Diversity Cruise**

*Cruise Length:* 10 days. The R.V. Celtic Explorer departed Killybegs on May 23rd (JD143) and docked in Galway, Co. Galway on June 1st (JD152) - Figure 4.10.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

*Chief Scientist:* Louise Allcock from the National University of Ireland Galway.

*Survey Route:* The CE headed in a west-south-westerly direction after leaving port. It cruised towards the shelf edge near 54.0°N and 12.4°W, where the majority of the survey was conducted. During the research cruise, the vessel was mostly off the continental shelf over the Rockall Trough. On May 28th (JD148), the ship headed towards Blacksod Bay, Co. Mayo, most likely seeking shelter due to a passing low system, and then returned to the survey area the following day. Once the cruise was completed on JD151, the ship headed for Galway Bay and port. Wind speeds peaked at the beginning and end of the survey at approximately 10 m/s. However, the average wind speed for the cruise was 5.9 m/s.

![Cruise Track - CE10004 - May 23rd(JD143) - June 1st(JD152)](image.png)

**Figure 4.10:** Cruise Track - CE10004 - May 23rd(JD143) - June 1st(JD152)

4.1.11 **CE 10008 - Glacial and Non-Glacial Sediment Transport in the Rockall Trough and Porcupine Bank (North Atlantic)**

*Cruise Length:* 15 days. The ship departed Galway, Co Galway on June 3rd (JD154). The CE returned to Galway on June 17th (JD168) - Figure 4.11.

*Chief Scientist:* Aggeliki Georgiopoulo from University College Dublin.
Chapter 4. Analysis of the Shipboard pCO\textsubscript{2} Data and PSI CO\textsubscript{2}-Pro Performance

*Survey Route:* After leaving Galway Harbour, the CE headed west parallel to the coastline. The ship travelled in a north-westerly direction towards the continental shelf edge and the Rockall Trough. The majority of the cruise was conducted over the Rockall Trough, approximately between 54.0°N - 56.0°N and 10.0°W - 14.0°W. During June 13th (JD164), the ship headed towards Killybegs, Co. Donegal, arriving offshore during the following day. The ship remained offshore for a very short period of time, before heading back out to the survey area off the continental shelf. The vessel moved back over the shelf for the remaining two days of the survey, before returning to port. The beginning of the cruise was relatively calm (1 - 7 m/s). However, wind speeds peaked at approximately 12 m/s three times during the remainder of the survey.

![Figure 4.11: Cruise Track - CE10008 - June 3rd (JD154) - 17th (JD168) (1)](image)

4.1.12 CE10012 - Northwest Herring Acoustic Survey

*Cruise Length:* 19 days. The vessel departed Galway, Co. Galway on June 18th (JD169) and returned to Galway, Co. Galway on July 6th (JD187) - Figure 4.12.

*Chief Scientist:* Ciaran O Donnell - Marine Institute.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

Survey Route: The CE headed west after leaving port and turned north-west after passing the Aran Islands. At 53.5°N, the ship travelled due west before turning north and then heading east towards the mainland. The ship entered Killary Harbour, Co. Mayo briefly before returning to the open ocean again. The cruise continued with the CE travelling back and forth between the continental shelf edge and the mainland, while overall moving north. The majority of the survey was conducted in this manner. Upon reaching 56.8°N, the survey was completed and the ship started heading for port by travelling in a SSW direction. Most of the survey observed wind speeds between 1 and 9 m/s. During JD178, wind speeds peaked at 16 m/s.

![Cruise Track - CE10012 - June 18th (JD169) - July 6th (JD187)](image)

4.1.13 CE10007 - Mackerel Egg Survey

Cruise Length: 21 days. The vessel departed Galway, Co. Galway on July 8th (JD189). The ship returned to Galway, Co. Galway on July 28th (JD209) - Figure 4.13.


Survey Route: Upon departing Galway Harbour, the CE headed south along the south-west coast of Ireland and across the Celtic Sea. The vessel passed close to the coast of France before turning in a westerly direction at 47.3°N. The ship travelled
back and forth both on and off the continental shelf and then passed very close to the English coast near Falmouth, Cornwall. The ship returned to the open ocean and travelled back and forth across the shelf, whilst overall moving north. During the remainder of the cruise, the CE surveyed water over the continental shelf, Rockall Trough, Porcupine Seabight and Porcupine Bank. The CE travelled as far north as 56.3°N, before returning to port. The average wind speed during the survey was 8.2 m/s. Wind speeds peaked near 18 m/s twice during the cruise: JD196 and JD203.

Figure 4.13: Cruise Track - CE10007 - July 8th (JD189) - 28th (JD209)

4.1.14 CE10018 - Bathymetric Survey

Cruise Length: Approximately 26 days. The R.V. Celtic Explorer departed Galway, Co. Galway on July 28th (JD209). The cruise was concluded when the CE docked in Horgan’s Quay, Cork, Co. Cork on August 22nd (JD234) - Figure 4.14.

Chief Scientist: Jon Rothwell from the Marine Institute.

Survey Route: Once the CE departed Galway, the ship headed south along the south-west coast and arrived at the survey area the following day. The majority of the survey was conducted in an area of the Celtic Sea at approximately 51.3°N and 8.15°W. During this cruise, the vessel travelled between the survey site and Cork Harbour several
times. The ship would dock at either Rushbrooke, Co. Cork or Horgan’s Quay, Co. Cork. As a result of this constant back and forth, there were several hours, if not days, when the ship was idle in port. Most of the ship track is along the same stretch of water between Cork Harbour and the survey site. The majority of the survey experienced wind speeds less than 10 m/s.

**Figure 4.14:** Cruise Track - CE10018 - July 28th (JD209) - August 22nd (JD234)

**4.1.15 CE10005 - MODOO MOdular Deep Ocean Observatory (MODOO) and its application in the Porcupine Abyssal Plain area**

*Cruise Length:* 7 days. The CE departed Milford Haven in the United Kingdom on September 16th (JD259), after a three week maintenance break. The ship docked in Galway, Co. Galway on September 22nd (JD265) at the end of the survey - Figure 4.15.

*Chief Scientist:* Jon Campbell from the Marine Institute.

*Survey Route:* After leaving port, the ship headed to the survey site immediately. The ship travelled in a south-westerly direction over the continental shelf and into deeper waters. The vessel arrived at the research area on September 18th (JD261), which was located at 49.0°N and 16.4°W. The CE stayed here for the majority of the
Chapter 4. Analysis of the Shipboard pCO₂ Data and PSI CO₂-Pro Performance

survey. The ship started heading for port on September 21st (JD264) and travelled in a north-east direction over the Porcupine Seabight and back over the shelf. Most of the survey experienced atmospheric pressure values above 1010 mb. However, towards the end of the cruise, values decreased below 1010 mb, inferring the likelihood of more unstable weather conditions.

Figure 4.15: Cruise Track - CE10005 - September 16th (JD259) - 22nd (JD265)

4.1.16 CE10015 - Irish Groundfish Survey 2010

Cruise Length: 12 days. The R.V. Celtic Explorer left Galway, Co. Galway on September 25th (JD267). The vessel returned to port in Galway, Co. Galway on October 6th (JD279) - Figure 4.16.

Chief Scientist: Dave Stokes - Marine Institute.

Survey Route: The CE departed Galway Bay and headed north along the west coast of Ireland towards continental shelf waters off the north-west coast. The ship surveyed waters close to the shelf edge, but mostly remained over the continental shelf. The majority of the survey was conducted over the continental shelf off north and north-western coasts of Ireland. At numerous times during the survey, the ship came very close to the mainland, entering both Lough Foyle and Lough Swilly, Kilalla Bay.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

and Donegal Bay. During October 5th (JD278), the CE made for port and travelled south towards Galway Bay. The average wind speed during the survey was 8.5 m/s.

![Image](image.png)

**Figure 4.16:** Cruise Track - CE10015 - September 25th (JD267) - October 6th (JD279)

### 4.1.17 CE10013 - Celtic Sea Herring Acoustic Survey

**Cruise Length:** 19 days. The ship departed Galway, Co. Galway on October 8th (JD281). The CE returned to port in Cork, Co. Cork on October 26th (JD299) - Figure 4.17.

**Chief Scientist:** Ryan Saunders from the Marine Institute.

**Survey Route:** After passing the Aran Islands, the CE headed south and remained very close to the mainland. This survey was conducted entirely over the continental shelf. The vessel entered waters part of the Shannon Estuary, Dingle Bay, Kenmare Bay and Bantry Bay on the south-west coast of Ireland. The survey continued off the southern coast, where the the CE travelled back and forth in a north/south direction at very small distances apart. The ship never sailed and further south than 51.0°N. After reaching St. Georges Channel, the cruise continued back in a westerly direction. Upon reaching the Old Head of Kinsale, Co. Cork, the ship travelled around the south-west coast once more, before returning to port. Wind speeds peaked at approximately 14
m/s at the very beginning of the survey and near the end. However, wind speed values were mostly between 1 and 10 m/s for the remainder of the cruise.

![Cruise Track - CE10013 - October 8th (JD281) - 26th (JD299)](image)

**Figure 4.17:** Cruise Track - CE10013 - October 8th (JD281) - 26th (JD299)

### 4.1.18 CE10017 - CBSH Survey No.4

*Cruise Length:* 18 days. The CE departed Cork, Co. Cork on October 28th (JD301), en-route to Germany, where it arrived on October 31st (JD304). The CE10017 survey began when the CE left port on November 1st (JD305). The ship returned to Hamburg on November 9th (JD313) and departed again on November 10th (JD314). It arrived back into Ireland, arriving into Galway, Co. Galway on November 14th (JD318) - Figure 4.18.

*Chief Scientist:* Achim Schulz from BSH.

*Survey Route:* After leaving port the CE headed south-east across the Celtic Sea and into the English Channel. After entering the North Sea, the vessel docked in port. All of the survey was conducted in the North Sea and when completed, the CE returned to Germany briefly. For the journey home, the ship headed NW across the North Sea, travelling around Scotland. The journey between Ireland and Germany was relatively calm with an average wind speed of approximately 6 m/s. However, during the actual survey, wind speeds peaked near 14 m/s several times.
4.1.19 CE10016 - Irish Groundfish Survey - Leg 2

*Cruise Length:* 18 days. The CE departed Galway, Co. Galway on November 15th (JD319) and returned to Galway on December 2nd (JD336) - Figure 4.19.

*Chief Scientist:* Hans Gerritsen - Marine Institute.

*Survey Route:* After departing port, the CE headed west before turning and travelling south towards the Shannon Estuary. During November 19th (JD323), the R.V. Celtic Explorer spent approximately two days in Smerwick Harbour, Co. Kerry, most likely due to a passing low system and the ship needed to seek shelter from hazardous weather. When the survey continued, the vessel proceeded in a southerly direction, passing close to the shelf edge and then travelled east into the Celtic Sea. The ship passed close to the southern coast of Ireland and spent sometime surveying waters in St. Georges Channel. The CE then headed in a westerly direction and returned to waters off the SW coast, before returning to port. High wind speeds (≥ 10 m/s) were recorded during the beginning of the cruise, but wind speeds decreased during the following days. However, wind speeds increased towards the end of the survey.
4.1.20 CE10016 - Irish Groundfish Survey - Leg 3

*Cruise Length:* 16 days. The CE departed Galway, Co. Galway on December 4th (JD338) and returned to Galway on December 19th (JD353) - Figure 4.20.

*Chief Scientist:* Hans Gerritsen from the Marine Institute.

*Survey Length:* The CE headed west after leaving port and then travelled north up to the shelf edge. On December 6th (JD340), the CE travelled back to Galway, although remaining just offshore. The survey continued after this small stop and the ship headed WSW to the continental shelf edge. The vessel travelled south along the shelf edge and into the Celtic Sea. Soon after, the ship started moving north-west towards the Porcupine Seabight. After passing the Seabight, the CE cruised north before turning south along the west coast, staying close to the mainland. During December 18th (JD352), the ship headed due west away from the Aran Islands before heading for port. Most of the cruise recorded high wind speeds (≥8 m/s). There were three distinct periods, each lasting about two days, where wind speeds peaked at approximately 15 m/s.
4.2 Preliminary Data Analysis

While the R.V. Celtic Explorer was in port between each survey, data from the previous cruise were collected from the PC on board the vessel, where it is logged and stored. Before the benchmarking of the instruments could be started, the sea-water pCO$_2$ data needed to be examined and filtered for certain situations that occurred at the beginning, middle and end of each of the surveys. These situations included:

1. Zeroing of the Instruments
2. Fresh water influences at the beginning of each survey
3. Non-toxic water supply being switched off in the middle and/or end of each survey
4. Noisy Data

4.2.1 Zeroing of the Instruments

In order to ensure the highest level of accuracy, the pCO$_2$ instruments zeroed themselves every three hours. However, when the zeroing process occurred, all data recorded and...
influenced during the zeroing process needed to be removed. An example of the zeroing process showing up in measured data is displayed in Figure 4.21. This example of data was recorded during the CE10007 survey on July 18th (JD199).

During the zeroing process, the pCO$_2$ instrument measures 0 $\mu$atm for approximately 10 - 15 seconds. Immediately afterwards, the measured data climbs steeply back up to pCO$_2$ concentrations more indicative of the sea-water passing through the tank. The cut-off point for zeroing influenced data was decided by visually inspecting the data. Located in Figure 4.22, is the same data set as displayed in Figure 4.21, but measurements influenced by the zeroing process have been removed. The remaining gaps in the data set are retained when the data is half-hour averaged.

Automatically removing all sea-water pCO$_2$ data measured during the zeroing process was considered and attempted. However, not all “contaminated” data was excluded during this filtering technique. As a result, it was decided to remove all data measured during the zeroing process by manual methods. Although slightly time consuming, confidence was achieved by filtering the data through this method.

### 4.2.2 Fresh Water Influences

Before the R.V. Celtic Explorer departed port, the tank containing the pCO$_2$ instruments was emptied, cleaned and filled with fresh water. The tank was secured and the instruments were powered up and started logging data. After the ship left port, the technician on board would open the inlet and allow saltwater to flow from the non toxic water supply into and through the tank. As a result, some data would be recorded while there was some fresh water inside the tank, and this data needed to be removed.
before further analysis could occur. An example of some pCO\(_2\) data measured while both fresh and salt water was inside the tank is located in Figure 4.23.

These data were measured during the beginning of the CE10010 survey. From the graph, it is very obvious when the transition from fresh water to salt water occurs - near the end of JD102. The length of time it took for all fresh water to leave the tank during this survey was roughly six hours. However, this amount of time varied at the beginning of each survey. After this point, it is presumed that measurements are being made in salt water only and are included. For each cruise, the transition period was identified and all fresh water data was removed. After the data displayed in Figure 4.23 has all fresh water influenced data removed, the resultant data set is plotted in Figure 4.24. It would have been advantageous to have a sensor that measured salinity installed inside the tank, as the transition between fresh water and sea-water could be identified more precisely. Unfortunately, no sensor was installed.

### 4.2.3 Non-Toxic Water Supply being switched off

During some of the surveys, the non toxic water supply was switched off in the middle of the cruise for some reason or another. Unfortunately, the crew do not record the exact times when the non-toxic water supply is switched off and on, as it would make this analysis much easier. When this occurred, the corresponding data needed to be removed. This particular situation occurred often during the CE10018 survey, as the ship was travelling back and forth from port on several occasions. A plot of all of the data recorded during this survey is displayed in Figure 4.25.
When the non toxic was switched off, there was a sudden and obvious change in the data signal. The recorded data increased sharply and there was a larger than normal difference between both of the instruments. The non toxic water supply was switched off during part of JD210 - 211, during JD212, JD217 - 219, during parts of JD225 - 226 and during JD228. During this particular survey, the non-toxic water supply was switched off because, the CE was in port. All of this data was removed and the remaining data was plotted in Figure 4.26.

Towards the end of each survey, as the R.V. Celtic Explorer came into port, the non toxic water supply was switched off. Similar to the non toxic being switched off mid-cruise, data is often recorded during this time frame and needs to be excluded from the data set. An example of this situation is plotted in Figure 4.27.

This example is taken from the CE10006 survey, where the non toxic water supply was switched off shortly after 00:00hrs on March 17th (JD076). Data that was recorded
when there was no flow of salt water though the tank appears very different from
when the non toxic is switched on. During this situation, the data recorded by both
instruments varies greatly, making it more easy to identify. The data that is included
is displayed in Figure 4.28.

4.2.4 Noisy Data

During some of the R.V. Celtic Explorer surveys, it was observed that some pCO₂ data
recorded by one or both of the PSI pCO₂ instruments would appear “noisy”, and not
“smooth”, which was the normality over the majority of surveys. An example of this
noisy data is displayed in Figure 4.29 and Figure 4.30.

At the beginning of the CE10002 survey, both sensors were recording data smoothly.
However, during the cruise, the pCO₂ signal from the PO2 instrument turned noisy for
a period of time, before ceasing by the end of the survey. During the CE10014 research
cruise, the PO2 instrument recorded noisy data over most of the survey. Note that the
PO1 appears to not have recorded any noisy data, its signal is smooth throughout both
cruises.

After contact with PSI, the cause for this noise in the pCO₂ signal was possibly as
a result of tiny droplets of water forming inside the gas line due to condensation. These
droplets were possibly created when the water temperature inside the tank dramatically
changed in a short period of time, or if the flow rate into the tank was high (>5 - 7
L/min). Fortunately, this noisy signal issue did not have a huge effect on the operation
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

of the instruments. Both sensors operated very well when compared to each other after the data was half-hour averaged.

4.3 Bench-marking of the PSI CO$_2$-Pro Instruments

Before the measured sea-water pCO$_2$ data could be studied any further, the accuracy of the PSI CO$_2$-Pro instruments needed to examined. This was conducted by using three different methods. These included

1. Bench-marking the two PSI CO$_2$-Pro Instruments, “PO1” and “PO2” against each other and see how well they compare.

2. Bench-marking a PSI CO$_2$-Pro Instrument against another pCO$_2$ system, the General Oceanics pCO$_2$ instrument.

3. Bench-marking the two PSI CO$_2$-Pro Instruments, “PO1” and “PO2” against pCO$_2$ concentrations calculated from water samples collected during corresponding cruises.

4.3.1 Bench-marking two PSI CO$_2$-Pro Instruments against each other

Only sea-water pCO$_2$ data recorded during 12 of the 19 surveys discussed in Section 4.1 were included when the two instruments were compared to each other. Three cruises - CE10003, CE10004 and CE10008, were not included as the instrument called “PO2”, was removed from the R.V. Celtic Explorer. Also, other cruises - CE10005, CE10015, CE10013 and CE10017, were not included, as there was a possible bio-fouling issue with the “PO1” instrument. All data was half-hour averaged before a comparative analysis of sea-water pCO$_2$ data from both instruments was conducted. Mean sea-water pCO$_2$ concentrations were calculated for each bench-marking survey. This is displayed by a black line: Figures 4.31. Also displayed, was the mean daily pCO$_2$ values for both sensors.
4.3.1.1 CE10001 - BSH Survey No.1

The sea-water pCO$_2$ concentrations measured by both instruments are plotted in Figure 4.31. Two gaps exist in the data set, these are as a result of when the R.V. Celtic Explorer was in port, and the pCO$_2$ instruments were switched off. The percentage difference data between both pCO$_2$ instruments is displayed in Figure 4.32.

![Figure 4.31: Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10001](image1)

![Figure 4.32: Percentage Difference of pCO$_2$ concentrations between both instruments - CE10001](image2)
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

4.3.1.2 CE10002 - Climate Change Oceanography, Biogeochemistry and Geology sections

Sea-water pCO$_2$ concentrations recorded by both instruments are plotted in Figure 4.33 and the percentage difference values between both sensors are plotted in Figure 4.34.

**Figure 4.33:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10002

**Figure 4.34:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10002

---

–94–
4.3.1.3 CE10009 - Cetaceans on the Frontier 2010

The measured sea-water pCO$_2$ concentrations by both instruments are plotted in Figure 4.35. The percentage difference values for the cruise CE10009 are displayed in Figure 4.36. A small gap appears in the data set during JD060. This was when the ship was in Cork Harbour for a few hours and no admissible data was recorded.

**Figure 4.35:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10009

**Figure 4.36:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10009
4.3.1.4 CE10006 - Mackerel Egg Survey

The measured sea-water pCO$_2$ concentrations by both instruments are plotted in Figure 4.37. Instrument comparison statistics for the survey are shown in Figure 4.38. At the beginning of this survey, there was a larger difference between “PO1” and “PO2”, when compared to the majority of the cruise. The reason for this larger difference is unknown. No data were plotted during part of JD066, as this was when the CE was anchored near port, and the measured data were unreliable.

![Seawater pCO$_2$ Concentrations - CE10006 Survey](image)

**Figure 4.37:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10006

![Percentage pCO$_2$ Difference between PO1 & PO2 - CE10006 Survey](image)

**Figure 4.38:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10006
4.3.1.5 CE10011 - Blue Whiting Acoustic Survey

Sea-water pCO$_2$ concentrations are plotted in Figure 4.39. During JD078 and JD079, sea-water pCO$_2$ concentrations varied sharply. Concentrations increased suddenly from around 330 $\mu$atm - 390 $\mu$atm. However, during this increase, there was a dip in pCO$_2$ concentrations. This sudden increase occurred as the ship travelled north away from the coast of Ireland, while the drop in pCO$_2$ concentrations was recorded as the vessel entered Killary Harbour. Percentage difference statistics for the survey are plotted in Figure 4.40.

![Seawater pCO$_2$ Concentrations - CE10011 Survey](image)

**Figure 4.39:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10011

![Percentage pCO$_2$ Difference between PO1 & PO2 - CE10011 Survey](image)

**Figure 4.40:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10011
4.3.1.6  CE10010 - Holland1 ROV/UL Sonar & MPPTRing/Cathx Video Imaging Systems - Integration & Shakedown Cruise

Measured pCO$_2$ concentrations by both of the Pro Oceanus instruments are plotted in Figure 4.41. No sea-water pCO$_2$ measurements were made between JD100 and JD103. The reason for this was the inlet of the tank was not opened, permitting no sea-water to flow through the tank. During JD105 and JD107, the CE was located in Galway Bay. A large variability in sea-water pCO$_2$ concentrations was observed. Some percentage difference values between the two instruments are plotted in Figure 4.42.

**Figure 4.41:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10010

**Figure 4.42:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10010

-98-
4.3.1.7 CE10014 - Deep Water Coral and Fish Interaction off the west coast of Ireland

The sea-water pCO$_2$ concentrations measured by both instruments are plotted in Figure 4.43. During JD127, pCO$_2$ concentrations dropped from around 360 µatm to 320 µatm. This decrease in carbon dioxide concentrations occurred as the CE travelled close to coast. A similar drop in sea-water pCO$_2$ concentrations was observed during JD130, as the ship passed close to the coast returning to port. The percentage difference data for the cruise CE10014 is plotted in Figure 4.44.

**Figure 4.43:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10014

**Figure 4.44:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10014
4.3.1.8 CE10012 - Northwest Herring Acoustic Survey

The pCO₂ concentrations measured during the CE10012 survey are plotted in Figure 4.45. During this cruise, the pCO₂ concentrations varied as the ship travelled back and forth across the continental shelf. Percentage difference data for both pCO₂ instruments is displayed in Figure 4.46.

**Figure 4.45:** Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10012

**Figure 4.46:** Percentage Difference of pCO₂ concentrations between both instruments - CE10012
4.3.1.9 CE10007 - Mackerel Egg Survey

The sea-water pCO₂ concentrations measured during this survey are shown in Figure 4.47. Sea-water carbon dioxide concentrations varied often over the duration of this survey. During JD191 sudden drops in sea-water pCO₂ concentrations were observed. These sharp drops occurred whilst the CE was in the Celtic Sea. The agreement statistics between each instrument are displayed in Figure 4.48. This survey showed the best agreement between both PSI CO₂-Pro Instruments.

![Seawater pCO₂ Concentrations - CE10007 Survey](image1)

**Figure 4.47:** Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10007

![Percentage pCO₂ Difference between PO1 & PO2 - CE10007 Survey](image2)

**Figure 4.48:** Percentage Difference of pCO₂ concentrations between both instruments - CE10007
4.3.1.10 CE10018 - Bathymetric Survey

The measured sea-water pCO$_2$ concentrations observed during this survey are plotted in Figure 4.49. Parts of this survey were located in or near Cork Harbour, causing a larger than normal amount of silt and particulate to accumulate inside the tank containing the two PSI CO$_2$-Pro instruments. The percentage difference data between both instruments is plotted in Figure 4.50.

**Figure 4.49:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10018

**Figure 4.50:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10018
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

4.3.1.11 CE10016 - Irish Groundfish Survey - Leg 2

The sea-water pCO$_2$ concentrations recorded by both instruments is plotted in Figure 4.51. There is a gap in the data (JD320 - JD322). This was when the CE was in a bay and poor data was recorded, thus removed. A spike in the pCO$_2$ data occurred during the evening of JD323. The cause for this spike is unknown. The percentage pCO$_2$ concentration difference statistics for the cruise CE10016 - Leg 2 are plotted in Figure 4.52.

![Seawater pCO$_2$ Concentrations](image1)

**Figure 4.51:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10016 - Leg 2

![Percentage Difference of pCO$_2$](image2)

**Figure 4.52:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10016 - Leg 2
4.3.1.12 CE10016 - Irish Groundfish Survey - Leg 3

The measurements made by the both pCO$_2$ measurements are plotted in Figure 4.53, showing the agreement between both instruments. The percentage difference results for the CE10016 - Leg 3 cruise are displayed in Figure 4.54.

**Figure 4.53:** Measured sea-water pCO$_2$ concentrations by both instruments - PO1 & PO2 - CE10016 - Leg 3

**Figure 4.54:** Percentage Difference of pCO$_2$ concentrations between both instruments - CE10016 - Leg 3
4.3.1.13 Total Benchmarking Cruise Analysis

When each of the benchmarking surveys were analysed as a whole, a picture of how well the two PSI CO$_2$-Pro instruments performed against each other becomes clearer. For each half-hour section, where both pCO$_2$ instruments were operating, average values were calculated between both instruments. Located in Figure 4.55, is a histogram of the standard deviation values for all of these half-hour sections in the benchmarking cruises. The amount of data less than a specific standard deviation is displayed in Table 4.4.

![Histogram of Standard Deviation Values](image)

**Figure 4.55: Standard Deviation values for All Benchmarking Cruises**

<table>
<thead>
<tr>
<th>Standard Deviation Value</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD - &lt; 3 µatm</td>
<td>61.2%</td>
</tr>
<tr>
<td>STD - &lt; 5 µatm</td>
<td>80.5%</td>
</tr>
<tr>
<td>STD - &lt; 7 µatm</td>
<td>91.8%</td>
</tr>
<tr>
<td>STD - &lt; 10 µatm</td>
<td>97.8%</td>
</tr>
</tbody>
</table>

**Table 4.4: Percentage Standard Deviation Values for all Benchmarking Cruises**

Some “large” standard deviation values (< 10 µatm) were calculated and observed in Figure 4.55. Although, accounting for only a fraction of the data, some possible reasons for these high values are discussed below.

- Between JD172 and JD176: Large standard deviation values were observed between these days. These occurred during the survey CE10012 - Blue Whiting
Acoustic Survey. This cruise was the first survey that the instrument PO2 operated, after being removed from the ship for one month, and lying idle. This might have had some impact on the operation of the instrument. However, towards the end of the survey, agreement between both instruments improved greatly.

- Around JD320 & JD323, some large standard deviations were observed. Some of these occurred at the beginning of the cruise CE10016 - Irish Groundfish Survey Leg 2. These values could be attributed to some fresh water possibly still residing inside the tank. During JD323, some standard deviations (14 - 18 µatm) were observed. These values were recorded as the ship was travelling in the open ocean south of the Irish coast and the reason for their occurrence is unknown.

The percentage difference statistics for all of the benchmarking cruises analysed as a whole are plotted in Figure 4.56. Approximately 50% of all recorded data from both instruments had a difference of 3 µatm or less. Also, just over two thirds of the data set had a difference of only 5 µatm or less.

![Figure 4.56: Percentage Difference Statistics for all Benchmarking Cruises](image)

On the next page, Figure 4.57 is a plot of various pCO₂ difference values, which were calculated for each of the benchmarking cruises.
Chapter 4. Analysis of the Shipboard pCO$_2$ Data and PSI CO$_2$-Pro Performance

**Figure 4.57:** Various Difference Values for all Benchmarking Cruises

![Graph showing various difference values for benchmarking cruises with labels: 01 - CE10001, 02 - CE10002, 09 - CE10009, 06 - CE10006, 11 - CE10011, 10 - CE10010, 14 - CE10014, 12 - CE10012, 07 - CE10007, 18 - CE10018, 16a - CE10016a, 16b - CE10016b.](image)

**Table 4.5:** Numbers from the x-axis in Figure 4.57 correspond to these benchmarking cruises

<table>
<thead>
<tr>
<th>Cruise Name</th>
<th>Benchmarking Survey</th>
</tr>
</thead>
<tbody>
<tr>
<td>01 - CE10001</td>
<td>06 - CE10006</td>
</tr>
<tr>
<td>02 - CE10002</td>
<td>11 - CE10011</td>
</tr>
<tr>
<td>09 - CE10009</td>
<td>10 - CE10010</td>
</tr>
<tr>
<td>14 - CE10014</td>
<td>12 - CE10012</td>
</tr>
<tr>
<td>18 - CE10018</td>
<td>16a - CE10016a</td>
</tr>
<tr>
<td>16b - CE10016b</td>
<td></td>
</tr>
</tbody>
</table>

The lowest half-hour average difference during each of the cruises is represented by the dark-green colour. As expected, all of the values were 0 µatm or very close to 0 µatm and are difficult to spot on the graph. The light-green bars are the highest half-hour difference that was observed during each survey. In theory, the total cruise average pCO$_2$ concentration for each instrument should be the same after each survey. Although, this was not the case during each of the benchmarking surveys, the total cruise averages for both instruments were very close to each other. Three-quarters of the surveys had a total cruise difference <5 µatm and the remaining cruises having differences <10 µatm. These differences are displayed by the yellow bars.

### 4.3.2 Bench-marking the PSI CO$_2$-Pro Instruments against the General Oceanics pCO$_2$ System

Along with the PSI-CO$_2$ Pro instruments, a General Oceanics (GO) pCO$_2$ system was also installed on-board the R.V. Celtic Explorer. The main objective of this set-up
was to try and benchmark the PSI pCO₂ instruments against the GO pCO₂ system. This objective was achieved during the CE10015 - Irish Groundfish Survey 2010. A comparison of sea-water pCO₂ data from both instruments is plotted in Figure 4.58.

The Pro Oceanus instrument - PO2 operated during the majority of the survey, measuring data between September 26th (JD269) and October 6th (JD279). However, the GO system only recorded sea-water pCO₂ during the second half of the survey. As a result, pCO₂ data from both instruments can only be compared between JD274 and JD279. Only data measured during this time frame is plotted in Figure 4.58. During this six day period from JD274 to the end of the cruise, gaps in sea-water pCO₂ data from both instruments occurred. The PO2 instrument did not record any data during part of JD276 and JD277, as it was stopped logging for one reason or another. The percentage difference statistics between both pCO₂ sensors are displayed in Figure 4.59. Comparative statistics are also displayed, if the time period during JD275 and JD276 is omitted.
In total both instruments measured data during 178 half-hour sections, which is approximately 3.7 days. For a period of approximately 24 hours, covering part of JD275 and part of JD276, a large ΔpCO$_2$ difference was measured between both sensors, relative to other sections of the cruise. A large difference in sea-water temperature between water flowing through the GO system and the pCO$_2$ tank could possibly account for this difference, however this was not the case as shown in Figure 4.60. Ultimately, the reason for this large difference in pCO$_2$ concentrations is unknown.

**Figure 4.59:** Percentage difference of pCO$_2$ concentrations between PO2 and GO - CE10015

**Figure 4.60:** Seawater Temperature measured at three separate places
Figure 4.60 is a plot of the sea-water temperature that was measured by a Seabird SBE-39 instrument, which is inside the tank housing the the PSI pCO$_2$ instruments. Temperature measurements were also collected inside the equilibrator of the GO pCO$_2$ system and at the non-toxic inlet located at the bow of the R.V. Celtic Explorer. Data was continuously collected from all three sources, with the exception of the sensor inside the tank housing the Pro Oceanus pCO$_2$ instruments, as no temperature data was collected during part of JD276 and JD277. The difference in water temperature between the open ocean measurements and readings from on-board the ship stayed relatively constant at a value of approximately 0.4 $^\circ$C. As the GO and PSI pCO$_2$ systems received water from the same supply, their temperature measurements are in general agreement with each other.

4.3.3 Bench-marking the PSI CO$_2$-Pro Instruments against In-Situ samples

Another method of examining the accuracy of the of the PSI CO$_2$-Pro Instruments was to compare measurements made by the PSI pCO$_2$ sensors to in-situ measurements collected during corresponding surveys. Water samples were collected by Dr. Rachel Cave, Dr. Caroline Kivimae and Ms. Triona McGrath during two cruises in 2010 - CE10002: Climate Change Oceanography, Biogeochemistry and Geology Section and CE10003: Climate and Ecosystem Sections on the Irish Shelf, and one survey in 2009 - CE0911: Climate Change Survey.

An objective of this other research was to calculate the amount of carbon dioxide in sea-water samples. Numerous other variables were measured, including sea-water temperature, salinity, pressure (depth), silicate, phosphate, dissolved inorganic carbon (DIC) and total alkalinity (TA). All of these parameters were then input into a program called “CO2SYS”, which allows the sea-water pCO$_2$ concentrations to be calculated (Lewis and Wallace, 1998).

CE10002 Survey - Climate Change Oceanography, Biogeochemistry and Geology Sections:

Figure 4.61, is a plot comparing the sea-water pCO$_2$ concentrations measured by both PSI CO$_2$-Pro Instruments (PO1 & PO2), and the calculated sea-water pCO$_2$
concentrations from in-situ water samples collected during the CE10002 survey. The actual depth where each of the water samples were collected are displayed on the graph. During the CE10002 survey, the majority of the pCO₂ concentrations calculated from the in-situ measurements are approximately 10 - 20 µatm above measurements made the PSI pCO₂ measurements. However, some good agreement was achieved towards the end of the survey. A comparison of sea-water temperature data from the CE10002 cruise is plotted in Figure 4.62.

**Figure 4.61:** Comparison between sea-water pCO₂ concentrations measured by the PSI CO₂-Pro Instruments and pCO₂ concentrations from in-situ water samples - CE10002

**Figure 4.62:** Comparison of sea-water temperature data collected during the CE10002 survey

---

-111-
Chapter 4. Analysis of the Shipboard pCO\textsubscript{2} Data and PSI CO\textsubscript{2}-Pro Performance

As shown in Figure 4.60, when sea-water is pumped on-board the CE, the water temperature rises by approximately 0.4 °C. The inlet for the non-toxic water supply is located at the bow of the vessel at an approximate depth of 5 m. The sensor which measures sea-water temperature is located near the inlet, so that heating from the vessel is minimised. This increase in temperature can change the CO\textsubscript{2} content in the sea-water. As a result, sea-water pCO\textsubscript{2} concentrations can be corrected, in order to represent the actual pCO\textsubscript{2} concentrations in the open ocean. As the in-situ measurements were calculated from water samples collected directly from the sea, this correction was necessary and was applied to sea-water pCO\textsubscript{2} data displayed in Figure 4.61.

This correction was applied by using an equation mentioned in Takahashi et al. (2002), which is displayed in Equation 4.1.

\[
pCO\textsubscript{2} @ T_{SST} = (pCO\textsubscript{2})_{Tank} \times \exp[0.0423(T_{SST} - T_{Tank})] \tag{4.1}
\]

- \(T_{SST}\) is the annual average sea-water temperature in °C
- \(T_{Tank}\) is the measured sea-water temperature in °C
- \((pCO\textsubscript{2})_{Tank}\) is the measured partial pressure of CO\textsubscript{2} in \(\mu\text{atm}\)

As expected, there was an approximate difference of 0.4 °C between sea-water temperature readings measured inside the pCO\textsubscript{2} tank and those measured by the temperature sensor that is part of the non-toxic water supply. Temperature readings derived from collected water samples were in excellent agreement with water temperature data measured by the sensor located at the inlet of the non-toxic water supply.

**CE10003 Survey - Climate and Ecosystem Sections on the Irish Shelf:**

Water samples were also collected during the CE10003 survey. pCO\textsubscript{2} data measured by the Pro-Oceanus instrument and in-situ pCO\textsubscript{2} measurements are plotted in Figure 4.63. During this survey, only the PO1 instrument was operational on the Celtic Explorer, as the PO2 pCO\textsubscript{2} instrument was removed.

Sea-water pCO\textsubscript{2} concentrations that were measured inside the tank have been corrected so that they represent pCO\textsubscript{2} concentrations that would be measured in the open
Figure 4.63: Comparison between sea-water pCO$_2$ concentrations measured by the PSI CO$_2$-Pro Instruments and pCO$_2$ concentrations from in-situ water samples - CE10003

Ocean, as per Equation 4.1. During this cruise, sea-water pCO$_2$ concentrations calculated from the collected water samples were in very good agreement with pCO$_2$ data measured by the Pro Oceanus pCO$_2$ instrument - PO1. Sea-water temperature data from the CE10003 survey are displayed in Figure 4.64. Again, in-situ measurements are in very close agreement with data measured by instrumentation located at the bow of the ship, where sea-water is pumped on board.

Figure 4.64: Comparison between various sea-water temperature measurements collected during the CE10003 survey
CE0911 Survey - Climate Change Survey:

Sea-water pCO$_2$ Concentrations & In-Situ Measurements - CE0911 Survey

![Graph showing pCO$_2$ concentrations and in-situ measurements](image)

**Figure 4.65**: Comparison between sea-water pCO$_2$ concentrations measured by the PSI CO$_2$-Pro instrument and pCO$_2$ concentrations from in-situ water samples - CE0911

For a brief period of time in June 2009, the PSI pCO$_2$ instrument - PO1 was installed on-board the CE, during the CE0911 - Climate Change Survey. In-situ water samples were also collected. A comparative plot of sea-water pCO$_2$ concentrations calculated from both the collected water samples and the Pro Oceanus instrument are plotted in Figure 4.65. Data measured by the pCO$_2$ instrument have been corrected, as per Equation 4.1 At the beginning of the cruise, between JD166 and JD169, sea-water pCO$_2$ concentrations calculated from the in-situ samples were in poor agreement with pCO$_2$ concentrations measured by the PSI sensors. However, towards the end of the cruise between JD171 and JD172, some better agreement was achieved.

Sea-water temperature data measured inside the tank housing the PSI pCO$_2$ instruments, along with temperature data measured at the bow of the Celtic Explorer plus temperature data calculated from the collected water samples are plotted in Figure 4.66.

Again, sea-surface temperature data calculated from the in-situ samples are in very good agreement with temperature data measured at the sea-water inlet of the Celtic Explorer. Whereas sea-water temperature readings inside the pCO$_2$ tank are approximately 0.4 °C higher.
It should be noted that all error bars which are fitted to the sea-water pCO$_2$ in-situ data points have an error of approximately $+/- 9 \mu$atm.

**Figure 4.66:** Comparison between various sea-water temperature measurements collected during the CE0911 survey
Chapter 5

Sea-water pCO$_2$ Concentrations in Irish Waters

Concentrations of carbon dioxide in coastal ocean zones vary both temporarily and spatially. In these regions there is a movement of CO$_2$ in several directions: across the air-sea interface, from riverine sources into continental shelf seas and from shelf waters into deeper regions of the oceanic environment. The coastal ocean is the site of intense physical, chemical and biological processes (Mackenzie, 1991). Significantly higher rates of new primary production occur in continental margins than in the open ocean, due to the higher supply of nutrients from cross-shelf break upwelling (Chen and Borges, 2009). In order to try ascertain a complete picture of the variation of sea-water pCO$_2$ concentrations in Irish waters, data were collected in both the open ocean and over the continental shelf. Sea-water pCO$_2$ concentrations were also measured at a coastal site - Mace Head research station, to try and achieve a full understanding of the seasonal changes of sea-water carbon dioxide concentrations in all oceanic regions around Ireland.

5.1 Sea-water pCO$_2$ Concentrations measured on the R.V. Celtic Explorer

During all of the research cruises conducted in 2010, which are discussed in Section 4.1, the R.V. Celtic Explorer surveyed waters in the following areas:
Chapter 5. Sea-water pCO$_2$ Concentrations in Irish Waters

- Atlantic Ocean: over the continental shelf around Ireland, Rockall Trough and Rockall Plateau, Celtic Sea, northern fringes of Bay Of Biscay, Irish Sea and North Channel
- North Sea
- English Channel

All of the ship tracks undertaken by the CE are displayed in Figure 5.1. The collection of ship tracks on the far right-hand side of the map was when the ship was travelling to and from Germany, and when conducting the CE10001 and the CE10017 surveys in the North Sea.

![Ship tracks from all cruises conducted by the R.V. Celtic Explorer during 2010](image)

**Figure 5.1:** Ship tracks from all cruises conducted by the R.V. Celtic Explorer during 2010

The majority of the R.V. Celtic Explorer surveys were conducted in waters off north, west and south coasts of Ireland. It was decided that only pCO$_2$ data recorded in these areas would be included for further analysis in this thesis. Sea-water pCO$_2$ data recorded in the following areas were excluded: English Channel, North Sea and North Bay of Biscay. Once the unwanted areas were removed, the ship tracks that remained were displayed in Figures 5.2 to 5.5.
Figures 5.2 to 5.5 display the CE ship tracks divided up into each of the four seasons. Figure 5.2 covers all routes between January and March 2010. Figure 5.3 displays all routes between April and June 2010 - summer. Figure 5.4 shows all tracks between July and September 2010 - autumn. Figure 5.5 shows all tracks between October and December 2010 - winter.
during the autumn months of July to September 2010. Figure 5.5 covers all tracks between October and December 2010 - winter.

When all sea-water pCO$_2$ concentrations measured during these CE routes are analysed as a whole, the picture of the seasonal variability of the the amount of carbon dioxide in Irish waters is easier to visualise. Figure 5.6 is a plot of the sea-water pCO$_2$ concentrations measured during all of the cruises that are displayed in Figures 5.2 to 5.5.

![Air and Sea pCO$_2$ Concentrations in Irish Waters 2010](image)

**Figure 5.6:** All pCO$_2$ data measured during 2010

Sea-water pCO$_2$ concentrations have been divided into two categories: coastal and offshore. All coastal measurements were collected when the sea floor was at a depth of between 0 and 200 m. Any measurements that were gathered when the ocean bottom was at a depth greater than 200 m are regarded as offshore measurements.

It should be noted that the sea-water pCO$_2$ concentrations displayed in Figure 5.6 originate under the following conditions:

- When both PSI pCO$_2$ instruments operated on a given cruise, the average sea-water pCO$_2$ concentration was calculated between both sensors (PO1 & PO2), and it was this average value that was brought forward for further analysis. This criteria would have been applied during all of the benchmarking surveys.
During the end of May 2010 and the beginning of June 2010, only the PSI instrument - PO1 was onboard the CE. As this instrument was the only source of data, only measurements from this sensor was retained for further study.

During the CE10005, CE10015, CE10013 and CE10017 surveys, an issue arose with one of the PSI pCO$_2$ instruments. Both sensors were in disagreement with each other, and it was believed that the PO1 instrument was impaired, possibly due to bio-fouling from the CE10018 survey. As a result, only pCO$_2$ data from the PO2 instrument was brought forward for further analysis. The reasoning behind retaining pCO$_2$ data from this instrument was because it performed relatively well against the GO system during the CE10015 survey, as discussed in Section 4.3.2.

Atmospheric carbon dioxide concentrations were measured at the Mace Head research station. During all of April and some of May, no data were collected, hence the gap in the black line in Figure 5.6. Overall, pCO$_2$ concentrations in the air remained relatively constant compared to that of the ocean. Atmospheric pCO$_2$ concentrations were highest during the winter months with monthly average concentrations in December and January of $396.9 \pm 4.1 \mu$atm and $394.4 \pm 8.2 \mu$atm respectively. In 2010, lower concentrations were observed towards the end of summer in August and September with pCO$_2$ concentrations of $381.4 \pm 4.3 \mu$atm and $382.6 \pm 4.3 \mu$atm. The yearly average atmospheric pCO$_2$ concentration was $388.9 \pm 7.6 \mu$atm.

From an annual perspective sea-water pCO$_2$ concentrations varied more, compared to atmospheric concentrations, and were lowest during the summer months and highest during the winter months. From May - September the ocean was strongly undersaturated relative to the atmosphere. This would infer that there would be downward movement of CO$_2$ across the air-sea boundary. The lowest average monthly sea-water pCO$_2$ concentration was observed in June, with a value of $320.1 \pm 18.4 \mu$atm. From Figure 5.6, it appears that sea-water concentrations of carbon dioxide in Irish sea-waters peaked twice during the year. Once during February/March, where carbon dioxide concentrations in the ocean were close to atmospheric equilibrium. Also, for a second time towards the end of the year near November/December, where CO$_2$ concentrations in the sea-water were at equilibrium or greater than those in the atmosphere. Sea-water pCO$_2$ concentrations reached their first peak during March at an average
monthly concentration of 388.0 +/- 12.3 µatm and reached a maximum concentration in November with a concentration of 408.3 +/- 22.9 µatm. During these months, when the atmosphere and under-lying ocean are at/near equilibrium, the movement of CO₂ across the air-sea interface would be very weak, if not non-existent. A plot of the mean monthly values for air and sea-water pCO₂ concentrations are displayed in Figure 5.7.

The error bars in Figure 5.7 represent the variability in the data for each month. The error bars are one standard deviation in length.

The General Oceanics pCO₂ system also measured air pCO₂ concentrations, however the instrument only operated during one survey in 2010: CE10015 - Irish Groundfish Survey 2010. A comparative plot of atmospheric pCO₂ concentrations measured on the CE and at Mace Head are plotted in Figure 5.8. During most of the time frame, the difference between both data sets is approximately 10 - 15 µatm. It should be noted that the CE was surveying waters off the north coast of Ireland, far from the Mace Head Research Station. However, during JD279 the CE passed off shore from Mace Head on its return to Galway. Yet there is still a difference of approximately 10 µatm between both instruments. The exact cause of this difference is unknown. Air pCO₂ concentrations measured on the CE are calculated by the GO instrumentation located in the wetlab of the ship. A long piece of tubing connects the instrument to the roof of the bridge (at a height of 35 m), where the air is sampled. Mace Head air pCO₂ concentrations are calculated from the LI-COR 6252 instrument.
Between JD274 and JD280, atmospheric pCO$_2$ data recorded by the GO system appears to vary diurnally, although weakly. During some days, air pCO$_2$ concentrations peak during the night-time hours and reach a low during the early afternoon. This diurnal activity is most pronounced during JD274, JD276 and JD278. Atmospheric and sea-water pCO$_2$ concentrations measured between JD274 and JD280 are plotted in Figure 5.9.

**Figure 5.8:** Air pCO$_2$ data between September 24th and October 7th 2010

**Figure 5.9:** Air and Sea-water pCO$_2$ concentrations between September 24th and October 7th 2010
Miyaoka et al. (2007) reported diurnal variations in atmospheric pCO$_2$ concentrations. However, these measurements were recorded over land and were documented to be influenced by both anthropogenic and natural processes. During this period of time, there was also a possible diurnal signal in the sea-water pCO$_2$ data. pCO$_2$ concentrations in the ocean would reach a peak during the nighttime hours and a low during the middle of the day. McGillis et al. (2004) states that over the open ocean, variability in air CO$_2$ concentrations will be a function of the variability in pCO$_2$ at the ocean surface. This weak diurnal signal in atmospheric pCO$_2$ concentrations could be as a result of the changing sea-water pCO$_2$ concentrations. Sea-water pCO$_2$ concentrations could be varying diurnally as a result of the autumn phytoplankton bloom. Photophysiological reactions, in the phytoplankton, could occur during the middle of the day, which would cause a decrease in carbon dioxide concentrations in the sea-water. pCO$_2$ concentrations would then increase during the night as no reactions would occur.

During some of the CE surveys, the variations in sea-water pCO$_2$ concentrations was easily visualised due to a high density of data points in a small area. These surveys included CE10011, CE10012, CE10013 and CE10015. pCO$_2$ data that was recorded during each of these cruise are displayed in Figures 5.10 to 5.13.

During the CE10011: Blue Whiting Acoustic survey, which was conducted between March 19th and April 6th 2010, higher concentrations (≈400 μatm) were observed over the open ocean compared to over the continental shelf closer to the mainland.
Chapter 5. Sea-water pCO₂ Concentrations in Irish Waters

The CE10012: Northwest Herring Acoustic survey was conducted between June 18th and July 6th 2010. It was during this time frame that some of the lowest sea-water pCO₂ concentrations were measured during 2010 in the north-east Atlantic Ocean. As the CE moved north over the continental shelf, carbon dioxide concentrations in the ocean steadily increased. These low pCO₂ concentrations can most likely be attributed to the phytoplankton bloom which occurs in waters off Ireland during the months of May and June. This is discussed further later on.

![Figure 5.12](image1.png)  
**Figure 5.12:** Sea-water pCO₂ concentrations measured during the CE10015 cruise

![Figure 5.13](image2.png)  
**Figure 5.13:** Sea-water pCO₂ concentrations measured during the CE10013 cruise

The CE10015: Irish Groundfish Survey 2010 was conducted between September 25th and October 6th 2010. During this cruise the highest sea-water pCO₂ concentrations were measured closer to the mainland, while higher concentrations were observed further into the open ocean. The CE10013: Celtic Sea Herring Acoustic survey was conducted throughout most of October 2010. Similar to the CE10015 cruise, higher sea-water pCO₂ concentrations were measured closer to the coast, while lower concentrations were observed in deeper waters.

5.1.1 Sea-Surface Temperature and Biological Effects on Sea-water pCO₂ concentrations

Sea-water pCO₂ concentrations varied between coastal regions and waters far from shore on a seasonal basis. During the early months of summer: April to early June,
pCO$_2$ concentrations in coastal regions and over the continental shelf were lower than those measured far from the mainland on the shelf edge and deeper waters of the Atlantic Ocean. Figure 5.14 shows the variation in sea-water concentrations of carbon dioxide in the ocean off Ireland.

**Figure 5.14:** Sea-water pCO$_2$ concentrations measured between April 10th and June 2nd 2010

**Figure 5.15:** Sea-water pCO$_2$ concentrations measured between November 15th and December 15th 2010

During the early summer months, pCO$_2$ concentrations measured near the coast
were in the range of 250 - 320 µatm (purple and blue), whereas sea-water pCO$_2$ concentrations further away from the mainland were in the region of 330 - 380 µatm (green). However, during the winter months of November and December, the opposite occurred, as displayed in Figure 5.15. Over the duration of the winter months, coastal sea-water pCO$_2$ concentrations were substantially higher than those observed during the summer months, mostly between 400 - 450 µatm (orange). Sea-water concentrations of CO$_2$ in deeper waters were approximately unchanged and very similar to concentrations recorded during the summer months.

Chlorophyll fluorescence data was collected during all Celtic Explorer cruises. It was measured by a fluorometer which was installed in the wetlab. The accuracy of the fluorometer on-board the CE is not exact, due to the instrument not being calibrated frequently enough. However, chlorophyll fluorescence levels are still a good indicator of the amount of phytoplankton in the surrounding sea-water. During the early summer months, when sea-water pCO$_2$ concentrations are at their lowest, some very high chlorophyll fluorescence levels were observed. During this time period, algal blooms occur in sea-water around Ireland, leading to elevated concentrations of phytoplankton, which in turn remove carbon dioxide from the ocean. In Figure 5.14, very low pCO$_2$ concentrations ($\sim$ 250 - 300 µatm) were observed close to the Irish mainland over the
continental shelf. It was in this region, off the south-west coast, that some of the highest chlorophyll fluorescence levels (≈ 0.055 - 0.065 V) were measured. During the winter months, when higher sea-water pCO$_2$ concentrations (≈ 380 - 450 µatm) were recorded, some chlorophyll fluorescence data were lower than those observed during the summer (≈ 0.04 V), implying lower phytoplankton concentrations.

Sea-water pCO$_2$ concentration measurements were collected in the coastal regions around the island of Ireland. Readings were also taken over the continental shelf and off the shelf edge over deep Atlantic waters. Located in Figure 5.18, is a plot of all sea-water pCO$_2$ measurements divided up into each of these three categories.

![Coastal, On-Shelf and Off-Shelf Sea-water pCO$_2$ Concentrations](image)

**Figure 5.18:** All sea-water pCO$_2$ measurements divided into coastal, on-shelf and off-shelf categories

All coastal and shelf data (blue circles) were measured when the CE was located in waters where the ocean floor was at depths between 0 - 200 m. “Shelf Edge” data (green circles) consists of all data that was collected on the edge of the continental shelf when the ship was surveying waters that had depths of between 200 and 500 m. When the CE travelled past the shelf boundary, all measurements collected were denoted as “Off-Shelf” (black circles), where the sea floor was at depths mostly greater than 500 m. From Figure 5.18, it can be seen that there is more of an seasonal variability in sea-water pCO$_2$ concentrations measured in coastal and on-shelf areas than in deeper waters off the continental shelf. Both the annual minimum and maximum values were
measured in these regions. Also, during the early summer months from April - June, the lowest pCO$_2$ concentrations were in the waters closer to the coast and over the continental shelf. These concentrations were in the region of 30 - 40 µatm lower than those measured over deeper waters.

Understanding the contribution of temperature effects and biological effects on the variation of sea-water pCO$_2$ concentrations is important not only for understanding the time space variability for the sea-air CO$_2$ exchange (Takahashi et al., 2002). Sea-water temperatures in Irish waters naturally vary over an entire year: with colder waters observed during the winter months and warmer waters experienced during the summer months. This warming of sea-waters reduces the solubility of the ocean, and could possibly impact on the amount CO$_2$ that can reside in the ocean, thus lowering it. A plot a sea surface temperature (SST) measured during all cruises specified in Figures 5.2 to 5.5, is displayed in Figure 5.19. Sea surface temperatures peak during July at approximately 18 °C and reach a yearly low in February with a value of approximately 7.5 °C. A plot of the sea-water temperature data averaged for each month in 2010 is also included. The annual average water temperature was 12.8 °C.

![Figure 5.19: SST during surveys conducted in Irish waters in 2010](image)

In order to remove the effects of temperature on sea-water pCO$_2$ concentrations, values can be normalised to 12.8 °C. Normalised pCO$_2$ data and actual measured pCO$_2$
data are plotted in Figure 5.20. Normalised sea-water pCO$_2$ is calculated by Equation 4.1, which was discussed previously.

\[ \text{Normalised sea-water pCO}_2 \]

Both normalised sea-water pCO$_2$ data and actual measured sea-water pCO$_2$ data vary in the same direction seasonally. However, sea-water pCO$_2$ concentrations that have been normalised to 12.8 °C appear to vary more in magnitude compared to the actual measured data. The seasonal change in temperature could have a damping effect on the air-sea exchange of CO$_2$. It is very clear that there is a springtime decrease in sea-water pCO$_2$ concentrations from March to June, in the measured and normalised pCO$_2$ data. This drop in carbon dioxide is most likely due to the annual phytoplankton bloom which occurs in temperate latitudes every year. During the months of June - September, pCO$_2$ @ 12.8 °C stayed relatively constant near 300 µatm. Then, from September to October, sea-water pCO$_2$ begin to climb steadily, most likely as a result as primary production starts slowing down.

Satellite images from the NASA (National Aeronautics and Space Administration) website can be used to study the phytoplankton blooms from space. Most days are of poor quality due to cloud cover, but phytoplankton blooms were observed during the months of May and June 2010. Images of the bloom are displayed in Figure 5.21 and Figure 5.22.
In Figure 5.21, the bloom is the light blue/turquoise colors off the south-west coast of Ireland. Figure 5.22 shows the bloom continuing off the south-west coast, in addition to the west coast over the continental shelf and close to the mainland off Co. Clare, Co. Galway and Co. Donegal. It was during the months of May and June that observed the lowest sea-water pCO$_2$ concentrations (250 - 300 $\mu$atm), see Figure 5.6 data measured during 2010.

The relative importance of biological (B) and temperature (T) effects on sea-water pCO$_2$ concentrations can be expressed as a ratio. This analysis was discussed by Takahashi et al. (2002), where three individual sites were studied to investigate what effect biology and temperature had on sea-water pCO$_2$ concentrations, and which was more influential. In order to calculate the biology/temperature ratio for data collected in the north-east Atlantic Ocean, the effect that temperature changes would have on measured sea-water pCO$_2$ concentrations have to be calculated. This is achieved through Equation 5.1, where calculated values are pCO$_2$ values that would be expected from temperature changes, if a parcel of water with an average annual pCO$_2$ value of 360.46 $\mu$atm is subjected to seasonal temperature changes under isochemical conditions. 360.46 $\mu$atm was the average sea-water pCO$_2$ concentration for all of the cruises plotted in Figures 5.2 to 5.5.
Chapter 5. Sea-water pCO\textsubscript{2} Concentrations in Irish Waters

\[ pCO_2 \text{ @ } T_{obs} = (\text{Mean annual } pCO_2) \times e^{0.0423(T_{obs} - T_{mean})} \]  \hspace{1cm} (5.1)

- \( T_{obs} \) is the actual observed water temperature in °C
- \( T_{mean} \) is the average water temperature in °C
- \((pCO_2)_{T_{obs}}\) is the sea-water pCO\textsubscript{2} values expected at a given temperature in \( \mu \text{atm} \)

These calculated sea-water pCO\textsubscript{2} values along with sea-water pCO\textsubscript{2} concentrations normalised to an annual average sea-water temperature of 12.8 °C are plotted in Figure 5.23.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Sea-water pCO\textsubscript{2} concentrations normalised to the annual mean sea-water temperature and pCO\textsubscript{2} concentrations expected with changes in SST}
\end{figure}

This biology/temperature ratio can be attained, by calculating the range between the maximum and minimum sea-water pCO\textsubscript{2} values for both data sets displayed in Figure 5.23. For pCO\textsubscript{2} data that was normalised to the annual mean SST value of 12.8 °C, the max and min pCO\textsubscript{2} values were 540.32 and 228.86 \( \mu \text{atm} \) respectively, leading to a range of 311.46 \( \mu \text{atm} \). The max and min pCO\textsubscript{2} values for the the pCO\textsubscript{2} concentrations that would be expected from a change in water temperature were 472.44 and 273.48 \( \mu \text{atm} \) respectively, which had a range of 198.96 \( \mu \text{atm} \).
The (T/B) ratio is approximately 0.63 (198.96/311.46) or (T - B) is -112.50 µatm (198.96 - 311.46). In oceanic areas where the (T/B) ratio is between 0 and 1 or (T - B) is negative, biological influences have a greater effect than temperature on sea-water pCO$_2$ concentrations. It is this type of situation that occurred in the north-east Atlantic Ocean during 2010. When (T - B) is positive and and the (T/B) ratio is greater than 1, temperature effects are more influential than biological effects. Both effects cancel each other in oceanic areas where the (T/B) ratio is 1 or (T - B) is 0.

5.2 Air and Sea-water pCO$_2$ analysis from Mace Head

An all weather data buoy was installed at Mace Head and was discussed in Section 3.2.2. Several pieces of instrumentation were installed on the buoy while it operated between November 2008 and November 2009. An analysis of the various parameters that were measured are discussed in the following sections.

5.2.1 Air and Sea-water pCO$_2$ concentrations

A Pro-Oceanus CO$_2$ Pro pCO$_2$ system was installed on the buoy and sea-water carbon dioxide concentrations were measured. The observed pCO$_2$ concentrations are plotted in Figure 5.24. Also plotted are the air pCO$_2$ concentrations which were measured by the LI-COR LI-6252 instrument at the Mace Head research station.

Air concentrations of carbon dioxide remained relatively constant compared to sea-water pCO$_2$ concentrations. Between November 1st 2008 and November 30th 2009 the average air pCO$_2$ concentration was 386.54 $\pm$ 8.25 µatm. Between the winter months of November 2008 and February 2009, sea-water pCO$_2$ concentrations were mostly less than or near equilibrium with atmospheric CO$_2$ concentrations. However, there were two brief episodes where sea-water concentrations did climb higher than those observed in the overlying air. During the summer months of April to July, sea-water concentrations of CO$_2$ varied dramatically, whilst mostly remaining higher than atmospheric concentrations. pCO$_2$ concentrations were highest at the very end of April when a concentration of approximately 973 µatm was recorded. Sea-water pCO$_2$ concentrations sharply increased and decreased over a time frame of few days during the very beginning of June and again towards the end of July.
With regard to atmospheric carbon dioxide concentrations, they were highest during the first six months of 2009, peaking between 400 and 410 μatm during the months of January, March and June, as displayed in Figure 5.25. However, air CO₂ did sharply decrease towards the end of January, reaching a low of approximately 375 μatm. Air concentrations again dipped this low towards the end of the summer season during the months of July - September, as expected.
5.2.2 Chlorophyll Levels

Chlorophyll fluorescence levels can be used to gauge how much phytoplankton is in the surrounding sea-water. These microscopic organisms are capable of performing photosynthetic reactions which remove CO$_2$ from the sea-water, thus lowering its dissolved concentration. Fluorescence measurements were conducted by the Wetlabs Water Quality Monitor (WQM) instrument which was installed on the Mace Head buoy. The principle underlying chlorophyll fluorescence analysis is relatively straightforward. Light energy is emitted from the instrument, which is turn is absorbed by the chlorophyll molecules in the plankton floating in the surrounding sea-water. The light energy that is absorbed by chlorophyll molecules can undergo one of three fates: it can be used to drive photosynthesis (photochemistry), excess energy can be dissipated as heat or it can be re-emitted as light - chlorophyll fluorescence. These three processes occur in competition with each other, where any increase in the efficiency of one will lead to a decrease in yield of the other two (Maxwell and Johnson, 2000). Light energy which is re-emitted by the plankton is detected by the instrument. The more plankton in the water, the likelihood that more light energy that will be detected by the instrument.

**Figure 5.26:** Chlorophyll fluorescence levels measured by the WQM installed on the Mace Head buoy between November 2008 and November 2009
Located in Figure 5.26 is a plot of all chlorophyll fluorescence data that was measured by the WQM instrument on the buoy. In sea-waters around Mace Head, biological activity was low (< 1 µg/L) during the winter months. However, during the summer months when phytoplankton concentrations tend to be higher, chlorophyll fluorescence levels were also elevated, as expected. Between April and October, chlorophyll fluorescence levels were higher than those experienced during the winter months. Levels spiked dramatically towards the end of April with measurements greater than 4 µg/L observed. Chlorophyll fluorescence levels increased again in the last week of July and the first week of August. During this time period, levels measured were approximately 2 - 3 µg/L.

5.2.3 SST and Salinity

Sea-surface temperature and salinity data were also measured by the WQM instrument installed on the buoy. Data sets for both of these variables are plotted in Figure 5.27 and Figure 5.28.

![Salinity - Mace Head - November 2008 - November 2009](image)

**Figure 5.27:** Salinity levels measured by the WQM installed on the Mace Head buoy between November 2008 and November 2009

The average salinity level for sea-waters at Mace Head was approximately 34 PSU (practical salinity units) during the time frame of this experimental work. However, there were times when salinity levels dropped below the average level, as shown by
Figure 5.27. These drops in salinity could be attributed to fresh water circulating through the area, possibly from either rainfall or riverine sources.

Sea-surface temperature data is plotted in Figure 5.28. The average sea-surface temperature between November 2008 and November 2009 was $11.05 \pm 2.8^\circ C$. At Mace Head, sea-water temperatures followed the typical yearly cycle that would be observed at temperate latitudes. The annual low occurs at the very end of winter or early spring. The lowest value recorded was approximately $6.77^\circ C$ on January 24th 2009. As the year proceeded, the sea-water temperature at Mace Head increased and reached its peak in early June with a reading of $17.57^\circ C$. Gaps appear in both the salinity and SST data sets. These gaps arise due to the WQM instrument not working, thus no data were recorded.

5.2.4 Sea-water pCO$_2$ Concentration “Spikes”

The coastal oceanic environment is a very active region with regard to changing concentrations of carbon dioxide. This is due to the fact that there are many factors at play which can influence the amount of CO$_2$ which reside in the sea-water during a given time period. Figure 5.25 is a plot of all air and sea-water pCO$_2$ data measured at Mace Head between November 2008 and November 2009. During the summer
months, pCO$_2$ concentrations were more varied than those observed during the winter months. A section of pCO$_2$ data from these summer months, measured between April and August 2009 is displayed in Figure 5.29.

![Air and Sea pCO$_2$ Conc. @ Mace Head - April - August 2009](image)

**Figure 5.29**: Air and Sea-water pCO$_2$ data measured at Mace Head between April and August 2009

Over the course of these months sea-water pCO$_2$ concentrations sharply increased and then suddenly decreased during three separate time frames, each lasting on average for around two weeks. Each of these “spikes” occurred between the following dates:

- **Spike 1**: April 24th - May 9th
- **Spike 2**: May 29th - June 10th
- **Spike 3**: July 13th - July 31st

The first spike lasted approximately sixteen days and a maximum sea-water pCO$_2$ concentration of 979 µatm was recorded. Soon after the peak was reached, pCO$_2$ concentrations began to drop rapidly. The second spike, which occurred during the beginning of June, resulted in a peak pCO$_2$ concentration of 845 µatm. The final sharp rise in sea-water pCO$_2$ concentrations had a maximum value of 877 µatm. During each of the sharp rises and falls of sea-water pCO$_2$ concentrations, atmospheric concentrations remained relatively constant.
Chlorophyll fluorescence, salinity and sea-surface temperature readings were also quite variable during each of these months. Plots for each of these data sets, including sea-water pCO$_2$ concentrations, where only the summer months are displayed are shown in Figures 5.30 to 5.32. In these graphs, each of these data sets have been “smoothed” for visual appearances.

During the first spike, when there was a sudden rise in pCO$_2$, this was accompanied by a sharp increase in chlorophyll fluorescence levels, while both SST and salinity levels remain relatively unchanged. The sudden increase in chlorophyll fluorescence levels occurs a few days after the pCO$_2$ peak. This situation could be as a result of deeper water coming to the surface, which is rich in carbon dioxide and nutrients. These nutrients, which include phosphorous and nitrogen, stimulate the beginning of the phytoplankton bloom.

The second spike in sea-water pCO$_2$ concentrations coincides with a sharp drop in salinity levels plus a rise in sea-surface temperature. It appears that a warm freshwater parcel of water passed though the area, causing these sudden changes in each of these variables. However, this is only a suggestion, as there are no large fresh-water rivers meeting the sea near Mace Head. Also, this fresh-water source was not due to precipitation, as early June was extremely dry and experienced very little rainfall.
The third spike in $pCO_2$ data occurred when there was also a slight rise in chlorophyll fluorescence levels, whilst SST and salinity stayed stable. This situation could have arisen due to $CO_2$ rich water arriving from deeper depths again, similar to the first spike.

**Figure 5.31:** Salinity and sea-water $pCO_2$ data measured at Mace Head between April and August 2009

**Figure 5.32:** Sea-surface temperature and sea-water $pCO_2$ data measured at Mace Head between April and August 2009

–139–
Figure 5.33 shows how chlorophyll fluorescence and salinity levels varied during April and August 2009.

Figure 5.33: Chlorophyll fluorescence and salinity data measured at Mace Head between April and August 2009
Chapter 6

CO$_2$ Fluxes and Gas Transfer

Velocity of Carbon Dioxide

6.1 Meteorological Data

6.1.1 Wind Speed and Wind Direction

The Mace Head Research station is located on the extreme west coast of Ireland. Its exact location is displayed in Figure 3.10. Air flow is mostly oceanic in origin, however wind speeds and wind directions varied throughout the time frame of this experimental work. The average monthly wind speed and wind direction values are displayed in Figure 6.1 and Figure 6.2.

**Figure 6.1:** Average Monthly Wind Direction at Mace Head

**Figure 6.2:** Average Monthly Wind Speed at Mace Head
All months with the exception of February and June had an average monthly wind direction that was oceanic in origin. Maritime winds at Mace Head occur between 190° and 300° approximately. Figure 6.3 displays the frequency of wind direction measurements at Mace Head, binned into groups of 10°. The most frequent wind direction was from the westerly direction between 260° & 270°. Figure 6.4 shows the frequency of wind speed measurements. These readings are placed in groups of 1 m/s. The highest recorded wind speed was roughly 21 m/s, observed on both May 7th and October 24th 2009. All wind speed and wind direction data were measured during times when no precipitation was observed, as all data measured during periods of rainfall were removed in the filtering process, which is explained in Section 6.3.2.2. As a result, higher wind speeds might have been observed, yet not included in the data set.

Wind direction and wind speed data were calculated from data measured by the sonic anemometer, which is described in Section 3.2.1.3. Data was measured at a rate of 10 Hz and then half-hour averaged. Equations 6.1 and 6.2 were used to calculate the respective variables.

\[
WD = (180 + (0 - \arctan2(v/u)))
\]

\[
WS = \sqrt{u^2 + v^2 + w^2}
\]
where \( u, v \) and \( w \) are the orthogonal wind components measured by the sonic anemometer. \( \text{atan2} \) is the four-quadrant inverse tangent function in Matlab. All wind direction and wind speed data were compared to other wind speed/direction data measured by other instrumentation at Mace Head. By comparing both data sets, further confidence in the anemometer data could be achieved.

Figure 6.5 is a comparative plot of wind direction data recorded by the anemometer and the Vector Instruments W200P instrument installed at the Mace Head research station. This instrument is discussed further in Section 3.2.3.2. Located in Figure 6.6 is a plot of wind speed measurements made by both the sonic anemometer and the Vector Instruments A100L instrument at Mace Head, which also measures wind speed.

The Vector W200P and A100L instruments were located beside “The Cottage” laboratory at Mace Head, which is at the top of a hill at ground level. This laboratory is approximately 100 m inland from the sonic anemometer. This comparative analysis was conducted so that further confidence could be achieved in the data measured by the anemometer. In both plots, the blue dots represent data that was measured after the rain filtering step was performed on all data sets. This data accounts for approximately 51.5% of all data that was recorded. The black dots correspond to data points that remained after all of the filtering stages were applied. The filtering process is discussed in Section 6.3.2. This data was approximately 1.2% of the whole data set. In Section 6.4.1, the relationship between wind speed and gas transfer velocity is quantified. The data points used to calculate the correlation between these two variables correspond to the same half-hour sections, that the black dots represent above. The red line marks the 1:1 relationship between both data sets.
In Figure 6.5, it is clear that there was a degree of scatter and disagreement between both instruments that measured the wind direction at Mace Head. As both sensors are in two separate locations, this could explain why there are many measurements that are not in agreement with each other. The majority of the data fall slightly below the 1:1 dotted line. The majority of black dots are close to the 1:1 dotted line. The wind speed measurements, located in Figure 6.6, appear less scattered and the data points fall along the 1:1 line. All measurements that were retained for final analysis are represented by the black dots.

6.1.2 Air Temperature and Atmospheric Pressure

Air temperature at Mace Head does not vary dramatically, as it is located on the edge of the Atlantic Ocean in temperate latitudes. Air temperature data recorded at Mace Head are plotted in Figure 6.7. The lowest and highest temperature observed at Mace Head was -2.2°C and 23.6°C respectively. A plot of atmospheric pressure data is shown in Figure 6.8, with measurements ranging between 963 mb and 1037 mb. Both data sets have been hourly averaged. The instruments that conducted both air temperature and atmospheric pressure measurements are discussed in Sections 3.2.3.4 and 3.2.3.3.

Air temperature values could also be calculated from SoS (Speed of Sound) measurements made by the sonic anemometer. The sonic temperature, $T_s$, is closely approximated to the virtual temperature of the air and is calculated by Equation 6.3.

\[
T_s = \frac{(SoS)^2}{403} \quad (6.3)
\]
Chapter 6. CO$_2$ Fluxes and Gas Transfer Velocity of Carbon Dioxide

- $T_s$ is the sonic temperature - K
- SoS is the Speed of Sound - m/s

The true air temperature is then calculated by Equation 6.4.

$$T = \frac{T_s}{1 + 0.32q^2 \rho}$$  \hspace{1cm} (6.4)

- $T$ is the true air temperature - K
- $T_s$ is the sonic temperature - K
- $q$ is water vapour air concentration - mmol/m$^3$
- $\rho$ is the standard air density - mmol/m$^3$

The standard density of air is $\approx$1.27 kg/m$^3$. This value was converted to mmol/m$^3$ by dividing by the molar mass of air which is $\approx$0.0000289644 kg/mmol.

6.1.3 Relative Humidity & Air CO$_2$ Concentration

Relative humidity data could be obtained from H$_2$O concentration data recorded by the LI-COR 7500 IRGA instrument. Values were obtained through a series of equations starting with Equation 6.5, where the water vapour mass density is converted to the mole fraction.

$$H = \frac{NR T}{P}$$  \hspace{1cm} (6.5)

- $H$ is the H$_2$O mole fraction - mmol/mol
- $N$ is the H$_2$O mass density - mmol/m$^3$
- $P$ is the atmospheric pressure - Pa
- $R$ is the universal gas constant - J/K/mol
Chapter 6. CO$_2$ Fluxes and Gas Transfer Velocity of Carbon Dioxide

The next step is to calculate the dew point temperature, $T_d$, from the water vapour mole fraction. This is achieved through Equations 6.6 and 6.7.

\[ x = \ln \left( \frac{H_{613.65}}{P} \right) \]  
(6.6)

\[ T_d = \frac{240.97 \times x}{17.502 - x} \]  
(6.7)

- $T_d$ is the Dew Point temperature - °C

After the dew point temperature is calculated, it can be converted into relative humidity via Equation 6.8.

\[ RH = 100 - 5(T - T_d) \]  
(6.8)

- RH is the relative humidity - %
- T is the Air temperature - °C

Although these relative humidity values are not extremely accurate and are an approximation, they can be compared to other relative humidity data measured at Mace Head. A comparative plot of relative humidity data from both the LI-7500 instrument and the Vaisala instrument at Mace Head is displayed in Figure 6.9.

The blue dots are data points retained after the rainfall filtering has been applied to the data. The black dots are the half-hour sections where the wind speed/gas transfer relationship was calculated. The red line is the 1:1 linear relationship between both data sets. A large degree of scatter was observed between both the instruments. It should be noted that the Mace Head instrument was located near the “Cottage” laboratory, and the LI-7500 was at the top of the tower. However, in the final data set (black dots), the remaining data fell along the 1:1 line. The LI-7500 measured RH values greater than 100%, which is impossible. Because of this error, all half-hour sections with an average relative humidity value of >95% was excluded from the data set.
Carbon dioxide concentrations in the atmosphere will be discussed in detail in later stages, but it will be briefly mentioned here. Atmospheric CO$_2$ concentrations are measured by the LI-7500 and the LI-6252 instrumentation. A comparison between both instruments is plotted in Figure 6.10.

The majority of the data is slightly the left of the 1:1 dashed line, meaning that the LI-6252 recorded air CO$_2$ concentrations slightly higher than the LI-7500 during a given
half-hour period. The LI-6252 instrument would be more accurate as it is calibrated more often than the LI-7500 instrument. As a result of this, when CO$_2$ measurements are required, this data set was used. During this experimental work, air pCO$_2$ and ∆pCO$_2$ values were calculated using the LI-6252 data set.

6.2 Micro-Meteorology

Relative to some meteorological motions, turbulent motions are of a micro-meteorological scale (Stull, 1988). There are several micrometeorological variables which can help to build a clearer picture of turbulent motion in the boundary layer at a given point in time. Some of these parameters include: friction velocity, drag coefficient and roughness length, which are all discussed below.

6.2.1 Friction velocity, $u^*$

Friction velocity values were calculated by Equation 2.18. Friction velocities calculated during this experimental work are displayed in Figure 6.11.

![Friction Velocities](image)

**Figure 6.11:** Friction velocities before and after filtering

The blue dots represent data points that remained after the data was rainfall filtered. The black dots are the half hour sections that were passed through all filtering stages.
6.2.2 Drag Coefficient, $C_D$

Drag coefficient values were calculated by using Equation 2.19. Rougher surfaces lead to higher drag coefficients. Values measured at Mace Head at the beginning and end of the filtering process are plotted in Figure 6.12.

![Drag Coefficient before and After Filtering](image)

**Figure 6.12:** Drag coefficients before and after filtering

6.2.3 Roughness Length, $z_o$

![Roughness Length Before and After Filtering](image)

**Figure 6.13:** Roughness lengths before and after filtering
Figure 6.13 shows roughness lengths calculated at Mace Head during this research. Again, the blue dots represent data after being rainfall filtered, where the black dots correspond to half-hour sections that remained after all the necessary filtering stages were applied. All roughness lengths were calculated using Equation 2.20.

6.3 CO₂ Flux Data

6.3.1 Data Collection

Instrumentation used in the measurement and collection of carbon dioxide fluxes were discussed in detail in Section 3.2.1. As data were recorded via the DLS, discussed in Section 3.2.1.5, they were stored on a PC in the shore laboratory at the base of the tower at Mace Head. Data were logged continuously to an ASCII file. Every few weeks, the logging programme was interrupted and the latest flux data were offloaded from the computer. The logging program would be restarted and a new ASCII file was created.

An example of the flux data as it appeared in an ASCII file is displayed in Table 6.1.

<table>
<thead>
<tr>
<th>JD</th>
<th>u</th>
<th>v</th>
<th>w</th>
<th>SoS</th>
<th>H₂O</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.62880387</td>
<td>6.48</td>
<td>-3.10</td>
<td>0.21</td>
<td>337.03</td>
<td>471.5576</td>
<td>16.5680</td>
</tr>
</tbody>
</table>

- JD - Julian Day - Day of the Year
- u - streamwise wind speed component - m/s
- v - transverse wind speed component - m/s
- w - vertical wind speed component - m/s
- SoS - Speed of Sound - m/s
- H₂O - Water vapour concentration - mmol/m³
- CO₂ - Carbon dioxide concentration - mmol/m³
The first line of the large flux data file, which was approximately 1 - 2 GB in size, was manually removed as it was normally of very poor quality. The large file was then split into daily files, ~ 50MB in size, as this made the data processing more manageable. Flux data were collected between November 1st 2008 and February 2nd 2009 and February 27th to November 30th 2009 for a total of 271 days. The flux system was non-operational during part of February 2009.

6.3.2 Data Processing

In order for the flux data to be correctly and completely analyzed, the raw data needed to pass through a series of filtering steps. These steps are outlined below.

6.3.2.1 Despiking

During the timeframe of data collection, it was noticed that random “spikes” could sometimes occur in the raw data. A spike is described as a sudden sharp increase in magnitude of a variable being measured, lasting only milliseconds. Although occurring very infrequently, these spikes needed to be filtered out from the data set. An example of some spikes observed in the raw data set are displayed in Figure 6.14. Half hour sections that contained “spikes” were removed via the cut-off technique, which is discussed further in Section 6.3.2.2 or though manual removal methods.

![Figure 6.14: Air CO₂ concentration data recorded during June 29th 2009 - JD180. All data coloured green was removed and all blue data was retained](image-url)
6.3.2.2 Rainfall Influences

During periods of time when rainfall or other forms of precipitation occurred at the Mace Head research station, data recorded by the CO\textsubscript{2}/H\textsubscript{2}O gas analyzer were adversely influenced and the instrument appeared not to be performing correctly. When water droplets coalesced on the sapphire windows of the instrument or passed through the path of the infrared beam, the beam was blocked or distorted, which in turn affected the measurements made by the analyzer. As a result, all flux data recorded during periods of precipitation needed to be removed.

As the Mace Head Research Station is located on the west coast of Ireland, rainfall events were very frequent. Over the course of the time frame when flux data was measured, only 31 days or 8.4% of the total data set were free from rainfall or any other forms of precipitation. Because rainfall events were so common, the altered data could not be removed solely by manual means. Therefore an automatic removal technique was applied to the data set, in conjunction with some manual removal methods.

Flux data recorded on November 11th 2009 contains examples of rainfall contaminated data, which is displayed in Figure 6.15. Data that is altered, which needs to be removed is coloured green. During this time frame very erratic CO\textsubscript{2} concentrations were measured, ranging between 16.5 mmol/m\textsuperscript{3} and 25 mmol/m\textsuperscript{3}. It should be noted that these very high and erratic values are not the sensor measuring the concentration of CO\textsubscript{2} in the passing rainfall. Acceptable data is coloured blue, which was observed to be in the range of 16 mmol/m\textsuperscript{3} and 16.5 mmol/m\textsuperscript{3}.

![Figure 6.15: CO\textsubscript{2} Flux Data measured during periods of precipitation](image1)

![Figure 6.16: Standard Deviation values for half hour periods of CO\textsubscript{2} Flux Data during JD315](image2)
In order to remove the “rainfall data”, the flux data is binned into half-hour periods and the standard deviation for each half-hour period is calculated. A cut-off point is selected and any half-hour periods that have a standard deviation above the cut-off are removed. In the case of November 11th - JD315, the selected cut-off point was 0.05. The half-hour standard deviations calculated during JD315 are displayed more clearly in Figure 6.16. Standard deviations in blue were acceptable, while those in green were deemed poor.

In certain cases, some half-hour periods had a standard deviation value less than the cut-off point, yet still some corresponding CO₂ concentration data was distorted by precipitation. When this situation occurred, the half-hour period was manually removed. Although time consuming, as the data was inspected one day at a time, this type of filtering was possible. The cut-off selected for each day varied. However, it did not differ far from 0.05. Figure 6.17 is a plot of the monthly average cut-off selected for half-hour periods over the course of data collection.

![Monthly Average Acceptable Cut-Off Point](image)

**Figure 6.17:** Monthly Average Standard Deviation Values for acceptable half-hour sections

Standard deviation values were calculated using the *std* function in Matlab. The *std* command is defined as follows

\[
std = \left[ \sum_{i=1}^{n} (x_i - \bar{x})^2 \right]^{1/2}
\]  

(6.9)
6.3.2.3 Wind Direction

The next data filtering step was to remove any data that were recorded when the wind direction was between 301° and 189°. During these wind directions, the air flow over Mace Head is coming from terrestrial sources - from the British Isles and mainland Europe. These regions are sources of air pollution, which could lead to incorrect air CO₂ concentration measurements. As a result of this altered data, inaccurate flux measurements could be incorporated into the final data set. Only data recorded when the wind direction was between 190° and 300° were included. During these wind directions, the air flow was coming from oceanic sources over the Atlantic Ocean.

As shown in Figure 6.3, the most frequent wind direction measured at Mace Head was between 260° and 270°, which is roughly due west of the research station and is from a purely marine source. Overall, 46.3% of the recorded data was measured during wind directions of oceanic origin.

6.3.2.4 Atmospheric Stability, ζ

All data sets were filtered for atmospheric stability, where only values of ζ between 0 and 2 were retained. When ζ is positive, the atmosphere is stable. It is between this range that mechanical and thermal forcing mechanisms in the boundary layer are equal (McGillis et al., 2001b).

6.3.2.5 Other Parameters

In order to maximize the quality of the flux data, certain parameters measured by the flux system were compared to other instrumentation at Mace Head. Such variables included wind speed, wind direction and relative humidity. If there was a large enough difference between two instruments, the corresponding half-hour was removed. The following parameters were compared

Wind Direction and Wind Speed. Both data sets measured by the sonic anemometer and the Mace Head instrument were compared. Only half-hour periods where \( \delta WS \leq 3 \text{ m/s} \) and \( \delta WD \leq 50° \) were acceptable. A comparison plot of these variables against the Mace Head instrument are displayed in Figure 6.5 and 6.6.
Relative Humidity. RH data calculated from the CO$_2$/H$_2$O analyzer and the Mace Head instrument were compared. Only half-hour periods where $\delta$RH $\leq$ 30% and RH data calculated from the CO$_2$/H$_2$O analyzer < 95% were acceptable. RH data from both instruments are plotted in Figure 6.9.

The constraints from each parameter were obtained from McVeigh and O’Dowd (private communication). It should be noted that the filtering steps discussed in Sections 6.3.2.3 - 6.3.2.5 were applied after the flux data was calculated.

6.3.3 Calculation of Flux Data

In order to calculate atmospheric CO$_2$ fluxes, the eddy covariance technique which is discussed in detail in Section 2.2 was used. The following section discusses and explains the processing conducted on the data both before and after calculating the fluxes.

6.3.3.1 Running Mean

A running mean, as discussed in Section 2.3, was applied using a time constant($\tau$) of 5 minutes or a running mean of order $N = 3000$. An example of CO$_2$ concentration data that has been running mean averaged - $\bar{c}$, is displayed in Figure 6.18.

![Raw and Running Mean Averaged CO$_2$ Concentration Data](image)

**Figure 6.18:** CO$_2$ concentration data measured during JD274. Raw data is light blue and running mean averaged data is blue.
Chapter 6. CO₂ Fluxes and Gas Transfer Velocity of Carbon Dioxide

After the running mean was calculated at each point, it was subtracted from the raw measured data of each parameter. This leads to the creation of the fluctuating part or deviation of the variable from its mean, as per Equation 2.1. Once completed, the variances and covariances of each variable are calculated.

6.3.3.2 Cross Sensitivity of Water Vapour Correction

Eddy correlation measurements of air-sea CO₂ fluxes conducted by open-path systems have been reported to be larger than those estimated by other methods or sensors. It was thought that this was as a result of water vapour in the optical path of the LI-7500 instrument (Prytherch et al., 2010). In order to try and compensate for this issue, a correction method was discussed by Prytherch et al. (2010) and a variation of this application technique was applied during this experimental work.

Prytherch et al. (2010) outlined that the vertical gradient of a scalar quantity $s$ is given by Geernaert (1990)

$$\frac{K z \delta \bar{s}}{s^* \frac{\partial}{\partial z}} = \phi_s$$  \hspace{1cm} (6.10)

where $K$ is the von Karman constant and $z$ is the height of measurement and $s^* = \frac{\omega' s'}{u'}$. Assuming that the dimensionless profile for CO₂ mixing ratio and water vapour mixing ratio are the same, Prytherch et al. (2010) arrived at Equation 6.11.

$$\frac{\delta c}{\delta q} = \frac{c^*}{q^*}$$  \hspace{1cm} (6.11)

They proposed a correction technique for the correlation between $RH$ and $c$ by fitting a 3rd order polynomial to the data and making $\frac{\delta c}{\delta RH} = 0$. However, despite this adjustment, data still exhibited a $w'c'$ correlation, which allowed them to calculate an initial estimate for $c^*$. This value and the observed $q^*$ are used in Equation 6.11 to readjust the CO₂ data in an iterative process until a stable CO₂ flux value is obtained.

During this experimental work, $q$ was used instead of relative humidity, as $RH$ data was not as readily available. Over the open ocean temperature fluctuations are small,
making the relationship between $q$ and $RH$ virtually linear. If we assume that $\phi_s$ is the same for the $H_2O$ and $CO_2$ air concentrations, then

$$\frac{\delta c}{\delta q} = \frac{\delta q}{\delta q}$$  \hspace{1cm} (6.12)

which can be transformed into

$$\frac{\delta c}{\delta q} = \frac{c'}{q'}$$  \hspace{1cm} (6.13)

A cubic fit can be applied to the correlation between $q'$ and $c'$ in order to remove the gradient between them. The 3rd order polynomial fit was applied via the Matlab functions `polyfit` and `polyval`. The “response”, $c_R'$, of the CO$_2$ fluctuations to those of the H$_2$O fluctuations can be calculated though Equation 6.14

$$c_R' = A(q'^3) + B(q'^2) + C(q)$$  \hspace{1cm} (6.14)

where the dimensionless water vapour concentrations $\hat{q} = \frac{q'}{\sigma q'}$. $A$, $B$ and $C$ are polynomial coefficients used to describe the cubic fit between $c'$ and $q'$. For a particular day - JD190, the correlation between $q'$ and $c'$ and the corresponding cubic fit, plus the response of $c'$ to $q'$, $c_R'$, are all displayed in Figure 6.19.

![Figure 6.19: The correlation between c' and q', plus the cubic fit of the data. The response of c' to q', c_R' for the day - JD190](image)
Figure 6.19 shows the negative correlation that exists between $c'$ and $q'$, as mentioned by Prytherch et al. (2010).

In order to incorporate the response correction, it can be applied directly either to the CO$_2$ fluctuations, $c'$ or to the CO$_2$ flux, $F_C$. In either case, the correction can be applied through Equations 6.15 and 6.16.

\[
c_{\text{new}}' = c' - c_R' \tag{6.15}
\]

- $c_{\text{new}}'$ is the response corrected CO$_2$ fluctuation
- $c'$ is the original CO$_2$ fluctuation
- $c_R'$ is the actual response fluctuation

\[
F_{\text{cnew}} = F_{\text{raw}} - F_R \tag{6.16}
\]

- $F_{\text{cnew}}$ is the response corrected vertical CO$_2$ flux
- $F_{\text{raw}}$ is the original CO$_2$ vertical flux
- $F_R$ is the response flux

After the response correction has been applied, $c'$ and $c_{\text{new}}'$ can be compared, as shown in Figure 6.20 to verify its incorporation into the data set. This data set is the same data that was displayed in Figure 6.19.

After the cross sensitivity correction was applied the average daily flux reduced from -44.9111 mol/m$^2$/yr to -4.3818 mol/m$^2$/yr.

### 6.3.3.3 Co-Ordinate Rotations

Co-ordinate rotation transformations are applied to the variances and covariances before the fluxes are calculated. This is so, because wind flow in the vertical direction can be altered due to local terrain. Also, it is quite difficult to level the sonic anemometer so
that its w-axis is perpendicular to the Earth's surface. These rotations helped overcome these issues and reduce any possible errors that could arise in the flux calculations.

Rotations were performed so that \( \bar{u} \) was pointed into the direction of the incident wind flow, making \( \bar{v} \) and \( \bar{w} \) perpendicular to the wind flow, causing their averages to approach zero. The required angles used to perform the rotations are defined in Equation 6.17 and Equation 6.18.

\[
\theta = \arctan\left(\frac{\bar{v}}{\bar{u}}\right) \quad \text{or} \quad \theta = \arcsin\left(\frac{\bar{v}}{\sqrt{\bar{u}^2 + \bar{v}^2}}\right) \quad (6.17)
\]

\[
\phi = \arctan\left(\frac{\bar{w}}{\sqrt{\bar{u}^2 + \bar{v}^2}}\right) \quad \text{or} \quad \phi = \arcsin\left(\frac{\bar{w}}{\sqrt{\bar{u}^2 + \bar{v}^2 + \bar{w}^2}}\right) \quad (6.18)
\]

The rotated means for \( \tilde{u} \), \( \tilde{v} \) and \( \tilde{w} \) are calculated by Equations 6.19 to 6.21.

\[
\tilde{u} = \bar{u} \cos \theta \cos \phi + \bar{v} \sin \theta \cos \phi + \bar{w} \sin \phi \quad (6.19)
\]

\[
\tilde{v} = \bar{v} \cos \theta - \bar{u} \sin \theta \quad (6.20)
\]
\[ \dot{w} = \dot{w} \cos \phi - \dot{u} \cos \theta \sin \phi - \dot{v} \sin \theta \sin \phi \]  
(6.21)

The rotated variances are calculated by Equations 6.22 through 6.24.

\[ \sigma_{\dot{u}}^2 = \sigma_u^2 \cos^2 \theta \cos^2 \phi + \sigma_v^2 \sin^2 \theta \cos^2 \phi + \sigma_w^2 \sin^2 \phi + 2 \sigma_{uv} \sin \theta \cos \theta \cos^2 \phi + 2 \sigma_{uw} \cos \theta \sin \phi \cos \phi \]  
(6.22)

\[ \sigma_{\dot{v}}^2 = \sigma_v^2 \cos^2 \theta + \sigma_a^2 \sin^2 \theta - 2 \sigma_{uv} \sin \theta \cos \theta \]  
(6.23)

\[ \sigma_{\dot{w}}^2 = \sigma_w^2 \cos^2 \phi + \sigma_u^2 \cos^2 \theta \sin^2 \phi + \sigma_v^2 \sin^2 \theta \sin^2 \phi - 2 \sigma_{uw} \cos \theta \sin \phi \cos \phi - 2 \sigma_{vw} \sin \theta \sin \phi \cos \phi + 2 \sigma_{uv} \sin \theta \cos \theta \sin^2 \phi \]  
(6.24)

The rotated covariances are defined by Equation 6.25 to 6.27.

\[ \sigma_{\dot{u}\dot{w}} = \sigma_{uw} \cos \theta (\cos^2 \phi - \sin^2 \phi) + \sigma_{vw} \sin \theta (\cos^2 \phi - \sin^2 \phi) - 2 \sigma_{uv} \sin \theta \cos \theta \sin \phi \cos \phi - \sigma_u^2 \cos^2 \theta \sin \phi \cos \phi - \sigma_v^2 \sin^2 \theta \sin \phi \cos \phi + \sigma_w^2 \sin \phi \cos \phi \]  
(6.25)

\[ \sigma_{\dot{u}\dot{v}} = \sigma_{uv} \cos \theta (\cos^2 \theta - \sin^2 \theta) + \sigma_{vw} \cos \theta \sin \phi - \sigma_{uv} \sin \theta \sin \phi + (\sigma_v^2 - \sigma_u^2) \sin \theta \cos \theta \cos \phi \]  
(6.26)
\[ \sigma_{\tilde{v}\tilde{w}} = \sigma_{vw} \cos \theta \cos \phi - \sigma_{uw} \sin \theta \cos \phi \]
\[ - \sigma_{uw} \sin \phi (\cos^2 \theta - \sin^2 \theta) + (\sigma_{u}^2 - \sigma_{v}^2) \sin \theta \cos \theta \sin \phi \]  

\[ (6.27) \]

\[ \sigma_{\tilde{u}s} = \sigma_{us} \cos \theta \cos \phi + \sigma_{vs} \sin \theta \cos \phi + \sigma_{ws} \sin \phi \]  

\[ (6.28) \]

\[ \sigma_{\tilde{v}s} = \sigma_{vs} \cos \theta - \sigma_{us} \sin \theta \]  

\[ (6.29) \]

\[ \sigma_{\tilde{w}s} = \sigma_{ws} \cos \phi - \sigma_{us} \cos \theta \sin \phi - \sigma_{vs} \sin \theta \sin \phi \]  

\[ (6.30) \]

and rotated scalars are defined by Equations 6.28 - 6.30.

\( s \) can be any scalar quantity such as water vapour, temperature or, in this case \( \text{CO}_2 \) concentration. The covariance, \( \sigma_{\tilde{w}s} \), of the vertical wind speed, \( w \), and scalar, \( s \), is the vertical turbulent flux of the scalar quantity in question - \( \text{CO}_2 \) fluxes.

As an example, the co-ordinate rotations were applied to the data on a given day - JD252. After the rotations were applied, both \( \tilde{v} \) and \( \tilde{w} \) approached 0 m/s, as displayed in Figure 6.21 and Figure 6.22. Also, after the rotations are incorporated into the data set, \( \tilde{u} \) approached values similar to \( U_{22} \). Both of these data sets are plotted in Figure 6.23.

### 6.3.3.4 Webb Correction

Webb et al. (1980) produced a paper discussing the eddy covariance technique in measuring atmospheric fluctuations of gases in the atmosphere. A particular correction (referred to as the Webb Correction during the research) can be applied to such flux measurements.
Figure 6.21: \( \bar{v} \) - component of wind speed before and after the application of co-ordinate rotations. After the application, \( \bar{v} \) approaches very close to zero.

Figure 6.22: \( \bar{w} \) - component of wind speed before and after the application of co-ordinate rotations. After the application, \( \bar{w} \) approaches very close to zero.

Figure 6.23: \( \bar{u} \) - component of wind speed after the application of co-ordinate rotations. After the application, \( \bar{u} \) approaches very close to \( U_{22} \).

Take for example, an eddy covariance flux system inside a particular parcel of air, where there are no turbulent fluctuations. Changes in water vapour and heat fluxes in the atmosphere can cause the density of air inside the parcel to increase or decrease. As a result of this change in air density, the air parcel will either ascend or descend, causing the flux system to register a vertical flux. This movement of air due to expansion and contraction is accounted for in the Webb Correction. As most sensors measure the mass density of a scalar (like \( \text{CO}_2 \) by the LI-7500) as opposed to the mixing ratio, the Webb Correction needs to be applied so that errors due to these variations in air density are taken into consideration. Equation 6.31 was used to calculate the \( \text{CO}_2 \) fluxes with the
Webb Correction included.

\[ F_W = w'\rho_c' + \mu \frac{\bar{\rho}_c}{\bar{\rho}_a} w'\rho_v' + (1 + \mu \sigma) \frac{\bar{\rho}_c}{\bar{T}} w'T' \]  

(6.31)

- \( w'\rho_c' \) is the un-corrected CO\(_2\) flux
- \( \mu \) is the ratio of the molecular masses of air (\( m_a \)) to water (\( m_v \)) and is 1.607
- \( \bar{\rho}_c \) is the running mean averaged concentration of CO\(_2\)
- \( \bar{\rho}_a \) is the mean density of dry air
- \( w'\rho_v' \) is the H\(_2\)O flux
- \( \sigma = \frac{\bar{\rho}_v}{\bar{\rho}_a} \), where \( \bar{\rho}_v \) is the running mean averaged water vapour concentration
- \( \bar{T} \) is the running mean averaged air temperature
- \( w'T' \) is the temperature flux

A slightly different version of Equation 6.31 was presented by McGillis et al. (2001a) and is displayed in Equation 6.32

\[ F_W = w'\rho_c' + \frac{m_a}{m_v} \frac{\bar{\rho}_a}{\rho_a} w'\rho_v' + (1 + \frac{m_a}{m_v} \frac{\rho_v}{\rho_a}) \frac{w'T'}{\bar{T}} = w'\rho_c' + \bar{w}c \]  

(6.32)

where \( \bar{w} \) can be interpreted as the small mean vertical velocity needed to maintain the density of dry air in the presence of sensible and heat fluxes (McGillis et al., 2001a).

Equation 6.31 is composed of two parts: a water vapour component and a temperature component. Burba and Anderson (2007) state that the Webb correction compensates for the effects of fluctuations of both temperature and water vapour on CO\(_2\) fluxes. However, the cross-sensitivity correction, discussed in Section 6.3.3.2, also corrects for water vapour fluctuations that influence atmospheric carbon dioxide fluxes. Therefore, if we were to apply the complete Webb correction, there is a possibility that we could be correcting for the presence of water vapour twice. This double correction...
could lead to an error in the calculation of the final \( \text{CO}_2 \) flux data. As a result, the water vapour term in Equation 6.31 was excluded, and the resultant equation was called the Half-Webb correction McVeigh and O'Dowd (private communication). It was this equation that was used when applying the Half-Webb correction.

Flux data measured on JD190 were used as an example when the CS correction was applied. If the full Webb correction was applied to this data set, the average daily flux would change from -4.3818 mol/m\(^2\)/year to 17.4418 mol/m\(^2\)/year. However, as only the Half-Webb correction was applied the final average daily flux value was -2.6391 mol/m\(^2\)/year.

6.3.4 Flux Analysis

6.3.4.1 Filtering Statistics

Once the flux data have been passed through the series of corrections and filtering stages, as outlined below, the analysis of the data can begin. A quick reminder of what order each of these filtering steps and corrections were applied is displayed as follows.

1. Removal of “spikes” and all rainfall contaminated data
2. Application of the cross-sensitivity correction
3. Co-Ordinate Rotations
4. Half Hour Averaging of the fluxes
5. Application of the Half Webb Correction
6. Filtering of data for wind direction (only marine air was retained)
7. Filtering of data for atmospheric stability
8. Filtering for other variables discussed in Section 6.3.2.5

A breakdown of how much data is lost during each of these steps is displayed in Figure 6.24.
Chapter 6. CO\textsubscript{2} Fluxes and Gas Transfer Velocity of Carbon Dioxide

Figure 6.24: A breakdown of how much data remains after each of the filtering steps

It is assumed that during the time frame between November 1st 2008 and November 30th 2009, all necessary data sets were being recorded 100\% of the time, even though gaps in several data sets did arise at one point or another. Once all rainfall contaminated data was removed, almost half of the data set was lost with only 51.5\% remaining. Once wind direction and atmospheric stability were taken into account less than 10\% of the total data set was retained. Ensuring further accuracy, data measured by the eddy-covariance system were compared to similar data sets from other instrumentation at Mace Head and any poor data were removed. When this questionable data was excluded, approximately 4.4\% of the initial data set is remaining.

The gas transfer velocity data is discussed in more detail in Section 6.4, but we will briefly mention it here. In order to calculate the transfer velocity of CO\textsubscript{2}, three separate data sets are required: CO\textsubscript{2} flux, \(\Delta p\text{CO}_2\) values and solubility. Over the course of the data collection time frame, some half-hour time periods were missing one or more of these data sets and as a result the transfer velocity could not be calculated. Of the half-hour periods that a gas-transfer velocity value could be calculated, these accounted for approximately 3.0\% of the total measurement time frame. Finally, when the transfer velocity was calculated, values were both positive and negative. All negative values were excluded, which resulted in a loss of approximately two-thirds of the remaining data.
6.3.4.2 Application of Flux Corrections

As both the cross-sensitivity (CS) and Half-Webb corrections were applied to the raw carbon dioxide flux data, the data changed in magnitude and direction. Exactly how the flux data changed after each correction is displayed in Figures 6.25 to 6.26. The flux data that is displayed has been filtered as far as the “Other Parameters” stage.

![Comparison of CO₂ Fluxes](image1.png)

**Figure 6.25:** Comparison of the CO₂ fluxes before and after the application of the cross sensitivity (CS) correction

![Comparison of CS and Half Webb Corrected Fluxes](image2.png)

**Figure 6.26:** Comparison of the CS corrected CO₂ fluxes and after the application of the Half-Webb correction
Figure 6.25, is a plot of the raw CO\textsubscript{2} flux data and the flux data after the cross-sensitivity correction is incorporated into the data set. During some half-hour periods, the data changed in magnitude and direction. Compared to the CS correction, the application of the Half-Webb correction did not dramatically change the flux magnitude or direction. During most of the data-set, the Half-Webb correction only slightly changed the flux values. A comparison of the CS corrected fluxes against the Half-Webb corrected fluxes are displayed in Figure 6.26.

### 6.3.4.3 Wind Speed Relationship

There are many environmental parameters that influence atmospheric CO\textsubscript{2} fluxes. One of the most important variables is wind speed. Figure 6.27, shows wind speed and the raw and fully corrected flux values plotted against each other.

![Wind Speed v Fluxes @ Mace Head](image)

**Figure 6.27:** Raw and fully corrected CO\textsubscript{2} fluxes plotted against wind speed

There is a slight negative correlation between wind speed and the CO\textsubscript{2} fluxes. At lower wind speeds, the data are less scattered. However, as wind speed increases, the scatter and uncertainty in the data also increases. When the fluxes are completely corrected, they are not as strongly correlated to wind speed compared to the raw fluxes. Best fits for both data sets are also displayed in Figure 6.27.
6.3.4.4 Seasonality

CO\textsubscript{2} fluxes were calculated during all months of the year, thus some insight into the variation of fluxes on a seasonal basis could be achieved. A bar graph showing the average monthly CO\textsubscript{2} flux values is plotted in Figure 6.28.

![Figure 6.28: Average monthly CO\textsubscript{2} flux values between November 2008 and November 2009. Also plotted are the corresponding errorbars, showing the range of data for each month.](image)

During the winter and spring months between November 2008 and April 2009, the flux was consistently in the downward direction. This general downwards movement of carbon dioxide would infer that CO\textsubscript{2} is moving from the atmosphere into the under-lying sea-water. This observation is in general agreement with the ΔpCO\textsubscript{2} concentrations, which are plotted in Figure 6.29.

During the summer months between May and August, only the months of July and August, show an average monthly positive flux. This upwards movement of carbon dioxide agrees with the positive ΔpCO\textsubscript{2} values observed during these months. However, the months of May and June recorded an average downward flux, while ΔpCO\textsubscript{2} levels were positive. Also, during all of these summer months sea-water pCO\textsubscript{2} concentrations varied sharply. During October, ΔpCO\textsubscript{2} values sharply change from being negative at the beginning of the month to positive during the second half October. Yet, the average monthly CO\textsubscript{2} flux value for October is strongly in the downwards direction.
Chapter 6. CO$_2$ Fluxes and Gas Transfer Velocity of Carbon Dioxide

Figure 6.29: $\Delta p$CO$_2$ concentrations at Mace Head from November 2008 to November 2009

Errorbars in Figure 6.29 show the range of CO$_2$ flux data for each month. It is very clear that the range of CO$_2$ flux data is very large.

6.3.4.5 Frequency Analysis

Spectrum analysis is a statistical tool that can used to study the workings of turbulence in further detail. When a time series of measurements are broken down to their frequency components, we can see how varying eddies contribute to the overall turbulence state (Stull, 1988).

**Discrete Fourier Transform:**

In order to transform the measured data into the Discrete Fourier Transform (DFT), the $fft$ command in Matlab was utilised. The transformation from the time domain into the frequency domain and visa versa is defined by Equation 6.33 and Equation 6.34.

$$F_A(n) = \sum_{k=0}^{N-1} \frac{A(k)}{N} e^{-i2\pi nk/N} \quad (6.33)$$
These two equations are known as the Fourier transform pairs. Equation 6.33 performs the forward transform, creating a representation of the original data series in frequency space. Whereas Equation 6.34 performs the inverse transform, converting the frequencies back into physical space (Stull, 1988).

$A(k) = \sum_{n=0}^{N-1} F_A(n) e^{i \frac{2\pi nk}{N}} \tag{6.34}$

$F_A(n)$ is a complex number and using Euler’s notation: $cos(x) + j sin(x)$, it can be represented by its real and imaginary parts.

$F_A(n) = \frac{1}{N} \sum_{k=0}^{N-1} A(k) \cos \left(\frac{2\pi nk}{N}\right) - i \frac{1}{N} \sum_{k=0}^{N-1} A(k) \sin \left(\frac{2\pi nk}{N}\right) \tag{6.35}$

One basic rule of discrete data analysis states that at least two points per cycle are needed in order to resolve a wave (Stull, 1988). During this research, measurements were made at a rate of 10 Hz. Therefore, the highest frequency that can be resolved in our Fourier transform is $n_f = N/2$. $n_f$ is known as the Nyquist frequency and is 5 Hz or 0.2 seconds. Aliasing could occur if the physical signal was not sampled at a high enough frequency. This is where higher frequencies in the signal would be folded or aliased into lower frequencies, creating an erroneous Fourier transform.

**Spectra of Two Variables:**

Aside from finding the spectrum of one variable, we can also find the spectrum for the product of two variables. Co-spectra are the distribution of the co-variance of $w'$ and a scalar (i.e. $c'$) by frequency. Co-spectra describe how much of the flux is transported at each frequency. They can also be seen as the Fourier transform of the time series into the frequency domain, with the integrated area under the non-dimensional co-spectra curve ideally equal to 1. This area represents 100% of the measured flux (Burba and Anderson, 2007).

Sonic anemometers that are manufactured in present day have the capability of sampling at a very fast rate with small errors. Along with $u$, $v$ and $w$, temperature data can be calculated from the anemometer data set. As a result, the co-spectra
of \( w'T' \) can be considered ideal, where no flux is lost due to frequency errors. Ideal co-spectra for a given height and condition can also be modelled after (Kaimal et al., 1972).

Cross spectrum analysis relates the spectra of two variables. The spectra for the variable \( A \) is represented by the expression \( F_A = F_{Ar} + iF_{Ai} \) and the spectra for the variable \( B \) is \( F_B = F_{Br} + iF_{Bi} \), where \( r \) and \( i \) denote the real and imaginary parts respectively. The spectral energy of the variable \( A \), is defined by Equation 6.36.

\[
G_A = (F_A^*)(F_A) = F_{Ar}^2 + F_{Ai}^2
\]  

(6.36)

where \( F_A^* \) is the complex conjugate of \( F_A \), the complex conjugate has the sign changed in front of the imaginary part. The cross spectrum of \( A \) and \( B \) is defined by Equation 6.37.

\[
G_{AB} = F_A^*F_B = F_{Ar}F_{Br} + iF_{Ar}F_{Bi} - iF_{Ai}F_{Br} - i^2F_{Ai}F_{Bi}
\]  

(6.37)

The real part of the cross spectrum is called the cospectrum, \( Co \), and the imaginary part is known as the quadrature spectrum, \( Q \), where

\[
Co = F_{Ar}F_{Br} + F_{Ai}F_{Bi}
\]  

(6.38)

and

\[
Q = F_{Ai}F_{Br} - F_{Ar}F_{Bi}
\]  

(6.39)

As, \( F_A \) and \( F_B \) are functions of \( n \), so will the cospectrum and quadrature spectrum: \( Co(n) \) and \( Q(n) \). Other spectra that can calculated from \( Co \) and \( Q \) include the amplitude spectrum, \( Am \), coherence spectrum, \( Coh \), and phase spectrum, \( \Phi \), where
Chapter 6. CO₂ Fluxes and Gas Transfer Velocity of Carbon Dioxide

\[ Am = Q^2 + Co^2 \]  \hspace{1cm} (6.40)

\[ Coh^2 = \frac{Q^2 + Co^2}{GA G_B} \]  \hspace{1cm} (6.41)

\[ \tan \Phi = \frac{Q}{Co} \]  \hspace{1cm} (6.42)

A plot of the co-spectra of the vertical wind speed, \( w \), and other variables including air temperature, \( T \), atmospheric carbon dioxide concentration, \( c \), and atmospheric water vapour concentration, \( q \), are plotted in Figure 6.30, Figure 6.31 and Figure 6.32 respectively.

Figure 6.30: Co-spectrum of vertical wind speed and air temperature
We can see from Figure 6.30, 6.31 and 6.32 that the majority of the fluxes are transported at lower frequencies (20).

Note: Parts of the section on calculating the co-spectra of various variables were sourced from Stull (1988).
6.4 Gas Transfer Velocity

The air-sea gas transfer velocity was discussed in Section 2.4. The gas transfer velocity of CO$_2$ can be directly determined by measuring CO$_2$ fluxes and air-sea concentration differences simultaneously: see Equation 2.25. Due to the various filtering steps performed in order to achieve the most accurate necessary data sets, the amount of overlapping data was sparse, to say the least. CO$_2$ transfer velocity data was calculated for approximately 3.00% of the entire data. However, during some half hour periods, ΔpCO$_2$ readings disagreed with CO$_2$ flux data with regard to the direction of movement. This resulted in negative gas transfer velocity measurements. All of these negative measurements were removed, reducing the data set further, to approximately 1.2% of the whole data set.

6.4.1 Wind Speed Relationship

When analyzing the transfer velocity of carbon dioxide, it is preferred to plot the transfer velocity data against wind speed, as shown by past experimental research, discussed in Sections 2.5.1 to 2.5.7. It has been observed that as wind speed increases, so should the gas transfer velocity value.

![Figure 6.33: Transfer velocity of CO$_2$ data plotted against wind speed](image)

Figure 6.33: Transfer velocity of CO$_2$ data plotted against wind speed

Plotted in Figure 6.33 is the resultant gas transfer velocity values from Mace Head after all corrections and filtering steps have been applied. Calculated gas transfer
velocity values have been normalised to a sea-water temperature of 20°C, per the Schmidt number dependence stated in Equation 2.26. Gas transfer velocity data was calculated using fluxes that have been corrected by both cross-sensitivity and Half-Webb corrections. Two half-hour periods corresponded to transfer velocity values of carbon dioxide that were substantially large. These values were believed to be incorrect and were excluded from the data set. With the removal of these points, the data could be better visualised in Figure 6.33. The half hour sections removed had the following measurements: 60736.06 cm/hr @ 9.1 m/s and 4432.65 cm/hr @ 8.3 m/s.

From Figure 6.33, as wind speeds increase, so does the gas transfer velocity, as expected. A positive quadratic fit is the best fit for the data set. However, there is still a large degree of scatter at wind speeds greater than 5 m/s. Some of these points are relatively high compared to the remainder of the data set and there is a possibility that some of these points could be incorrect.

Located in Figure 6.34 is a graph of ΔpCO₂ data plotted against the same gas transfer velocity data displayed in Figure 6.33.

![Figure 6.34: ΔpCO₂ values plotted against transfer velocity](image)

Some of the relatively high gas transfer velocity values observed in Figure 6.33, were recorded when the atmosphere and under-lying ocean were in equilibrium with each other, with regard to pCO₂ concentrations, as shown in Figure 6.34. If all data recorded when ΔpCO₂ values between -12 µatm and +12 µatm was excluded, the correlation
between wind speed and gas transfer velocity would be improved and the amount of scatter reduced. This correlation is displayed in Figure 6.35.

![Wind Speed vs Gas Transfer Velocity at Mace Head](image)

Figure 6.35: CO$_2$ transfer velocity data plotted against wind speed and values with a corresponding $\Delta$pCO$_2$ of +/- 12 µatm excluded

The majority of the large outliers that were observed in Figure 6.33 have been removed, as a result of the $\Delta$pCO$_2$ constraint mentioned above. The largest transfer velocity value remaining is approximately 200 cm/hr, calculated for a wind speed of approximately 15 m/s. There is still a lack of data available at high wind speeds (> 14 m/s), as this issue is quite difficult to overcome. Past experimental research has shown that there is an inherent problem when trying to quantify the relationship between wind speed and gas transfer velocity at these high wind speeds, due to the difficulty in obtaining such data.

The best fit for the data displayed in Figure 6.35 shows that the relationship between wind speed and CO$_2$ transfer velocity can be expressed through Equation 6.43.

$$k_{660} = 0.089x^2 + 0.084x + 4.5$$  \hspace{1cm} (6.43)

where $x$ is wind speed. This derived relationship is compared against other parameterisations calculated from other experimental work in Figure 6.36.
Chapter 6. CO\textsubscript{2} Fluxes and Gas Transfer Velocity of Carbon Dioxide

Figure 6.36: CO\textsubscript{2} transfer velocity data compared against past experimental work

The Mace Head best fit is most similar to that proposed by Liss and Merlivat (1986). Liss and Merlivat (1986) relationship was calculated from data collected from tank experiments and over a lake using the dual tracer technique. Data was collected over a time frame of 1 - 2 days. During this experimental work, wind speeds were only recorded as high as 8 m/s, while for higher wind speeds, experimental results were extrapolated (Wanninkhof, 1992). The Mace Head relationship is in good agreement with all other derived relationships at wind speeds less than 6 m/s. However, as wind speeds increase, each relationship diverges, with the Mace Head relationship being the lowest of them all. Ho et al. (2006) mentions that both the Nightingale et al. (2000b) and Wanninkhof (1992) relationships have potential shortcomings. Nightingale et al. (2000b) was based on data collected during February 1992 and 1993, using the dual tracer technique in a coastal environment. This type of experimental site could experience less developed wind fields and a higher occurrence of surfactants. While the Wanninkhof (1992) relationship was based on the $^{14}$C inventory of the global ocean. McGillis et al. (2004) relationship was based on data collected using the eddy covariance technique in the Equatorial Pacific Ocean over a time frame of 15 days. McGillis et al. (2004) also mentions that chemical enhancement could play a role in increasing measured gas transfer velocities at the study site. The Ho et al. (2006) parameterisation was derived from results collected during the SAGE experiment using the dual tracer technique. The experiment was conducted in the South Pacific Ocean off the coast of New Zealand, where very high wind speeds were observed (16 m/s).
Chapter 6. CO\textsubscript{2} Fluxes and Gas Transfer Velocity of Carbon Dioxide

Figure 6.37 is a plot of the CO\textsubscript{2} transfer velocity data calculated at Mace Head, where the gas transfer velocity values have been bin averaged and fitted with error bars. Also displayed are other parameterisations from past experimental work, plus the best fit calculated from the Mace Head data set.

![Gas Transfer Velocity Comparison](image)

**Figure 6.37:** CO\textsubscript{2} transfer velocity averaged per wind speed value and compared against past experimental best fits

![Frequency of Transfer Velocity Measurements at each Wind Speed](image)

**Figure 6.38:** Frequency of CO\textsubscript{2} transfer velocity measurements binned into 1 m/s wind speeds

The Wanninkhof and McGillis (1999) relationship was removed for visual purposes. At wind speeds from 0 - 9 m/s, data observed at Mace Head is in very good agreement
with all displayed past experimental research. From 10 m/s onwards, a difference starts to emerge between each of best fits and the Mace Head data set. However, after 10 m/s the amount of data available starts to decrease, as displayed in Figure 6.38.

If more data were available at higher wind speeds, the relationship between wind speed and gas transfer velocity might have been more clear.
Chapter 7

Conclusion

Atmospheric carbon dioxide concentrations have been steadily rising since the industrial revolution in the 1800’s. Over the past 60 years or so, CO\textsubscript{2} concentrations have started to increase at a faster rate and it is widely believed that this is as a result of anthropogenically produced CO\textsubscript{2}. The oceans both absorb and release carbon dioxide. However, with this increase in atmospheric CO\textsubscript{2} concentrations, how the oceans will respond, is open to debate. As a result, the need for a complete and thorough understanding of the movement of carbon dioxide across the air-sea interface is of paramount importance. During this experimental work, research was conducted into the transfer of CO\textsubscript{2} between the ocean and the overlying atmosphere off the western coast of Ireland in the north-east Atlantic Ocean. Valuable data were collected in both coastal and oceanic sites.

7.1 Pro Oceanus CO\textsubscript{2} Pro Instrument

Behind all experimental work lies a vast array of modern instrumentation that is necessary to conduct any scientific research. Confidence is vital in all instruments used. One of the core pieces of instrumentation used during this experimental work was the Pro Oceanus CO\textsubscript{2} Pro Instrument. This sensor measured the amount of carbon dioxide in sea-water at the Mace Head research station and on-board the R.V. Celtic Explorer. It was important that data measured by the instrument be as accurate as possible. This was achieved by bench-marking the instrument on board the CE.
Chapter 7. Conclusion

This pCO$_2$ instrument was bench-marked using three different methods. These methods were

1. Bench-marking two PSI CO$_2$ Pro instruments against each other

2. Bench-marking a PSI CO$_2$ Pro instrument against another pCO$_2$ instrument: General Oceanics pCO$_2$ sensor

3. Bench-marking a PSI CO$_2$ Pro instrument against pCO$_2$ data calculated from in-situ water samples

• For each half-hour section when both instruments operated, the average value was calculated. Of all these half-hour sections, 61.2% had a calculated STD value $< 3 \mu$atm and 97.8% had a calculated STD value $< 10 \mu$atm

• During each of these half-hour sections, 49.1% of the time, both instruments had an average difference $\leq 3 \mu$atm and 92.1% of the time, $\leq 10\mu$atm

• During 3/4 of all bench-marking surveys, the total average survey difference was $\leq 5 \mu$atm and all bench-marking surveys had a total average survey difference $\leq 10 \mu$atm

• When the PSI pCO$_2$ instrument was compared to the General Oceanics pCO$_2$ instrument: 22.5% of the total time, the difference was $\leq 3 \mu$atm and 69.7% of the time, the difference was $\leq 10 \mu$atm

• Data from the PSI pCO$_2$ instrument was compared to pCO$_2$ data calculated from in-situ water samples. Agreement between both data sets was excellent for one cruise.

Results from the bench-marking work showed that the Pro Oceanus CO$_2$ Pro was a highly accurate instrument.

7.2 Atmospheric and Sea-water pCO$_2$ Concentrations in Irish waters

Concentrations of carbon dioxide in the oceans vary both temporally and spatially on a large scale. Having a full understanding of the quantity of CO$_2$ in the upper few
metres of the sea surface is very important, as surface CO$_2$ concentrations control how much is released and absorbed by the ocean at the air-sea interface. Sea-water pCO$_2$ concentrations were measured by the Pro Oceanus pCO$_2$ instrument on board the R.V. Celtic Explorer as the vessel surveyed waters off the coast of Ireland in the north-east Atlantic Ocean.

During 2010, in Atlantic waters off the coast of Ireland, sea-water carbon dioxide concentrations varied strongly on a seasonal basis. Highest concentrations were observed during the spring and winter months, where sea-water pCO$_2$ concentrations peaked during March and November with values of 388.0 +/- 12.3 µatm and 408.3 +/- 22.9 µatm respectively. During the summer months, between the months of May and September, sea-water pCO$_2$ concentrations were approximately 60 - 70 µatm lower than atmospheric concentrations. The lowest average monthly sea-water pCO$_2$ concentration was 320.1 +/- 18.4 µatm, recorded in June. This strong undersaturation of carbon dioxide inferred that there would be downwards movement of CO$_2$ from the atmosphere into the ocean in Atlantic waters off the coast of Ireland. Whereas during the winter months, when the air and ocean are near or at equilibrium, the movement of carbon dioxide across the air/sea interface would be negligible. During 2010, the average air pCO$_2$ concentration was 388.9 +/- 7.6 µatm.

It was observed that one of the causes for the strong variation of CO$_2$ in Irish waters was due to biological activity. During the summer months when phytoplankton concentrations increased, this caused a rise in photosynthetic processes. Which in turn removed carbon dioxide from the surrounding sea-water. After the summer, when biological activity declined, pCO$_2$ concentrations in the ocean started to rise. Lower sea-water pCO$_2$ concentrations were observed over the continental shelf, compared to over deeper waters further from shore. It was also in this region, that the highest biological activity was recorded. Sea surface temperature also influences the amount of carbon dioxide in the upper few metres of the ocean. It was calculated that biological activity played a stronger role in influencing sea-water pCO$_2$ concentrations than sea-surface temperature in Atlantic waters off Ireland.

Sea-water pCO$_2$ concentrations were also collected at a coastal site: Mace Head, Co. Galway. Another Pro Oceanus pCO$_2$ instrument was installed on an all weather buoy moored off-shore from the research station. During the winter of 2008/2009, sea-water
pCO₂ concentrations were observed to be mostly less than atmospheric concentrations, inferring a downwards movement of carbon dioxide, into the coastal ocean. The average air pCO₂ concentration at Mace Head was 386.54 +/- 8.25 µatm. Between April and July 2009, concentrations of CO₂ in the sea-water were higher than concentrations recorded in the atmosphere. Sea-water pCO₂ concentrations varied dramatically during these summer months, reaching a maximum value of 973 µatm at the end of April. Sea-water concentrations peaked twice more in June and July at approximately 810 µatm and 835 µatm respectively. This constant over saturation of carbon dioxide suggests that the coastal ocean is a source of CO₂ for the atmosphere at Mace Head. Sometimes, the coastal ocean is neglected when studying the transfer of CO₂ across the air-sea boundary, but due to its high variation in CO₂ concentrations, a thorough understanding is important.

### 7.3 CO₂ Fluxes and CO₂ Transfer Velocity

Between November 2008 and November 2009, in conjunction with sea-water pCO₂ concentrations, CO₂ fluxes were also measured at the Mace Head research station. Between November 2008 and April 2009, CO₂ fluxes were predominantly in the downwards direction. This is in agreement with negative ΔpCO₂ concentrations at the time, as the surrounding ocean was undersaturated with carbon dioxide, relative to the over-lying atmosphere. The sea-water was a sink for CO₂ during these winter and spring months. Between May and August 2009, when the sea-water pCO₂ concentrations were variable, the agreement between the CO₂ fluxes and ΔpCO₂ concentrations was not as strong. Only July and August recorded an average positive flux, inferring that the ocean was a source of CO₂, which is in agreement with ΔpCO₂ concentrations.

CO₂ fluxes were corrected for atmospheric variables that can alter the flux measurements so that they are not a true representation of the movement of carbon dioxide in the atmosphere. The first correction applied was to take into account the cross-sensitivity of water vapour. Secondly, the effects of air temperature and water vapour, which change the density of air, were corrected by using the Webb Correction. With these corrections taken into consideration, it was felt that the atmospheric CO₂ fluxes measured at Mace Head, were a true representation of the movement of carbon dioxide in the atmosphere. Both raw and corrected CO₂ fluxes were plotted against wind.
speed. As wind speed increased, there was an increase in the downwards movement of carbon dioxide for both the raw and corrected fluxes. However, there was a decrease in the correlation of the fluxes against wind speed after the CO₂ fluxes were corrected.

The transfer velocity of carbon dioxide was also calculated at Mace Head. It was calculated by measuring the concentration of CO₂ in the atmosphere and under-lying ocean, coupled with CO₂ flux measurements in the atmosphere and solubility data from the ocean. The relationship between wind speed and CO₂ transfer velocity was quantified. As wind speed increased, so did the transfer velocity of carbon dioxide across the air-sea interface. At higher wind speeds, the CO₂ transfer velocity was not as high as past experimental work. There was also a lack of data at elevated wind speeds (>10 m/s). This issue is a major stumbling block when studying the wind speed/gas transfer velocity relationship. Unfortunately it was encountered when analysing data from Mace Head. Nevertheless, as wind speed increased, the rate of exchange of CO₂ across the air-sea interface also increased.
# Appendix A

## Gill Sonic Anemometer

<table>
<thead>
<tr>
<th>Table A.1: Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ultrasonic Measurement</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Wind Speed</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Direction</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Speed of Sound</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Digital Output</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Analogue Outputs</strong></td>
</tr>
<tr>
<td>(via PCIA Unit)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

185
### Table A.2: Specifications: continued

<table>
<thead>
<tr>
<th>Analogue Inputs (requires SIU)</th>
<th>Quantity</th>
<th>6 Differential Inputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Rate</td>
<td>100 s⁻¹</td>
<td></td>
</tr>
<tr>
<td>Input Range and Resolution</td>
<td>±5 V, 14 bits</td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>0.1% of FSR</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRT Input (PRT100 Not Supplied)</th>
<th>Input Resolution</th>
<th>0.01°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Input Accuracy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;0.01°C (0 to 50°C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;0.15°C (40 to +60°C)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inclinometer</th>
<th>Range and Resolution</th>
<th>±20° 0.01°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Null Repeatability</td>
<td>±0.15°</td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>±0.3 (from -10° to 10° of inclination)</td>
<td></td>
</tr>
</tbody>
</table>

| Power Requirement              | Anemometer           | 9 - 30 V DC <4W (e.g. <150 mA at 24 V DC or <300 mA at 12 V DC) |

<table>
<thead>
<tr>
<th>Environmental</th>
<th>Operational Temp.</th>
<th>-40 to +60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Ingress</td>
<td>IP65</td>
<td></td>
</tr>
<tr>
<td>Precipitation</td>
<td>Operation maintained to 300 mm/Hr</td>
<td></td>
</tr>
<tr>
<td>EMC</td>
<td>BS EN 50081 - 1 : 1992 (Emissions)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BS EN 50082 - 1 : 1992 (Immunity)</td>
<td></td>
</tr>
</tbody>
</table>

| General                        | Suitable for exposure to marine environment | |

---
Appendix B

LI-COR 7500 Gas Analyzer

- **Type**: Absolute, open-path, non-dispersive infrared gas analyzer.

- **Detector**: Thermo-electrically cooled lead selenide.

- **Bandwidth**: 5, 10, or 20 Hz. software selectable.

- **Path Length**: 12.5 cm (4.72").

- **Operating Temperature Range**: -25 to 50°C (-40 to 50°C optional).

- **User Interface**: Windows based software supports all setup, configuration and calibration functions through the RS-232 serial port.

- **Outputs**:
  - 2 user scalable 16-bit DAC’s updated at 300 Hz.
  - **RS – 232**: 20 Hz Maximum.
  - **SDM**: Greater than 40 Hz

- **Auxiliary Inputs**: 2 channels for temperature and pressure sensors (during calibration).

- **Auxiliary Input for Pressure Sensor**: 0 - 4.096 V (±5 V common mode rejection).

- **Power Requirements**: 10.5 to 30 V DC.

- **Power Consumption**: 30 W during warm-up, 10 W in steady state.
Appendix B. LI-COR 7500 Gas Analyzer

- **Dimensions**: Head
  - **Head**: Dia 6.5 cm, Length 30 cm. Designed for minimal wind flow disturbance.
  - **ControlBox**: 35 cm x 30 cm x 15 cm (external dimensions).
  - **IRGACable**: 5 metres standard, 10 metres available.
  - **Power, Serial, DAC, Auxiliary Input and SDM Cables**: 5 metres.
  - **Weight**: Head: 0.75 kg (1.65lb). Control box and Cables: 4.8 kg (10.5lb).

### Table B.1: LI-7500 Power Spectral Density and Noise Specifications

<table>
<thead>
<tr>
<th>CO₂</th>
<th>µmol mol⁻¹</th>
<th>mmol m⁻³†</th>
<th>mg m⁻³†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Range</td>
<td>0 - 3000</td>
<td>0 - 117</td>
<td>0 - 5148</td>
</tr>
<tr>
<td>RMS noise at ambient (370 ppm) Bandwidth</td>
<td>5 Hz</td>
<td>0.08</td>
<td>0.0031</td>
</tr>
<tr>
<td>PSD* = 35 ppb ÷ Hz typical</td>
<td>0.00043</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>70 ppb ÷ Hz max</td>
<td>0.0061</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>20 Hz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero drift with temperature Maximum (per °C)</td>
<td>±0.3</td>
<td>±0.012</td>
<td>±0.5</td>
</tr>
<tr>
<td>Typical</td>
<td>±0.1</td>
<td>±0.004</td>
<td>±0.2</td>
</tr>
<tr>
<td>Gain drift with temperature Maximum at 370 ppm (% of reading per °C)</td>
<td></td>
<td>±0.1%</td>
<td></td>
</tr>
<tr>
<td>Typical</td>
<td></td>
<td>±0.02%</td>
<td></td>
</tr>
<tr>
<td>Direct sensitivity to H₂O Maximum [mol CO₂/mol H₂O]</td>
<td>±4.00E−05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Typical</td>
<td></td>
<td>±2.00E−05</td>
<td></td>
</tr>
</tbody>
</table>

### Table B.2: LI-7500 Power Spectral Density and Noise Specifications

<table>
<thead>
<tr>
<th>H₂O</th>
<th>mmol mol⁻¹</th>
<th>mmol m⁻³†</th>
<th>g m⁻³†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Range</td>
<td>0 - 60</td>
<td>0 - 2340</td>
<td>0 - 42</td>
</tr>
<tr>
<td>RMS noise at ambient (370 ppm) Bandwidth</td>
<td>5 Hz</td>
<td>0.0034</td>
<td>0.13</td>
</tr>
<tr>
<td>PSD* = 35 ppb ÷ Hz typical</td>
<td>0.0047</td>
<td>0.18</td>
<td>0.0033</td>
</tr>
<tr>
<td>70 ppb ÷ Hz max</td>
<td>0.0067</td>
<td>0.26</td>
<td>0.0047</td>
</tr>
<tr>
<td>20 Hz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero drift with temperature Maximum (per °C)</td>
<td>±0.05</td>
<td>±2</td>
<td>±0.04</td>
</tr>
<tr>
<td>Typical</td>
<td>±0.03</td>
<td>±1</td>
<td>±0.02</td>
</tr>
<tr>
<td>Gain drift with temperature Maximum at 370 ppm (% of reading per °C)</td>
<td></td>
<td>±0.3%</td>
<td></td>
</tr>
<tr>
<td>Typical</td>
<td></td>
<td>±0.15%</td>
<td></td>
</tr>
<tr>
<td>Direct sensitivity to CO₂ Maximum [mol H₂O/mol CO₂]</td>
<td>±0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Typical</td>
<td></td>
<td>±0.02</td>
<td></td>
</tr>
</tbody>
</table>

* Power Spectral Density (PSD) = RMS noise/square root of bandwidth. To compute RMS noise at any bandwidth, multiply the PSD value by the square root of the bandwidth.

† at 26°C 96 kPa
Appendix C

Pro-Oceanus Systems Inc. (PSI)
CO₂ Pro

Table C.1: Accuracy and Precision specifications of the PSI pCO₂ instrument

<table>
<thead>
<tr>
<th>Parameter &amp; Accuracy or Precision</th>
<th>± 0.1ppm</th>
<th>± 1 mb</th>
<th>± 2 mb</th>
<th>0.01 ppm</th>
<th>1 mb</th>
<th>1 mb</th>
<th>600 ppm</th>
<th>0 - 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Stream Humidity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Stream Pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calibration Range</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature Range</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C.2: Physical Characteristics of the PSI pCO₂ instrument

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physical Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>length: 33.02 cm (+10 cm for connectors)</td>
</tr>
<tr>
<td></td>
<td>diameter: 17.27 cm at body</td>
</tr>
<tr>
<td></td>
<td>(max. diameter at locking ring 19.05 cm)</td>
</tr>
<tr>
<td>Weight</td>
<td>in water: 0.40 kg</td>
</tr>
<tr>
<td></td>
<td>in air: 0.3 kg</td>
</tr>
<tr>
<td>Housing</td>
<td>hard anodized aluminium</td>
</tr>
<tr>
<td></td>
<td>proof to 1000 m</td>
</tr>
</tbody>
</table>
**Table C.3: Electrical Characteristics of the PSI pCO$_2$ instrument**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Electrical Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Voltage</td>
<td>9.5 to 18 V DC</td>
</tr>
<tr>
<td>Power Consumption</td>
<td>0.8 A at 12 V for warmup</td>
</tr>
<tr>
<td>Data Storage</td>
<td>available when equipped with PSI data logger/controller; otherwise provides data via cable to external computer</td>
</tr>
<tr>
<td>Data Output</td>
<td>RS-232 serial output</td>
</tr>
<tr>
<td>Sample Rate</td>
<td>0.6 Hz; 0.31 Hz with data logger/controller</td>
</tr>
<tr>
<td>Equilibration Time Constant</td>
<td>about 3.5 minutes depending on the water temperature and ambient pressure</td>
</tr>
</tbody>
</table>
Appendix D

Equation Conversions

(1) mmol/m\(^3\) to \(\mu\)mol/mol:

The LI-COR 7500 measures the air concentration of CO\(_2\) in mmol/m\(^3\). This data can be converted into \(\mu\)mol/mol through Equation D.1. \(\mu\)mol/mol are the same as ppm (parts per million).

\[
C_f = \frac{C \cdot R \cdot (T + 273.15)}{P} \tag{D.1}
\]

where

- \(C_f\) is the concentration of CO\(_2\) in mmol/m\(^3\)
- \(C\) is the concentration of CO\(_2\) in \(\mu\)mol/mol
- \(R\) is the Universal Gas Constant: 8.314 N M mol\(^{-1}\) K\(^{-1}\)
- \(T\) is the air temperature in °C
- \(P\) is the atmospheric pressure in kPa
## List of Figures

1.1 Layers of the Atmosphere. From National Oceanographic and Atmospheric Administration (NOAA) .................................................. 3
1.2 Atmospheric CO$_2$ concentration measurements at Mauna Loa, Hawai’i. From Woods Hole Oceanographic Institute (WHOI) ............ 4
1.3 Carbon Cycle. From Environmental Protection Agency (EPA) ........... 5
1.4 Biological Pump of CO$_2$. From Woods Hole Oceanographic Institute (WHOI) ................................................................. 6

2.1 Planetary Boundary Layer. From National Oceanographic and Atmospheric Administration (NOAA) ................................. 10
2.2 Turbulent Eddies in the Atmosphere - (Burba and Anderson, 2007) .... 11
2.3 Schematic spectrum of wind speed near the ground estimated from a study by Van der Hoven (1957) - (Stull, 1988) ....................... 12
2.4 Two particular eddies at a given point in time and space - (Burba and Anderson, 2007) .............................................................. 13
2.5 Distribution of the climatological mean annual sea-air CO$_2$ flux (moles CO$_2$ m$^{-2}$ yr$^{-1}$) for the reference year 1995 representing non El-Niño conditions. This has been computed using the mean monthly distribution of sea-air pCO$_2$ difference, the climatological NCEP 41-year mean wind speed and the wind speed dependence of the CO$_2$ gas transfer velocity of (Wanninkhof, 1992). This map yields an annual oceanic uptake flux for CO$_2$ of 2.2 ± 0.4 Pg C yr$^{-1}$ (Takahashi et al., 2002) ............. 23
2.6 Commonly used short-term wind speed/gas exchange parameterizations, plotted along with $^{3}$He/SF$_6$ data points from coastal (open symbols) and open ocean (solid symbols) (Ho et al., 2006). ................................. 28

3.1 R.V. Celtic Explorer ................................................................. 39
3.2 Pro-Oceanus Systems Inc.(PSI) CO$_2$ Pro Instrument .................. 39
3.3 Schematic of the pCO$_2$ instrument ........................................... 40
3.4 Support structure for the gas transfer interface (on right side of instrument) ................................................................. 41
3.5 Chamber containing ascarite inside the instrument ...................... 44
3.6 Stainless steel tank housing the pCO$_2$ instruments .................... 47
3.7 Two (PSI) CO$_2$ Pro instruments and a Seabird SBE39 water temperature sensor installed inside tank ................................. 47
3.8 General Oceanics pCO$_2$ system drybox ................................. 48
3.9 General Oceanics pCO$_2$ system wetbox .................................. 48
3.10 Location of the Mace Head Research Station .......................... 49
3.11 The Mace Head Tower ........................................................... 51
3.12 A picture of the sonic anemometer and the CO$_2$ and H$_2$O gas analyzer .... 52
List of Figures

3.13 Calibration procedure of the LI-7500 analyzer ........................................... 57
3.14 Black Weatherproof Box .................................................................................. 58
3.15 Schematic of the Data Logger System ............................................................... 59
3.16 Offshore Data Buoy at Mace Head .................................................................... 61
3.17 Stainless steel frame supporting the Pro Oceanus pCO$_2$ sensor ..................... 62
3.18 Pulley System used to raise/lower the Pro Oceanus pCO$_2$ sensor from inside the nylon tube .......................................................... 62
3.19 LI-6252 Infrared Gas Analyzer ......................................................................... 63
3.20 Vector Instruments W200P potentiometer wind vane which collected wind direction data at Mace Head .............................................................. 64
3.21 Vector Instruments A100L cup anemometer which collected wind speed data at Mace Head ................................................................. 64
3.22 Vaisala Model HMP45D sensor which collected relative humidity data at Mace Head ................................................................. 64
3.23 Vaisala PTB220 barometer which collected atmospheric pressure data at Mace Head ................................................................. 64

4.1 Cruise Track - CE0911 - June 14th (JD165) - June 22nd (JD173) .................... 68
4.2 Cruise Track - CE10001 - January 15th (JD015) - February 2nd (JD033) ......... 69
4.3 Cruise Track - CE10002 - February 5th (JD036) - February 17th (JD048) ...... 70
4.4 Cruise Track - CE10009 - February 18th (JD049) - March 4th (JD063) ......... 71
4.5 Cruise Track - CE10006 - March 5th (JD064) - 17th (JD076) ......................... 72
4.6 Cruise Track - CE10011 - March 18th (JD077) - April 6th (JD096) ............... 73
4.7 Cruise Track - CE10010 - April 10th (JD100) - 16th (JD106) ......................... 74
4.8 Cruise Track - CE10014 - April 19th (JD109) - May 11th (JD131) ................. 75
4.9 Cruise Track - CE10003 - May 16th (JD136) - 22nd (JD142) ......................... 76
4.10 Cruise Track - CE10004 - May 23rd (JD143) - June 1st (JD152) ................... 77
4.11 Cruise Track - CE10008 - June 3rd (JD154) - 17th (JD168) ......................... 78
4.12 Cruise Track - CE10012 - June 18th (JD169) - July 6th (JD187) .................... 79
4.13 Cruise Track - CE10007 - July 8th (JD189) - 28th (JD209) ......................... 80
4.14 Cruise Track - CE10018 - July 28th (JD209) - August 22nd (JD234) .......... 81
4.15 Cruise Track - CE10005 - September 16th (JD259) - 22nd (JD265) .......... 82
4.16 Cruise Track - CE10015 - September 25th (JD267) - October 6th (JD279) .... 83
4.17 Cruise Track - CE10013 - October 8th (JD281) - 26th (JD299) ................. 84
4.18 Cruise Track - CE10017 - October 28th (JD301) - November 13th (JD318) ... 85
4.19 Cruise Track - CE100016 - Leg 2 - November 15th (JD319) - December 2nd (JD336) .................................................................................................................... 86
4.20 Cruise Track - CE100016 - Leg 3 - December 4th (JD338) - 19th (JD353) .... 87
4.21 An example of the zeroing process - CE10007 Survey ................................. 88
4.22 Accepted pCO$_2$ measurements - CE10007 Survey ...................................... 88
4.23 Fresh and Salt water pCO$_2$ measurements - CE10010 Survey .................. 89
4.24 Accepted pCO$_2$ measurements - CE10010 Survey ...................................... 89
4.25 CE10018 Survey - All data including data recorded when the non toxic was switched off ........................................................................................................ 90
4.26 Accepted pCO$_2$ measurements - CE10018 Survey ...................................... 90
4.27 CE10006 Survey - Data measured when the non toxic was switched off at the end of the survey ................................................................. 90
4.28 Accepted pCO$_2$ measurements - CE10006 Survey ...................................... 90
List of Figures

4.29 An example of noisy pCO₂ data measured during a CE10002 survey . . 91
4.30 An example of noisy pCO₂ data measured during a CE10014 survey . . 91
4.31 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10001 ................................. 93
4.32 Percentage Difference of pCO₂ concentrations between both instruments - CE10001 ........................................... 93
4.33 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10002 ................................. 94
4.34 Percentage Difference of pCO₂ concentrations between both instruments - CE10002 ........................................... 94
4.35 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10009 ................................. 95
4.36 Percentage Difference of pCO₂ concentrations between both instruments - CE10009 ........................................... 95
4.37 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10006 ................................. 96
4.38 Percentage Difference of pCO₂ concentrations between both instruments - CE10006 ........................................... 96
4.39 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10011 ................................. 97
4.40 Percentage Difference of pCO₂ concentrations between both instruments - CE10011 ........................................... 97
4.41 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10010 ................................. 98
4.42 Percentage Difference of pCO₂ concentrations between both instruments - CE10010 ........................................... 98
4.43 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10014 ................................. 99
4.44 Percentage Difference of pCO₂ concentrations between both instruments - CE10014 ........................................... 99
4.45 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10012 ................................. 100
4.46 Percentage Difference of pCO₂ concentrations between both instruments - CE10012 ........................................... 100
4.47 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10007 ................................. 101
4.48 Percentage Difference of pCO₂ concentrations between both instruments - CE10007 ........................................... 101
4.49 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10018 ................................. 102
4.50 Percentage Difference of pCO₂ concentrations between both instruments - CE10018 ........................................... 102
4.51 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10016 - Leg 2 ............................ 103
4.52 Percentage Difference of pCO₂ concentrations between both instruments - CE10016 - Leg 2 ............................ 103
4.53 Measured sea-water pCO₂ concentrations by both instruments - PO1 & PO2 - CE10016 - Leg 3 ............................ 104
4.54 Percentage Difference of pCO₂ concentrations between both instruments - CE10016 - Leg 3 .......................................................... 104
4.55 Standard Deviation values for All Benchmarking Cruises .................. 105
4.56 Percentage Difference Statistics for all Benchmarking Cruises ............. 106
4.57 Various Difference Values for all Benchmarking Cruises .................. 107
4.58 Comparison in sea-water pCO₂ concentrations between the PSI instrument (PO2) and the GO system .............................................. 108
4.59 Percentage difference of pCO₂ concentrations between PO2 and GO - CE10015 ................................................................. 109
4.60 Sea-water Temperature measured at three separate places ................. 109
4.61 Comparison between sea-water pCO₂ concentrations measured by the PSI CO₂-Pro Instruments and pCO₂ concentrations from in-situ water samples - CE10002 .................................................. 111
4.62 Comparison of sea-water temperature data collected during the CE10002 survey ................................................................. 111
4.63 Comparison between sea-water pCO₂ concentrations measured by the PSI CO₂-Pro Instruments and pCO₂ concentrations from in-situ water samples - CE10003 .................................................. 113
4.64 Comparison between various sea-water temperature measurements collected during the CE10003 survey .................................. 113
4.65 Comparison between sea-water pCO₂ concentrations measured by the PSI CO₂-Pro instrument and pCO₂ concentrations from in-situ water samples - CE0911 .................................................. 114
4.66 Comparison between various sea-water temperature measurements collected during the CE0911 survey .................................. 115

5.1 Ship tracks from all cruises conducted by the R.V. Celtic Explorer during 2010 ........................................................................... 117
5.2 CE cruise paths between January and March 2010 - Spring ............... 118
5.3 CE cruise paths between April and June 2010 - Summer .................... 118
5.4 CE cruise paths between July and September 2010 - Autumn .......... 118
5.5 CE cruise paths between October and December 2010 - Winter ........ 118
5.6 All pCO₂ data measured during 2010 ............................................ 119
5.7 Monthly averages of air and sea-water pCO₂ data during 2010 ......... 121
5.8 Air pCO₂ data between September 24th and October 7th 2010 .......... 122
5.9 Air and Sea-water pCO₂ concentrations between September 24th and October 7th 2010 ......................................................... 122
5.10 Sea-water pCO₂ concentrations measured during the CE10011 cruise .... 123
5.11 Sea-water pCO₂ concentrations measured during the CE10012 cruise .... 123
5.12 Sea-water pCO₂ concentrations measured during the CE10015 cruise .... 124
5.13 Sea-water pCO₂ concentrations measured during the CE10013 cruise .... 124
5.14 Sea-water pCO₂ concentrations measured between April 10th and June 2nd 2010 ................................................................. 125
5.15 Sea-water pCO₂ concentrations measured between November 15th and December 15th 2010 .................................................. 125
5.16 Chlorophyll fluorescence levels measured during cruises between April 10th and June 2nd 2010 ..................................................... 126
5.17 Chlorophyll fluorescence levels measured during cruises between Nov. 15th and Dec. 15th .................................................. 126
5.18 All sea-water pCO$_2$ measurements divided into coastal, on-shelf and off-shelf categories .................................................. 127
5.19 SST during surveys conducted in Irish waters in 2010 .................. 128
5.20 Sea-water pCO$_2$ concentrations and normalised pCO$_2$ concentrations monthly averaged during 2010 .......................... 129
5.21 Satellite imagery of the phytoplanton bloom on May 23rd .......... 130
5.22 Satellite imagery of the phytoplanton bloom on June 1st 2010 .... 130
5.23 Sea-water pCO$_2$ concentrations normalised to the annual mean sea-water temperature and pCO$_2$ concentrations expected with changes in SST ........................................... 131
5.24 Air and Sea-water pCO$_2$ concentrations measured at Mace Head between November 2008 and November 2009. The raw data and a smoothed version of the raw data are plotted .............................. 133
5.25 Air pCO$_2$ concentrations at Mace Head between November 2008 and November 2009. Measurements have been smoothed for a better visual appearance .......................................................... 133
5.26 Chlorophyll fluorescence levels measured by the WQM installed on the Mace Head buoy between November 2008 and November 2009 .................................................. 134
5.27 Salinity levels measured by the WQM installed on the Mace Head buoy between November 2008 and November 2009 .................. 135
5.28 Sea-surface temperature measurements at Mace Head between November 2008 and November 2009 ................................... 136
5.29 Air and Sea-water pCO$_2$ data measured at Mace Head between April and August 2009 ...................................................... 137
5.30 Chlorophyll fluorescence and sea-water pCO$_2$ data measured at Mace Head between April and August 2009 .......................... 138
5.31 Salinity and sea-water pCO$_2$ data measured at Mace Head between April and August 2009 ...................................................... 139
5.32 Sea-surface temperature and sea-water pCO$_2$ data measured at Mace Head between April and August 2009 .......................... 139
5.33 Chlorophyll fluorescence and salinity data measured at Mace Head between April and August 2009 ...................................................... 140
6.1 Average Monthly Wind Direction at Mace Head ........................ 141
6.2 Average Monthly Wind Speed at Mace Head ............................ 141
6.3 Frequency of Wind Direction Measurements at Mace Head - 260$^\circ$ - 270$^\circ$ most frequent .......................................................... 142
6.4 Frequency of Wind Speed Measurements at Mace Head - 8.0 m/s most frequent .......................................................... 142
6.5 Comparative plot of wind direction measurements at Mace Head .... 143
6.6 Comparative plot of wind speed measurements at Mace Head ....... 143
6.7 Air Temperature Data at Mace Head ....................................... 144
6.8 Atmospheric Pressure Data at Mace Head ............................... 144
6.9 A comparison of relative humidity data measured at Mace Head ... 147
6.10 A comparison of atmospheric CO$_2$ concentration data measured at Mace Head .......................................................... 147
6.11 Friction velocities before and after filtering ............................... 148
6.12 Drag coefficients before and after filtering .......................... 149
6.13 Roughness lengths before and after filtering .......................... 149
6.14 Air CO$_2$ concentration data recorded during June 29$^{th}$ 2009 - JD180.
   All data coloured green was removed and all blue data was retained .. 151
6.15 CO$_2$ Flux Data measured during periods of precipitation .......... 152
6.16 Standard Deviation values for half hour periods of CO$_2$ Flux Data during
   JD315 ............................................................................. 152
6.17 Monthly Average Standard Deviation Values for acceptable half-hour
   sections ............................................................................ 153
6.18 CO$_2$ concentration data measured during JD274. Raw data is light blue
   and running mean averaged data is blue ................................. 155
6.19 The correlation between c’ and q’, plus the cubic fit of the data. The
   response of c’ to q’, cR’ for the day - JD190 ............................. 157
6.20 Comparison of c’ and c$^{new'}$ after the response correction has been applied159
6.21 $\bar{v}$ - component of wind speed before and after the application of co-
   ordinate rotations. After the application, $\bar{v}$ approaches very close to
   zero. .................................................................................. 162
6.22 $\bar{w}$ - component of wind speed before and after the application of co-
   ordinate rotations. After the application, $\bar{w}$ approaches very close to
   zero. .................................................................................. 162
6.23 $\bar{u}$ - component of wind speed after the application of co-ordinate rota-
   tions. After the application, $\bar{u}$ approaches very close to $U_{22}$ ......... 162
6.24 A breakdown of how much data remains after each of the filtering steps 165
6.25 Comparison of the CO$_2$ fluxes before and after the application of the
   cross sensitivity (CS) correction .............................................. 166
6.26 Comparison of the CS corrected CO$_2$ fluxes and after the application of
   the Half-Webb correction ....................................................... 166
6.27 Raw and fully corrected CO$_2$ fluxes plotted against wind speed .... 167
6.28 Average monthly CO$_2$ flux values between November 2008 and November 2009. Also plotted are the corresponding errorbars, showing the range of data for each month ......................................................... 168
6.29 $\Delta$pCO$_2$ concentrations at Mace Head from November 2008 to November
   2009 .................................................................................. 169
6.30 Co-spectrum of vertical wind speed and air temperature ............... 172
6.31 Co-spectrum of vertical wind speed and air CO$_2$ concentration ...... 173
6.32 Co-spectrum of vertical wind speed and air H$_2$O concentration ...... 173
6.33 Transfer velocity of CO$_2$ data plotted against wind speed ............. 174
6.34 $\Delta$pCO$_2$ values plotted against transfer velocity ....................... 175
6.35 CO$_2$ transfer velocity data plotted against wind speed and values with
   a corresponding $\Delta$pCO$_2$ of +/- 12 µatm excluded ................... 176
6.36 CO$_2$ transfer velocity data compared against past experimental work .. 177
6.37 CO$_2$ transfer velocity averaged per wind speed value and compared
   against past experimental best fits ........................................... 178
6.38 Frequency of CO$_2$ transfer velocity measurements binned into 1 m/s
   wind speeds ........................................................................ 178
List of Tables

1.1 Composition of the atmosphere near the surface of the earth - Wallace and Hobbs (2006) ............................................................ 1

3.1 Sample data string output from the PSI CO$_2$ Pro ......................................... 45

4.1 Summary of CE cruises between June 14th and 22nd 2009 ................................. 66
4.2 Summary of CE cruises between January 15th and May 22nd 2010 .......................... 66
4.3 Summary of CE cruises between May 23rd and December 19th 2010 ...................... 67
4.4 Percentage Standard Deviation Values for all Benchmarking Cruises ....................... 105
4.5 Numbers from the x-axis in Figure 4.57 correspond to these benchmarking cruises ................................................................. 107

6.1 Sample data string output from the Data Logging System .................................... 150

A.1 Specifications ................................................................. 185
A.2 Specifications: continued ........................................................ 186

B.1 LI-7500 Power Spectral Density and Noise Specifications ................................. 188
B.2 LI-7500 Power Spectral Density and Noise Specifications ................................. 188

C.1 Accuracy and Precision specifications of the PSI pCO$_2$ instrument .................... 189
C.2 Physical Characteristics of the PSI pCO$_2$ instrument ........................................ 189
C.3 Electrical Characteristics of the PSI pCO$_2$ instrument ........................................ 190
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGC</td>
<td>Automatic Gain Control</td>
</tr>
<tr>
<td>ASCII</td>
<td>American Standard Code for Information Interchange</td>
</tr>
<tr>
<td>AZPC</td>
<td>Automatic Zero Point Calibration</td>
</tr>
<tr>
<td>CE</td>
<td>R.V. Celtic Explorer</td>
</tr>
<tr>
<td>CS</td>
<td>Cross Sensitivity</td>
</tr>
<tr>
<td>DLS</td>
<td>Data Logging System</td>
</tr>
<tr>
<td>EC</td>
<td>Eddy Covariance</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EPROM</td>
<td>Erasable Programable Read Only Memory</td>
</tr>
<tr>
<td>FTP</td>
<td>Field Training Preparation</td>
</tr>
<tr>
<td>GPRS</td>
<td>General Packet Radio Service</td>
</tr>
<tr>
<td>IRGA</td>
<td>Infra Red Gas Analyzer</td>
</tr>
<tr>
<td>MI</td>
<td>Marine Institute</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NDIR</td>
<td>Non Dispersive Infra Red</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Association</td>
</tr>
<tr>
<td>PO1</td>
<td>Pro Oceanus pCO2 Insturment - 1</td>
</tr>
<tr>
<td>PO2</td>
<td>Pro Oceanus pCO2 Insturment - 2</td>
</tr>
<tr>
<td>ppmv</td>
<td>parts per million by volume</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PSI</td>
<td>Pro Oceanus Systems Inc</td>
</tr>
<tr>
<td>PSU</td>
<td>Practical Salinity Units</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SBE</td>
<td>Sea Bird Electronics</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt Number</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>TMBB</td>
<td>TechWorks Marine Black Box</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>WD</td>
<td>Wind Direction</td>
</tr>
<tr>
<td>WHOI</td>
<td>Woods Hole Oceanographic Institute</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorological Organisation</td>
</tr>
<tr>
<td>WS</td>
<td>Wind Speed</td>
</tr>
</tbody>
</table>
Physical Constants

<table>
<thead>
<tr>
<th>Constant Name</th>
<th>Symbol</th>
<th>Constant Value (with units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity</td>
<td>$g$</td>
<td>9.81 m/s</td>
</tr>
<tr>
<td>Specific Heat of Air</td>
<td>$c_\rho$</td>
<td>$2.909\ 966\ 37 \times 10^{-2} \text{ J mmol}^{-1} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>at a Constant Pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Universal Gas Constant</td>
<td>$R$</td>
<td>8.314 J mol$^{-1}$ K</td>
</tr>
<tr>
<td>Von Karman</td>
<td>$\kappa$</td>
<td>0.4</td>
</tr>
</tbody>
</table>


