

Marine Research Sub-Programme  
(NDP 2007-'13) Series

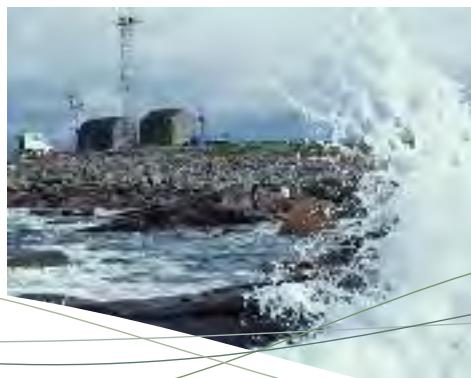


# Impacts of Increased Atmospheric CO<sub>2</sub> on Ocean Chemistry and Ecosystems

Project Based Award, Final Summary Report



Lead Partner: National University of  
Ireland, Galway



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1. Assist existing, and largely indigenous, marine sub-sectors to improve their overall competitiveness and engage in activity that adds value to their outputs by utilising knowledge and technology arising from research.
2. Build new research capacity and capability and utilise fundamental knowledge and technology to create new marine-related commercial opportunities and companies.
3. Inform public policy, governance and regulation by applying the knowledge derived from marine research and monitoring.
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# Marine Research Sub-Programme 2007-2013

## *Project-Based Award*

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### ***Impacts of Increased Atmospheric CO<sub>2</sub> on Ocean Chemistry and Ecosystems***

*(Project Reference: SS/CC/07/001)*

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Project Partners:	Marine Institute
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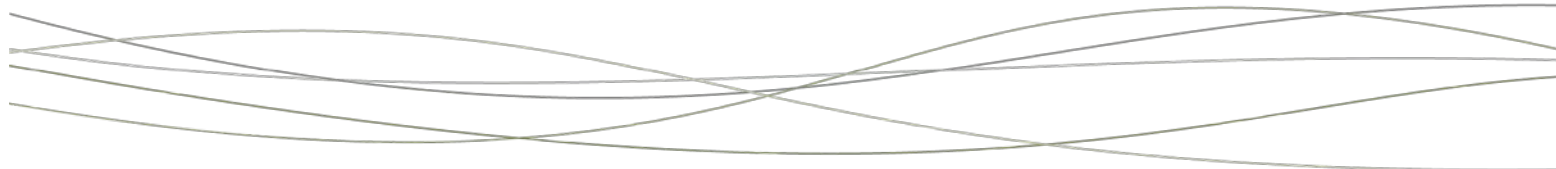
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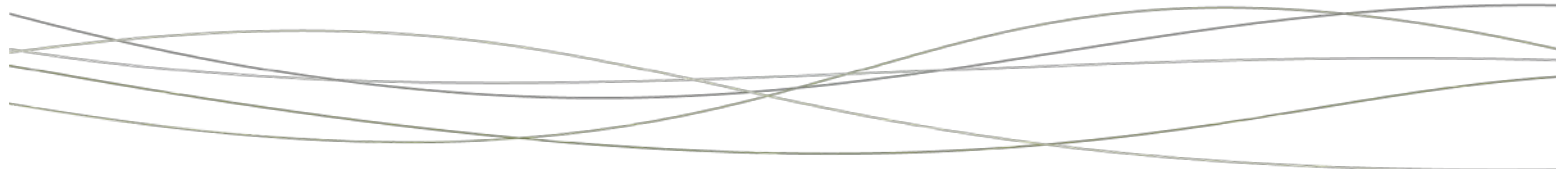
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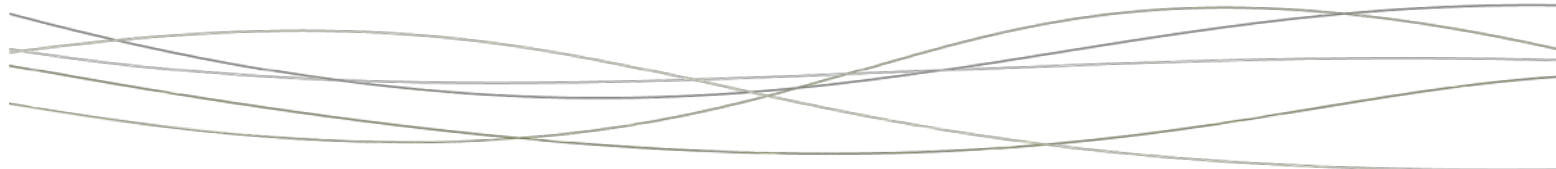


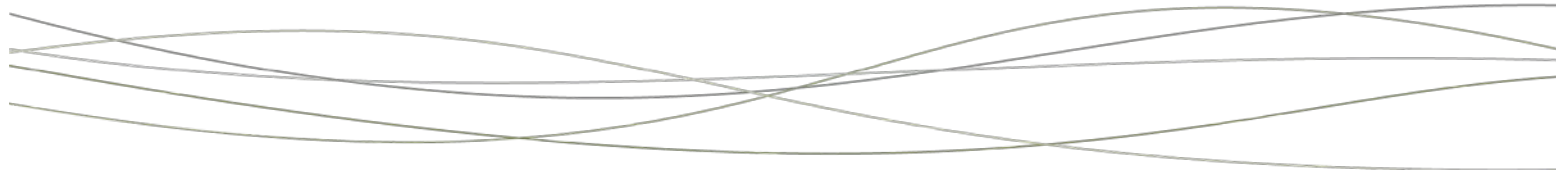
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## EXECUTIVE SUMMARY

Ocean  $pH$  is a function of the seawater carbonate system, which is a function of both the influx of  $CO_2$  from the atmosphere and the resulting concentration of  $CO_2$  in the water (i.e.  $pCO_2$ ). Uptake of anthropogenic carbon dioxide from the atmosphere is reducing ocean  $pH$ ; a phenomenon referred to as ocean acidification. It is estimated that there has been a decrease of 0.1  $pH$  units in the surface waters of the world's oceans since the start of the industrial revolution with a reduction of 0.3 – 0.5 forecast by 2100. There is growing concern over the potential consequences of ocean acidification for marine ecosystems and the services they provide for mankind. This project was aimed at enabling the capability and developing the expertise within Ireland to measure and quantify the flux of  $CO_2$  into (or out of) the ocean; to monitor seasonal trends in  $pCO_2$  and  $CO_2$  fluxes; to determine the current baseline state and variability of the carbonate system; and to evaluate the potential impact of future changes on ecosystems with the ultimate aim of contributing to more informed policy development.

The continuous monitoring aspect of this programme focused on coastal  $CO_2$  fluxes and  $pCO_2$  measurements and was centred at the Mace Head Atmospheric Research Station (a World Meteorological Organisation Global Atmosphere Watch Station), which included an off-shore marine chemistry buoy as part of its observational facilities. The coastal flux and  $pCO_2$  measurements were complemented by identical off-shore measurements on the *RV Celtic Explorer*. The determination of the carbonate system baseline was achieved through a series of *RV Celtic Explorer* cruise-transects of the continental shelf region and coastal seas during different seasons.

In order to measure future  $pH$  changes in water bodies within and beyond the continental shelf limits, a good characterisation of the baseline state and variability of the carbonate system is required. Measurement of carbonate system parameters (dissolved inorganic carbon -  $DIC$ , total alkalinity -  $TA$ ,  $pCO_2$  and  $pH$ ) in seawater to the required degree of accuracy is a specialised and challenging task. During this project a laboratory for carbonate measurement was established in NUI Galway with methodologies optimised for the sampling and accurate determination of  $DIC$  and  $TA$ . These parameters, when determined along with other parameters such as salinity and nutrients, enable calculation of  $pCO_2$  and  $pH$ . However, *in situ*



deployment of an electrode-based pH meter confirmed that currently available instruments are not yet sufficiently developed for direct high precision monitoring of ocean *pH*. An algorithm for estimating *TA* from sea salinity and temperature was also evaluated, showing promise.

During five deepwater and three coastal surveys, measurements of *TA*, *DIC*, dissolved inorganic nutrients, dissolved oxygen and salinity were undertaken, alongside complementary physical and biological oceanographic studies providing integrated datasets with good seasonal coverage. Winter surface seawater in the outer shelf and Rockall Trough in 2010 was observed to be more acidic by 0.02-0.04 pH units than surface seawater sampled in the same area in November 1996 during the World Ocean Circulation Experiment (WOCE). However, nutrient concentrations show that seasonal stratification may not have fully broken down during WOCE sampling and that biological activity may, at least in part, explain the *pH* differences. Many organisms secrete calcium carbonate, either as aragonite or calcite, to build their shells and skeletons. The aragonite and calcite saturation states are important parameters as any decrease in these will have implications for the amount of energy a given organism has to expend in order to produce its hard parts. Saturation Horizons are the water depths below which water is under-saturated with respect to aragonite or calcite and at which these minerals will begin to dissolve. These saturation horizons are predicted to become shallower due to oceanic uptake of increased atmospheric CO<sub>2</sub>. The Aragonite Saturation Horizon (ASH) was calculated to be at about 2500m. Little or no change is evident in aragonite saturation state in the southern Rockall Trough between 1996 and 2010. However, the saturation state in summer in the Porcupine Sea Bight, north of the Goban Spur, is lower throughout the water column in 2009 than determined in 1997 for a transect further to the south, and the ASH appears to be shallower by several hundred metres. Salinity and temperature data indicate that this may be due to physical factors, such as difference in geographical spread of sampling points and water mass mixing. These findings demonstrate the need for consistent regular integrated biogeochemical and oceanographic surveys, as the underlying physical and biological processes provide a natural variability which must be understood to get a true picture of changes to the overall acidification state of our marine waters.

In terms of the seasonal trend of *pCO*<sub>2</sub>, *pCO*<sub>2</sub> was generally lower in winter and higher in summer and was partly correlated to sea surface temperature. Coastal *pCO*<sub>2</sub> was generally elevated compared to open ocean *pCO*<sub>2</sub>. CO<sub>2</sub> fluxes were correlated to wind speed, with increased fluxes associated with increased wind speed. The coastal CO<sub>2</sub> fluxes were higher, by a factor of 3.5, than previously reported open ocean fluxes due to coastal shoaling effects, but

comparable to measurements over the North Sea. The maximum  $CO_2$  fluxes occurred during winter, with a secondary maximum occurring over summer months. It is concluded that the winter peak is driven by greater  $CO_2$  solubility in the colder winter waters combined with increased air-to-sea transfer of  $CO_2$  associated with higher winds. The secondary peak in summer is associated with  $CO_2$  uptake resulting from biological activity.

The ecological and socio-economic impacts are as yet uncertain but provide significant cause for concern. Calcifying organisms such as cold water corals and bivalve and gastropod molluscs, many of which support commercial fisheries, are most obviously at risk. A report detailing current scientific information on ocean acidification and its potential ecological impacts was published as part of the project. It also addressed the potential socio-economic consequences and broader policy considerations and elaborated recommendations for future research and monitoring. A short information leaflet for policy makers and the general public was also produced. **It is recommended that a long-term multi-disciplinary ocean acidification and marine climate change monitoring and research programme is established to support policy decisions on mitigation and adaptation. Specialist expertise and capacity developed under this programme should be sustained to deliver a viable and cost-effective monitoring programme into the future.**

## INTRODUCTION

It is estimated that the concentration of atmospheric CO<sub>2</sub> has increased from 280 ppm to 390ppm, the highest concentration in the last 420 kyr. This current rate of increase is unprecedented in the last 20 kyr, and is expected to continue to rise (Prentice *et al.*, 2001). This increase in atmospheric CO<sub>2</sub> since pre-industrial times has probably resulted in a corresponding decrease of 0.1 pH units in the world's oceans, although there is a spatial variability of about ± 0.3 units primarily governed by temperature and upwelling. Long-term monitoring at a number of North Atlantic locations has confirmed downward trends in pH; specifically Bermuda (-0.0017 pH units yr<sup>-1</sup>, Bates and Peters, 2007), Canary Islands (-0.0017 pH units yr<sup>-1</sup>, Santana-Casiano *et al.*, 2007) and the Iceland Sea (-0.0024 pH units yr<sup>-1</sup>, Olafsson *et al.*, 2009).

Model forecasts have indicated that with a 'business as usual' scenario (IPCC, 2010) there could be a reduction in surface ocean pH of ~0.3-0.5 by 2100 and of 0.7 units by 2300 (Caldeira and Wickett, 2003). Such pH changes are probably unprecedented in the past 300 million years with the possible exception of rare catastrophic events. Biogeochemical ocean models predict that dissolved inorganic carbon (DIC) will increase by > 12%, and the carbonate ion concentration will decrease by almost 60% (Feely *et al.*, 2004). The rate of this increase in atmospheric and consequently surface ocean CO<sub>2</sub> concentrations exceeds the ability of the ocean to sequester excess carbon in the deep ocean via mixing and the biological pump and also exceeds the oceans capacity to buffer the changes through release of carbonate from sediments. Measuring the pH of seawater to the required accuracy and precision to determine such changes is not a trivial task especially given that the predicted change is in the order of 0.003 units per annum.

Moreover, CO<sub>2</sub> solubility in seawater will decrease as the oceans warm, reducing the solubility pump which drives the air-sea flux of CO<sub>2</sub> (Ward *et al.*, 2004). Abrupt climate change scenarios expect that the thermohaline circulation of the ocean will diminish, thereby decreasing the efficiency of the biological pump, which transports carbon from the surface to the deep ocean. These changes require complex carbon cycle models for future climate predictions, whose accuracy can be determined only through measurements of ocean-atmosphere CO<sub>2</sub> flux to balance the global carbon budget. Despite the history of CO<sub>2</sub> ocean observations for the last several decades, there still remain large uncertainties in the budget.

The ecological consequences of increased oceanic CO<sub>2</sub> concentrations are much more uncertain. Many marine organisms such as corals and molluscs use calcium carbonate in the form of calcite or aragonite to produce shells or skeletons. With reduced pH the calcification rates of most calcifying species are reduced, and at certain critical carbonate concentrations (carbonate saturation concentrations), the chemical equilibrium is shifted such that carbonate structures actually start to dissolve. As this is pressure and temperature dependent there is a saturation horizon below which the ocean tends to be undersaturated. The aragonite saturation horizon is shallower than that for calcite. Modelled predictions using the IPCC IS92a “business as usual” scenario have indicated that the surface Southern Ocean will begin to become undersaturated with respect to aragonite by 2050 and that by 2100 this undersaturation could extend to the entire southern ocean and subarctic Pacific Ocean (Orr *et al.*, 2005). Arctic waters are most vulnerable and a recent study projected arctic surface waters to become locally undersaturated with respect to aragonite within a decade (Steinacher *et al.*, 2009). Example of animals that could be affected include corals, coccolithophores, foraminifera, pteropods and echinoderms, with larval stages most strongly affected due to their secretion of amorphous forms of calcium carbonate, which are most vulnerable to dissolution (Fabry *et al.*, 2008). The likely effects and consequences to the health of the organisms is still a matter for research as are the potential knock-on ecosystem effects. For example the potential impact on habitats such as corals, which are often important nursery grounds for fish, needs to be better understood and this includes deep cold water corals (e.g. *Lophelia pertusa*) that occur on the Atlantic shelf edge to the west of Ireland. The direct physiological response of marine organisms to increased CO<sub>2</sub> concentrations (e.g. acidosis) are also matters for concern as are the indirect effects due to changing water chemistry (trace element speciation, nutrient availability). Economic effects on fisheries may be considerable (e.g. Cooley and Doney, 2009). Ultimately, ocean acidification may also have feedback mechanisms on climate change by reducing the transport of biogenic carbonate from the surface ocean or reducing the albedo effect associated with coccolithophores (Riesbesell *et al.*, 2000).

## PROJECT OBJECTIVES

### The project objectives were as follows:

- **To initiate research into ocean carbon processes in Irish shelf sea waters, including investigation of CO<sub>2</sub> fluxes.**

The project aimed to develop the capabilities and for measuring pCO<sub>2</sub>, CO<sub>2</sub> flux, and inorganic carbon chemistry and pH in Irish waters and to initiate research into:

- CO<sub>2</sub> air-sea flux processes for Irish shelf waters. This information is essential given the uncertainties associated with CO<sub>2</sub> budgets.
  - Carbonate system in key water masses to the west of Ireland. This will provide a basis for longer-term assessment of changes in the carbonate system and small but critical changes in ocean pH (acidification) ultimately required to predict risk to marine ecosystems.
  - The project aimed to put in place key infrastructure while maximising use of available resources and platforms, including access to the Mace Head Atmospheric Monitoring station, M1 Metbuoy system, and existing & ongoing research programmes and surveys.
- **To establish high-quality chemical measurement capabilities to describe inorganic carbon chemistry in seawater.**

Using equipment procured under the work programme, methodologies were to be optimised and validated to measure the inorganic carbon system (TA, TCO<sub>2</sub>, pCO<sub>2</sub>, and calculate pH –from other parameters) in Irish shelf waters with a high level of precision required given the relatively small annual change in oceanic pH expected.

- **To deploy automated systems on moorings and shipboard systems for measurement of pCO<sub>2</sub> in seawater (such as a proposed buoy at Mace head and research vessels).**

The aim was to establish and test a network of autonomous pCO<sub>2</sub> sensors at a Mace Head mooring, and the M1 and M6 Metbuoys currently operated by the Marine Institute, to provide a transect of semi-continuous pCO<sub>2</sub> and other key measurements in surface waters in coastal waters, offshore shelf and at 3000m isobath and to complement atmospheric pCO<sub>2</sub> measurements made at the Mace Head Research Station.

- **To investigate potential indicators of ecological impact of ocean acidification.**  
A desk study was to be undertaken to review ecological impacts of ocean acidification that are likely to occur in Irish waters and potential indicators.
- **To make recommendations for future Irish research and long-term monitoring in this field.**  
Based on the above, work recommendations were to be made for future Irish research and long-term monitoring and assessment, taking account of initiatives by other countries in this field, such as the UK.

*Additional objectives included:*

- Building capacity and expertise in CO<sub>2</sub> air-sea exchange and ocean carbon chemistry in Ireland;
- Establishing an interdisciplinary research team;
- Making best use of existing infrastructure and resources to provide key measurements of CO<sub>2</sub> flux and carbonate chemistry and providing unique access to the continental margin and oceans to the west of Ireland;
- Acquisition and testing of essential equipment;
- Recommending a research agenda for subsequent needs and feedback to policy makers;
- Maintaining links with the Marine Institute Rapid Climate Change team. Ultimately the information generated by this activity will input into coupled climate and ecosystem models being developed by the Marine Institute under this programme;
- Establishing links with other leading researchers in the field, particularly in the UK and the US.

# I. ESTABLISHMENT OF A NETWORK OF AUTONOMOUS pCO<sub>2</sub> MEASUREMENT SYSTEMS

## I.1 Aims and Overview of Outcomes

The overall aim of this activity was to put in place the measurement infrastructure for pCO<sub>2</sub> measurements on a continuous basis in Irish waters. There were two approaches to enabling this infrastructure: (1) to deploy a number of buoy-mounted pCO<sub>2</sub> instruments in different waters, ranging from coastal to shelf, to open ocean waters and to operate these measurements year-round and on a continuous basis; (2) to deploy a pCO<sub>2</sub> measurement system on the R.V. Celtic Explorer to provide additional spatial coverage to complement the detailed temporal data from the buoy network. For technical reasons, enabling of pCO<sub>2</sub> measurements on the off-shore buoys proved not to be possible given the current power requirements on these buoys. Instead, effort was focused on maintenance of the Mace Head buoy. The Mace Head buoy has been operating since mid-2008; however, data coverage is approximately only 60%. The primary reason for 40% downtime relates to access to the buoy to replace and maintain equipment – access is difficult due to a combination of converging currents, high wind speeds and shallow fetch leading to extremely choppy wave conditions.

The measurements of pCO<sub>2</sub> onboard the Celtic Explorer proved also challenging and there were considerable technical difficulties with the pCO<sub>2</sub> instrument. In fact, two instruments were operated as a method of quality control. Even with this approach, the instruments at times deviated from each other and had to be returned a number of times to the manufacturer for recalibrations. Nevertheless, good datasets were gathered on a number of cruises both in-shore and off-shore. Sample results are presented from each platform below.

## I.2 Mace Head Buoy

Mace Head is an atmospheric research and monitoring station operated by the Centre for Climate and Air Pollution Studies and the School of Physics, National University of Ireland Galway (Jennings *et al.*, 2003). It is located on the west coast of Ireland, at the North East Atlantic interface (52° 20'N, 9° 54'W) and is ideally suited for monitoring atmospheric composition and essential climate variables in both clean and background marine air entering into Europe along with polluted continental air exiting from Europe out over the North East Atlantic. It has a long term record of CO<sub>2</sub>, ozone CFCs and HFCs extending back more than

twenty years and aerosol research has been conducted there since 1958. More recently, research has included micrometeorological flux studies, aerosol flux studies and CO<sub>2</sub> flux studies. CO<sub>2</sub> flux measurements, combined with atmospheric CO<sub>2</sub> and water side CO<sub>2</sub> measurements can be combined to determine the transfer coefficient of CO<sub>2</sub>, or its gas transfer velocity, as a function of key environmental conditions (e.g. wind speed or white cap coverage or biological activity).

In July 2008, a coastal marine meteorology and chemistry buoy was deployed approximately 2 km off-shore from the Mace Head Atmospheric Research Station. The location and distance from the shore was optimised to provide water side CO<sub>2</sub> concentrations (pCO<sub>2</sub>) as close as possible to the peak in the flux footprint of the continuous CO<sub>2</sub> micrometeorological flux measurements conducted from the 22 m tower at Mace Head. Figure 1.1 illustrates the location of the buoy at Mace Head while Figure 1.2 provides a photograph of the buoy.

The buoy was equipped with a Pro-Oceanus pCO<sub>2</sub> instrument, which measures the concentration of carbon dioxide in the seawater along with instruments to provide measurements of Chlorophyll Fluorescence, Dissolved Oxygen Concentration, Salinity, Sea Surface Temperature, Barometric Pressure, Air Relative Humidity, Air Temperature, Average Wind Direction and Average Wind Speed. Data were transmitted in realtime *via* GSM technology.

A year long pCO<sub>2</sub> dataset, measured at Mace Head between November 2008 and November 2009, is shown in Figure 1.3. Over the time frame atmospheric levels of carbon dioxide remained stable and did not vary much; however, seawater pCO<sub>2</sub> levels varied dramatically. During the winter of 2008, seawater levels were in the vicinity of 300 – 400 µatm. In the summer of 2009, a series of “spikes” in seawater carbon dioxide levels was recorded, with peak concentrations reaching 900 µatm (Figure 1.4). Associated with these large concentrations of pCO<sub>2</sub> were high chlorophyll-*a* concentrations and reduced salinity. It is possible that such trends result from an influx of fresh water into the bay area where nutrient and pCO<sub>2</sub> levels are high and salinity low.



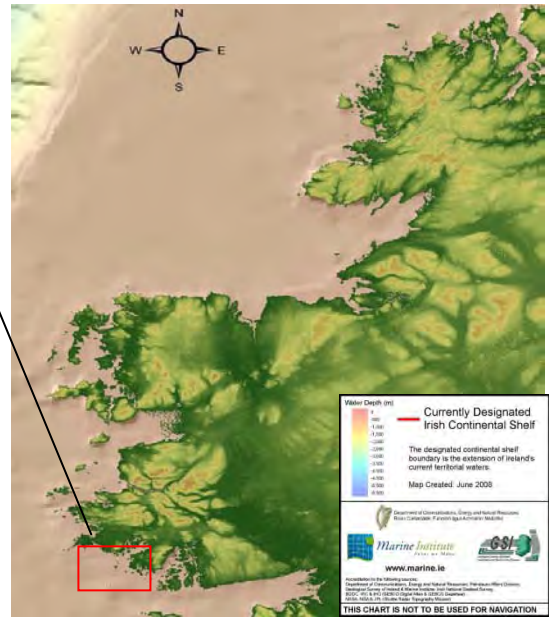
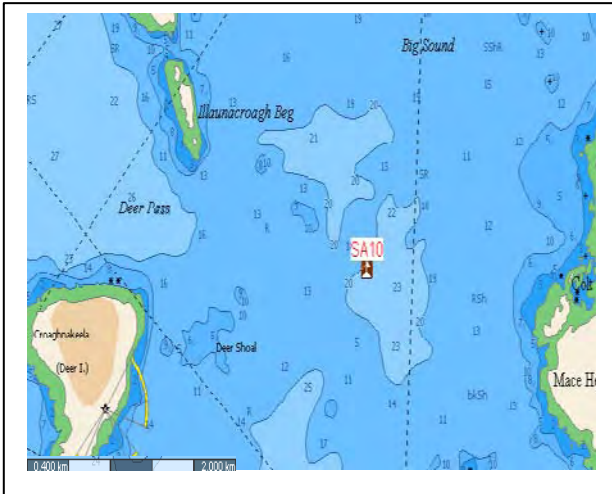


Figure 1.1: Map showing the Mace Head Atmospheric Research Station and the buoy location (SA10)



Figure 1.2: Photograph of the Mace Head Buoy.

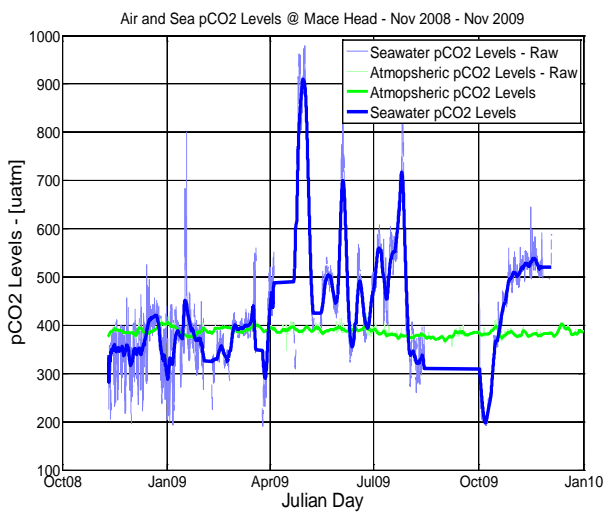


Figure 1.3: Annual pCO<sub>2</sub> and atmospheric CO<sub>2</sub> concentrations at Mace Head. Raw data and smoothed data are shown.

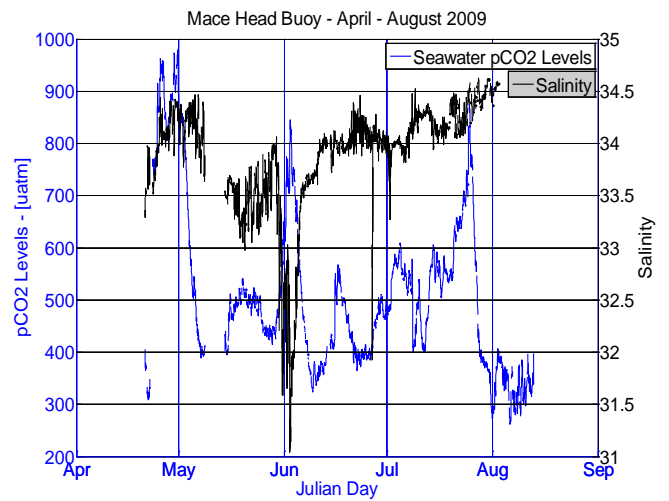


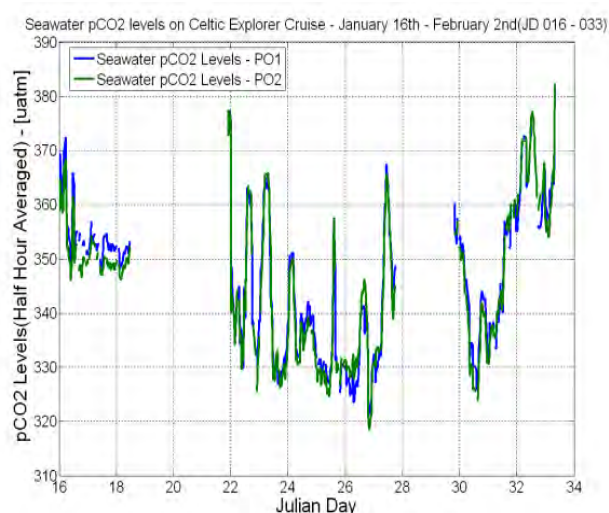
Figure 1.4: Periods of increases in pCO<sub>2</sub> associated with decreases in salinity.

### 1.3 Celtic Explorer

The Celtic Explorer, shown in Figure 1.5, is owned and operated by the Marine Institute and is Ireland's primary research vessel. During this research programme, the initial stages focused on the simultaneous operations of the gold-standard  $p\text{CO}_2$  instrument, the General Oceanics, with the newly-developed Pro-Oceanus  $p\text{CO}_2$  instrument. The former is calibrated during the measurement cycle in-situ while the latter instrument is calibrated yearly in the laboratory. Simultaneous measurements were tried on four cruises; however, due to technical failures of both instruments at different times, no overlapping "cross-calibration" data were gathered. In light of this, two Pro-Oceanus instruments were deployed in parallel to improve the confidence level in that instrument. After various difficulties, a number of cruises (see Figure 1.9) were performed where both instruments agreed to within a few percent. An example of excellent agreement between the two instruments is illustrated in Figure 1.6 for a cruise between 16<sup>th</sup> January and 2<sup>nd</sup> February 2010.

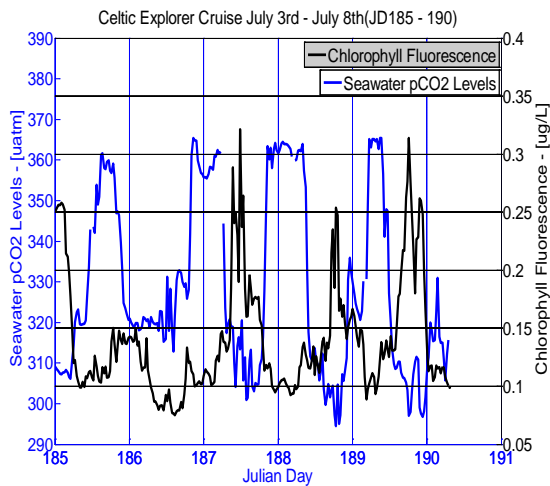


**Figure 1.5:** The R.V. Celtic Explorer. The  $\text{CO}_2$  flux mast is seen at the front of the bow.

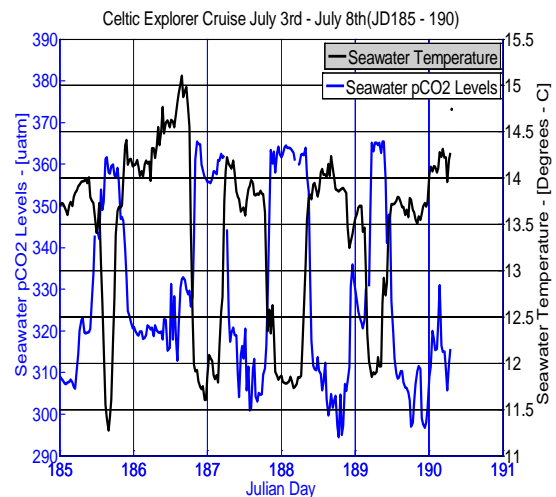


**Figure 1.6:** Intercomparison of two Pro-Oceanus Instruments on board the R.V. Celtic Explorer.

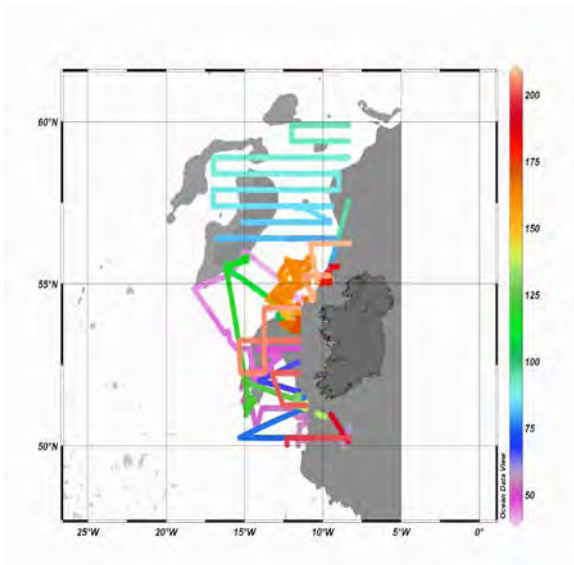
An interesting pCO<sub>2</sub> pattern was seen during a period of calm weather over 5 days in July 2009 in off-shore waters and is shown in Figure 1.7 and Figure 1.8. During this period, pCO<sub>2</sub> was observed to have a strong diurnal variation from ~300 µatm in the afternoon till late evening and lasting approximately 12 hours, after which there was a sudden and sharp rise to ~360 µatm, remaining at the elevated levels for approximately 12 hours. The pCO<sub>2</sub> values were anti-correlated with chlorophyll-a fluorescence and similarly anti-correlated with sea-water temperature which oscillated by 3.5 Degrees.



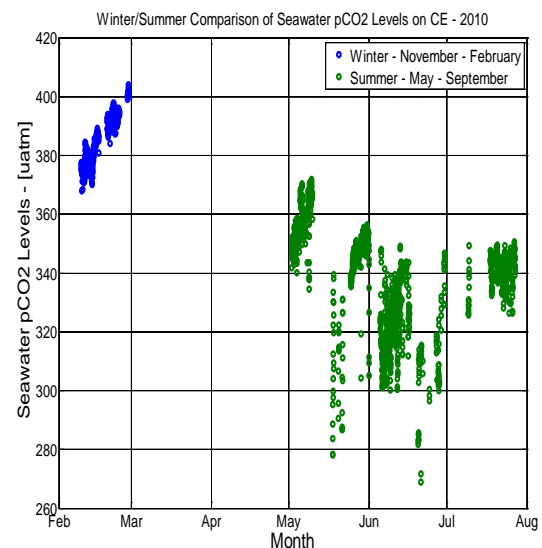
**Figure 1.7:** Case study of chlorophyll fluorescence and pCO<sub>2</sub>, July 2009.



**Figure 1.8:** Case study of sea surface temperature versus pCO<sub>2</sub>, July 2009.



**Figure 1.9:** Cruise track for 2010 cruises up to end of July. The colour bar represents day of year (January 1<sup>st</sup> is day 1). Coastal data were filtered out of subsequent analysis.



**Figure 1.10:** Off-shore pCO<sub>2</sub> for Winter (February) and Summer (May, June, July) periods in 2010.

## **I.4 Activity Synthesis**

While the complete infrastructure, initially envisaged, was not enabled due to technical challenges in a harsh environment, significant progress was achieved in both the long-term continuous point measurements (i.e. the Mace Head buoy) and in the spatial and seasonality distribution of measurements on the R.V. Celtic Explorer. The development of methodologies to implement and maintain the Pro-Oceanus PSI CO<sub>2</sub>-Pro sensor in vessel mounted flow through mode, and buoy mounted discrete sampling mode, was a key element of this work. To this end very significant technical and procedural challenges were overcome and a level of successful data acquisition achieved. The capacity now exists to undertake this work on a routine and ongoing basis and represents a significant step forwards, with knock-on benefits to other work programmes. Future work should include detailed and on-going *in-situ* validation of all parameters. Clear patterns are evident in both near-shore pCO<sub>2</sub> trends and off-shore trends with notable differences observed at the interface between continental shelf and open ocean waters along with strong effects seen in conjunction with what is thought to be fresh water influences in near-shore coastal data.

## 2. DEVELOPMENT AND VALIDATION OF CAPABILITIES FOR MEASURING TA, TCO<sub>2</sub>, pH

### 2.1 Aims and overview of outcomes

The aim of this activity was to establish laboratory and shipboard capabilities for the measurement of total alkalinity (TA) and total dissolved inorganic carbon (TCO<sub>2</sub> or DIC). These two parameters can be used to calculate seawater pH. It should be borne in mind that two other parameters which are routinely sampled for - salinity and nutrients - need to be sampled for in conjunction with TA and DIC as they are required for the calculation of pH.

A VINDTA-3C instrument and a UIC Coulometer were purchased and installed in the NUI Galway Chemical Oceanography laboratory. Several months of setup, testing and adjustment by an experienced postdoctoral researcher were required before the instrument was giving consistently stable, high-precision results allowing actual samples to be run. Throughout the pilot study a postgraduate researcher received ongoing training on the instrumentation. Samples were collected on eight research surveys over the two years of the project, in order that both multi-annual and seasonal sampling data would be available to establish the baseline for Irish waters (see Ch. 3), and including open ocean, continental shelf and coastal waters. The VINDTA was successfully trialled at sea for TA analysis only, as it was judged that given the sensitive nature of the coulometer, it would be both risky to bring it to sea in the first place, and unlikely to produce useful results. RV Celtic Explorer has adequate lab space and facilities for carrying out TA analysis at sea, but this would not be feasible on the RV Celtic Voyager. Due to the setup time, the instrument should only be brought to sea if the voyage will be of reasonable duration, e.g., 10 days or more. Running samples on board reduces the amount of refrigeration space required.

A Seabird SBE-18 pH sensor was tested at sea and results compared with pH calculated from TA and DIC measurements. Results indicate that the instrumentation and protocols are not yet sufficiently developed for direct high precision monitoring of ocean pH. Standard solutions for calibrating pH sensors are designed to cover a much broader range of pH values (2-12) than are found in the oceans, which generally hover around a pH of 8. Development of calibration standards giving several points between pH of 7 and 9 would be a significant step forward.

The instrumentation for the analysis of TA and DIC is complex, and analysis of samples to the precision required for ocean acidification research requires a high degree of skill and understanding of carbonate chemistry. Instrumentation is not available 'off-the-shelf', rather it is hand-built to order, and is in use in only a handful of laboratories worldwide. The retention of trained personnel is therefore critical to the maintenance of a monitoring capability for ocean acidification in Ireland.

## 2.2 Background

Measurements of TA, DIC, pH and pCO<sub>2</sub> have been made in ocean waters with increasing regularity since the GEOSECS expeditions of the 1970s (Takahashi *et al.*, 1980, 1981), as part of programmes such as the Joint Global Ocean Flux Study, the Ocean Atmosphere Carbon Exchange Study, and the World Ocean Circulation Experiment. The knowledge of any two of these parameters, along with the temperature, salinity, pressure, abundances of other constituents of seawater, and the relevant equilibrium constants, allows the determination of the other two parameters. In GEOSECS measurements of TA, a number of variables including the effects of OH, phosphate, and silicate were neglected, but included in the later Peng *et al.* (1987), definition. TA is largely controlled by salinity, and recently, region-specific algorithms have been derived which allow the calculation of TA from sea surface salinity (SSS) and sea surface temperature (SST) (Lee *et al.*, 2006). A number of instruments for measuring TA and DIC in seawater samples are commercially available, using combinations of potentiometric titration for TA and coulometric determination for DIC. Certified reference materials (based on natural sea water) are available routinely for total dissolved inorganic carbon and for total alkalinity from Scripps Institute of Oceanography. The Guide to Best Practices for Ocean CO<sub>2</sub> measurements (Dickson *et al.*, 2008) describes the standard methods now in use for determination of these parameters by researchers worldwide.

Recent work indicates that high concentrations of organic bases and acids may affect the total alkalinity of coastal waters, where present (Hernandez-Ayon *et al.*, 2007; Muller and Bleie, 2008). Where pH is to be calculated from measured TA and DIC in coastal waters, this unknown contribution may lead to a small but measurable error in the pH calculation. This can only be accounted for by simultaneous measurement of the pH in closed-cell titrations.

## 2.3 Set up of laboratory and shipboard analysis

A team was recruited consisting of a postdoctoral researcher (Dr Caroline Kivimäe) with previous expertise in making measurements of carbonate parameters in marine waters, and a postgraduate with an interest in both physical and chemical oceanography (Ms. Triona McGrath). A VINDTA-3C instrument, hand-built by Dr. Ludger Mintrop of Marianda Inc., was purchased and installed in the Chemical Oceanography laboratory at NUI Galway (Figure 2.1), together with a UIC CM5014 Coulometer with CMI33-079 501 I Emulation modification supplied by RL Slaughter. The VINDTA-3C instrument measures total alkalinity (TA) and dissolved inorganic carbon (DIC, also known as  $\text{TCO}_2$ ) on the same sample. It is designed for use at sea as well as in the lab, and was successfully trialled at sea on board RV Celtic Explorer.



**Figure 2.1:** The VINDTA-3C (main picture, centre) with UIC coulometer (right) and water bath (left) for maintaining sample temperature at 25°C, in the lab at NUI Galway. Inset – the VINDTA installed in the chemistry lab on Celtic Explorer.

TA and DIC sampling and analysis were carried out in accordance with the Guide to Best Practices for Ocean  $\text{CO}_2$  measurements (Dickson *et al.*, 2008). Certified reference materials obtained from Prof. Andrew Dickson at Scripps Institute of Oceanography were used throughout the project to validate the TA and DIC analyses, which were carried out either on

board (TA only) or in the lab (TA and DIC) by Kivimäe and McGrath, using the VINDTA-3C. In addition to the carbonate parameters, marine waters were sampled for oxygen, nutrients, and organic carbon. O<sub>2</sub> analyses were carried out on board, using a Metrohm 848 Titrino Plus, while dissolved nutrient analyses (total oxidised nitrogen, nitrite, orthophosphate and silicate) were carried out by McGrath at the Marine Institute, using a Skalar San++ Continuous Flow Analyser. The Marine Institute is accredited to ISO 17025 for nutrient analysis in seawater and routinely participates in QUASIMEME proficiency testing scheme exercises for nutrients in seawater. Dissolved and Total Organic carbon (DOC/TOC) analysis was carried out at the Southampton Oceanography Centre, UK, as facilities suitable for measuring the low values found in ocean waters are not available in Ireland. Salinity samples were analysed at the Marine Institute by McGrath, using a Guildline Portasal Salinometer and by McGrath and Kivimäe at NUI, Galway using a Guildline Autosal salinometer.

A pH sensor, rated for depths down to 1200m, was deployed on one survey, CE10002, and results have been compared with pH calculated from carbonate parameters (Figure 2.2). Instruments for the direct measurement of pCO<sub>2</sub> in seawater were deployed on all the surveys carried out on RV Celtic Explorer, and are described in Chapters 1 and 4.

A number of difficulties were encountered during DIC analyses. The VINDTA-3C was originally designed to work with a UIC 5011 Coulometer, and when UIC changed to the 5014 model, an emulator had to be designed to allow it to work with 5011-compatible instruments. The emulator was included with the Coulometer when purchased, but it proved very difficult to achieve adequate precision of DIC measurements. Several months of testing and tweaking, and the replacement of both the lamp and the cell in the coulometer, were required before the instrument was giving consistently stable, high-precision results (Table 2.1) allowing samples to be run.

**Table 2.1:** Precision of DIC and TA analysis (µmol/kg)

Survey	DIC +/-	TA +/-
<b>CE0807</b>	3.2	n/a
<b>CV0824</b>	1.8	n/a
<b>CE0903</b>	1.9	0.9
<b>CV0911</b>	3.4	1.2
<b>CE0911</b>	1.8	1.4
<b>CV0924</b>	2.1	1.6
<b>CE10002</b>	2.8	1.4



## 2.4 Sampling

Sampling for carbonate parameters was carried out on 8 research surveys over the two years by Kivimäe, McGrath, and Cave (Table 2.2). A number of undergraduate students also participated in the surveys and were trained in sampling methods. 5 deepwater surveys took place on RV Celtic Explorer, with the remaining 3 coastal water surveys on RV Celtic Voyager (Table 2.2). Details of these surveys and sampling protocols are given in Chapter 3. Shipboard sampling requires a minimum of two people per watch, as samples for TA/DIC must be poisoned and sealed immediately after being drawn from the rosette, and salinity and nutrient samples must be collected simultaneously. Oxygen samples may also be taken and should be analysed on board.

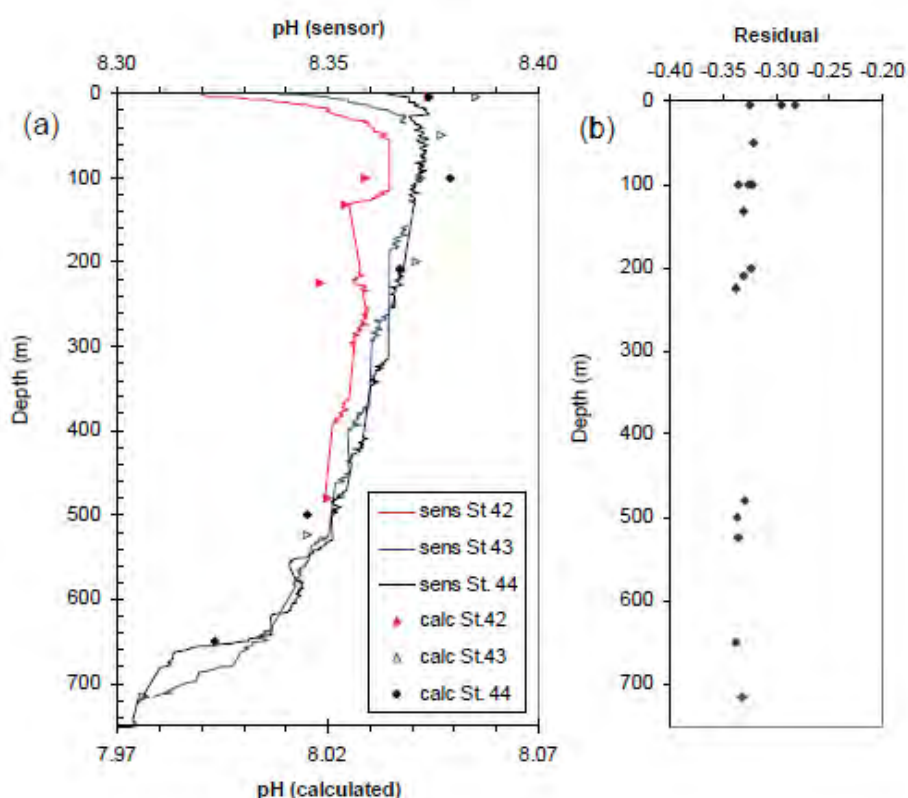
**Table 2.2:** Research surveys on which ocean carbonate parameters were sampled. CExxxx = RV Celtic Explorer CVxxxx = RV Celtic Voyager. The first two digits after the ship identifier denote the year.

\* denotes samples from CE0919 which are still under analysis.

Survey	CE0807	CV0824	CE0903	CV0911
Date	26 - 29 May 2008	4 – 7 Sept 2008	5 - 15 Feb 2009	3 - 7 May 2009
	Irish West & South coast shelf	Irish West coast shelf, 52 - 53°N	53°N and Rockall Trough	West coast, 53°N to Erris Head
DIC	n= 55	n= 38	n= 62	n= 27
TA	Lost	Lost	n= 62	n= 27
Oxygen	Not sampled	Not sampled	Lost	n= 37
Nutrients	n= 73	n= 38	n= 139	n= 78
Salinity	n= 73	n= 38	n= 139	n= 42
Survey	CE0911	CV0924	CE0919	CE10002
Date	14 - 22 June 2009	7 – 12 Sept 2009	15 Dec 2009	17 Feb 2010
	Western Shelf, Porcupine Bank	Shannon to Galway Bay	Western Shelf-break, off-shelf	53°N, Rockall Trough
DIC	n= 177	n= 31	n= 60*	n= 60
TA	n= 177	n= 31	n= 60*	n= 107
Oxygen	n= 250	Not sampled	Not sampled	n= 71
Nutrients	n= 253	n= 68	n= 60	n= 355
Salinity	n= 258	n= 122	n= 60	n= 270

## 2.5 Comparison of measured with calculated pH

A Seabird SBE-18 pH sensor was deployed as part of the instrument package for part of CE10002. This sensor is only rated to 1200m, so could only be deployed for the first 3 stations (Figure 2.2). The sensor generally shows an abnormally high pH value, with an almost constant offset of 0.33 between the pH measured by the sensor, and the pH calculated using TA and DIC, with two exceptions. At 800m, the offset was significantly smaller (0.07) than for all the readings above this depth, and this may be related to the sudden change in water mass properties below 700m, where the temperature and salinity both drop sharply and the speed of descent may not have allowed the sensor to equilibrate. At 990m, the sensor gave an anomalously high reading of  $\text{pH} = 11$ , and this is likely to be a simple failure as it was approaching its maximum rated depth. Measurements right at the surface may also vary due to the very rapid changes in properties at the surface not being adequately captured due to the difference in the depth of the water measured by the sensor, and that sampled by the bottle.



**Figure 2.2:** (a) Comparison of pH sensor with pH calculated from TA and DIC of samples on CE10002. Solid lines are the continuous sensor data, symbols are the calculated pH from TA and DIC of water samples. (b) The residual pH (calculated pH – sensor pH) for each water sample. The two deepest points (not shown) have residuals of -0.07 (800m) and -3.24 (990m). From McGrath *et al.*, in prep.

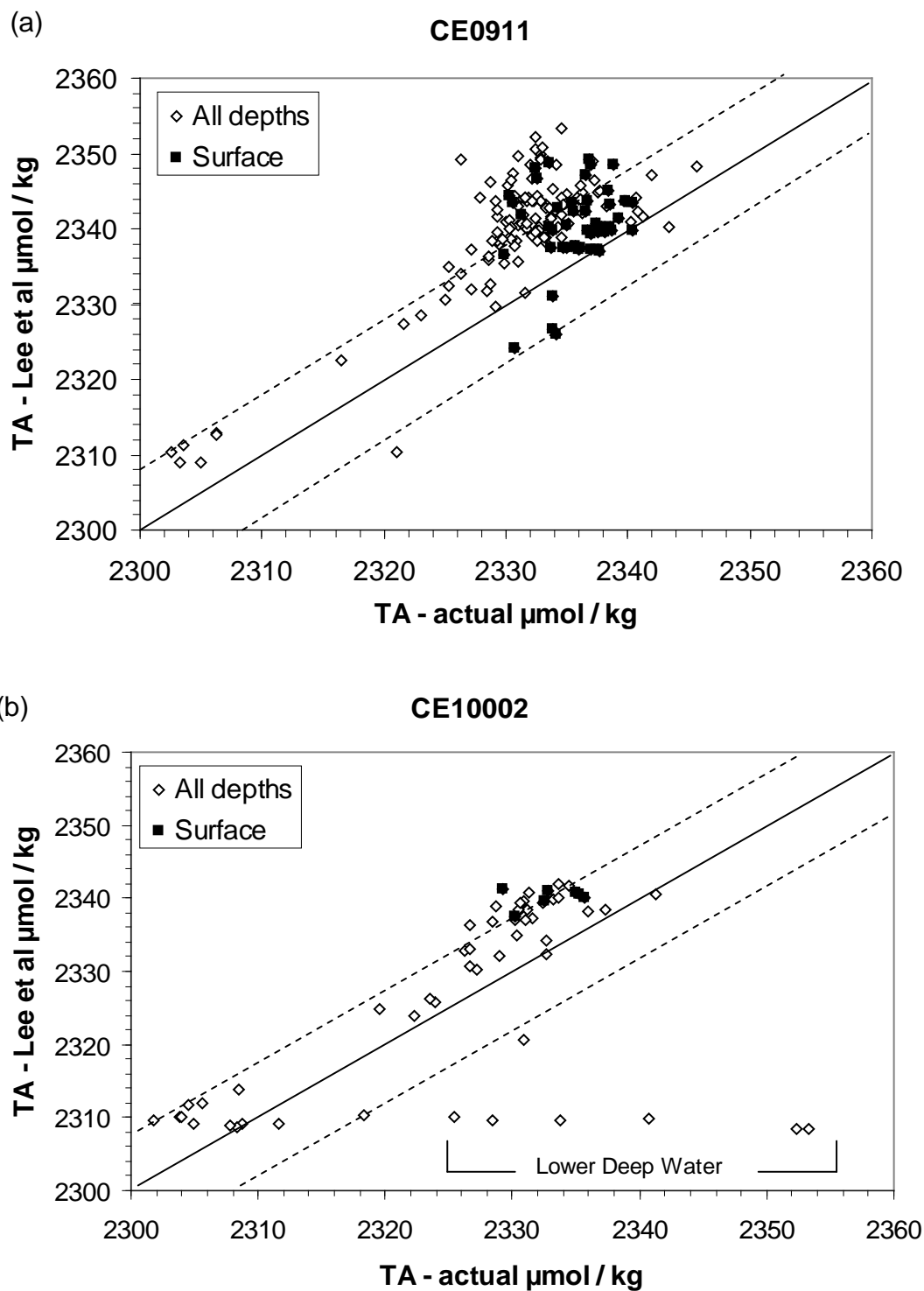
The pH sensor was factory-calibrated. Sea-Bird calibrates the pH sensor against precision buffer solutions (4, 7, and 10 pH  $\pm$  0.02 pH). These calibration results are tabulated on a certificate furnished with each sensor. However, the calibration scale vastly exceeds the range of pH values likely to be found in the oceans (pH 8-8.5), where differences in pH of 0.01 are considered significant. pH sensors in general are slow to adapt to changing conditions, and usually require time for the readings to settle down. If such sensors are to be considered for routine measurements of ocean pH in the future, then they need to be rated for a much narrower pH range, and calibrated to a precision better than 0.01. They also need either to respond more rapidly to changing salinity and temperature, or protocols need to be put in place such that where clear changes in temperature or salinity are encountered, the winch should be stopped for a few minutes to allow the sensor to acclimatise. At present, the instrumentation and protocols are not sufficiently developed for high precision direct monitoring of ocean pH.2.6

## 2.6 Comparison of TA data with algorithms for N. Atlantic

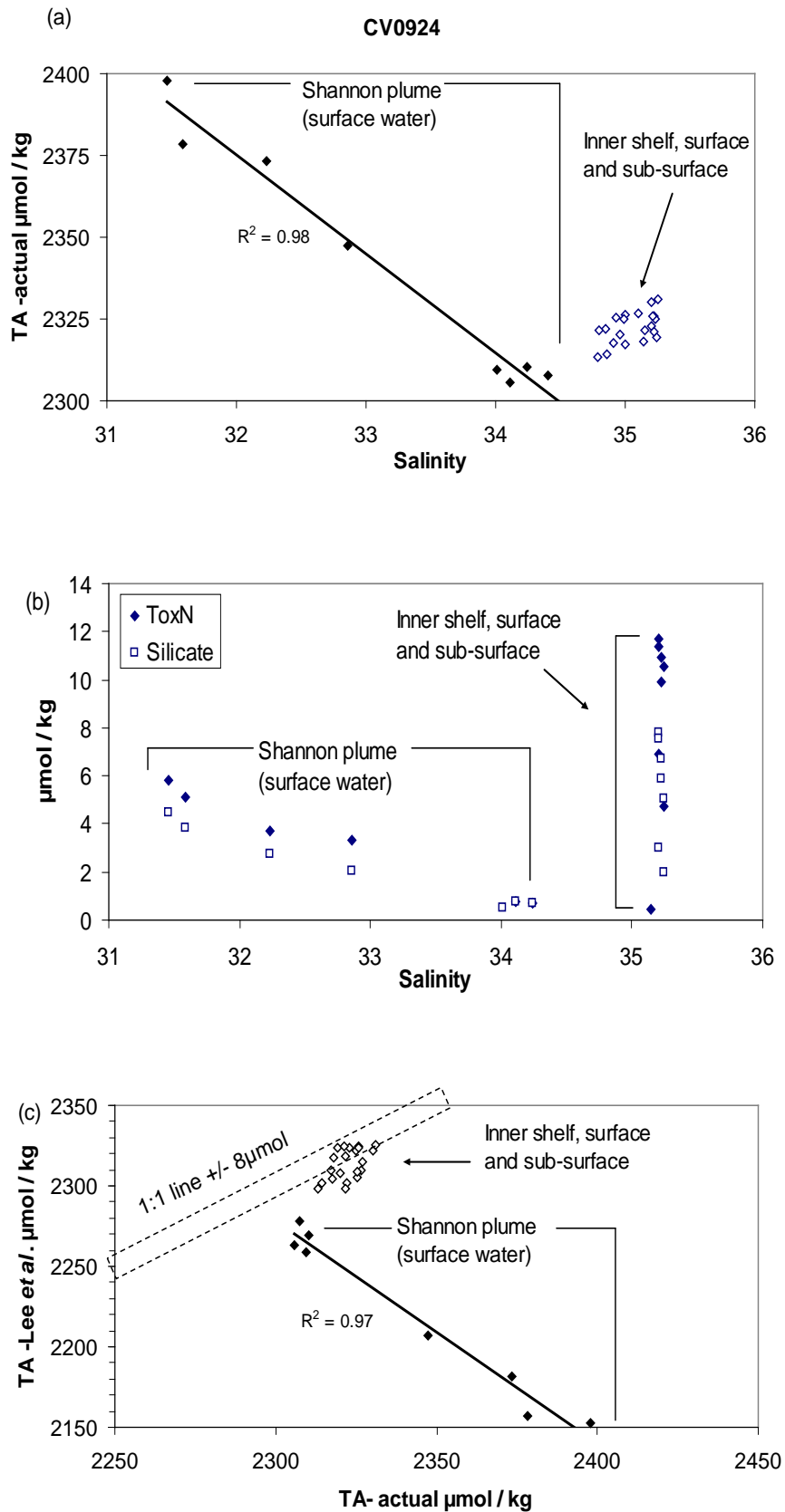
Lee et al (2006) published algorithms for all the ocean basins, relating sea surface salinity (SSS) and sea surface temperature (SST) to the total alkalinity of surface water (TA). For latitudes north of 30°N, Lee, *et al.* used samples of SSS, SST and TA from water depths above 30m from the Joint Global Ocean Flux Study, the Ocean Atmosphere Carbon Exchange Study, and the World Ocean Circulation Experiment. One objective of the pilot study was to test the algorithm for the N. Atlantic Ocean against our data in order to see in which regions the algorithm is valid, and where it breaks down. We expected that the algorithm would be robust for open ocean waters across the Porcupine Bank and Rockall Trough, but might break down in more productive waters closer to the coast, where the presence of organic acids might be expected to play a role in TA (Hernandez-Ayon *et al.*, 2007; Muller and Bleie, 2008).

The algorithms showed that TA was largely a function of salinity and temperature, for a range of salinity from 31 to 37, and temperature from 0°C to 20°C. The majority of samples in our study, whether from surface or deeper water, fall close to the 1:1 line for measured TA versus TA calculated using this algorithm, and are generally well within the  $\pm$  8  $\mu$ mol/kg uncertainty of Lee *et al.*, (Figure 2.3). It is clear that there is considerably less scatter in the samples from CE10002, the Rockall Trough area in winter, with the exception of the very deep Lower Deep Water (below 2500m), which has a high silicate content, increasing its TA with respect to salinity (Figure 2.3b). Waters across the Porcupine Bank in summer (CE0911)

are expected to be quite productive, creating the greater scatter seen in Figure 2.3a, and it can be seen that the algorithm, in general, overestimates the TA whether in winter or summer. For coastal water, the Lee *et al.* algorithm is not expected to work well, due to the effects of low salinity water on the one hand, and the high content of dissolved organic material in coastal waters on the other (Figure 2.4c). However in these waters, the algorithm may be used to highlight different water masses or processes. A comparison of actual TA against salinity for waters along the west coast between the Shannon estuary and Galway bay is shown in Figure 2.4a. The influence of the Shannon on TA is clearly seen, with plume waters having high TA, which reduces with dilution with seawater, until a salinity of about 34.5, after which the TA starts to rise. The high TA in plume waters cannot be attributed simply to high nutrients (nitrate, silicate) as there are also high nutrients in water below the surface mixed layer outside the plume (Figure 2.4b), and must therefore also be a function of dissolved organic matter. Overall, for waters where salinity exceeds 34.5 in this area, i.e. outside the direct influence of the Shannon plume, the Lee *et al.* algorithm tends to underestimate the TA, whereas in waters further offshore, the algorithm overestimates the TA.



**Figure 2.3:** Comparison of TA calculated using N. Atlantic algorithm from Lee et al, (2006) -where TA is a function of salinity and temperature -with measured TA which takes nutrients into account. Dotted lines indicate the precision of  $\pm 8 \mu\text{mol}/\text{kg}$  of Lee et al. (2006). CE0911 sampled over the Porcupine Bank, while CE10002 sampled in the Rockall Trough. From Cave et al. in prep.



**Figure 2.4:** Comparison of coastal and Shannon plume water salinity with TA and nutrients. It can be seen that different relationships exist for waters of salinity < 34.5 and salinity > 34.5. From Cave *et al.* in prep.

## 2.7 Activity Synthesis

The laboratory for measuring total alkalinity (TA) and dissolved inorganic carbon (DIC or  $\text{TCO}_2$ ) was successfully established, and the VINDTA instrument was successfully trialled at sea. Skills in both sampling and analysis of these key parameters were transferred from postdoctoral to postgraduate researcher. However, the continued operation of such a laboratory requires the retention of skilled personnel, and the curtailment of the project after two years means that the skills acquired may be lost. A pH sensor was tested at sea and compared to calculated pH. Results indicate that the instrumentation and protocols are not sufficiently developed for high precision monitoring of ocean pH. Comparisons between actual measurements of TA, and algorithms which relate sea surface salinity (SSS) and sea-surface temperature (SST) to total alkalinity (TA), were carried out for surface and sub-surface coastal and offshore waters, to establish the limitations of the use of algorithms.

## 3. BASELINE MONITORING

### 3.1 Aims and overview of outcomes

The aims of this activity were twofold: (1) to develop and implement sampling protocols, based on international best practice, for the collection, preservation and storage of seawater samples for the analysis of carbonate parameters, and to review these protocols in order to develop routine sampling procedures for the measurement of carbonate parameters in Irish waters; (2) to produce a set of baseline data for carbonate parameters in Irish waters, against which future changes could be assessed. Sampling was carried out on five deepwater and three coastal water surveys over the course of the project, more than twice as many as originally envisaged, providing both seasonal and multiannual baseline data. Revisions of protocols were made between surveys incorporating lessons learned each time. A robust set of protocols has resulted, including pre-cruise preparation protocols, which have been integrated with those used by the Marine Institute for their oceanographic surveys. Results indicate measurable differences between the *pH* of samples collected in the mid-1990's during the World Ocean Circulation Experiment and *pH* of samples collected in 2009/10, however these differences in *pH* may be attributable to differences in physical oceanography between the surveys.

### 3.2 Baseline surveys of Irish waters

Five deepwater surveys took place on RV Celtic Explorer, with the remaining three coastal water surveys on RV Celtic Voyager (Table 2.2). This was well in excess of the three surveys envisaged in the original proposal, and was made possible by a combination of outstanding effort on the part of the sea-going staff, and the extra access granted by the Marine Institute and other users to berths on a range of surveys. Ships tracks and location of CTD sampling stations can be seen in Figure 3.1. Stations on CE0903 sampled in Feb. 2009 were repeated on CE10002 in Feb. 2010, in conjunction with the annual Marine Institute Ocean Science Services survey, to examine interannual variability, and seasonal variation was examined by comparing these with stations from CE0911, sampled in June 2009. Water masses below the mixed layer were also targeted for sampling (Table 3.1) as these can be identified from CTD data.

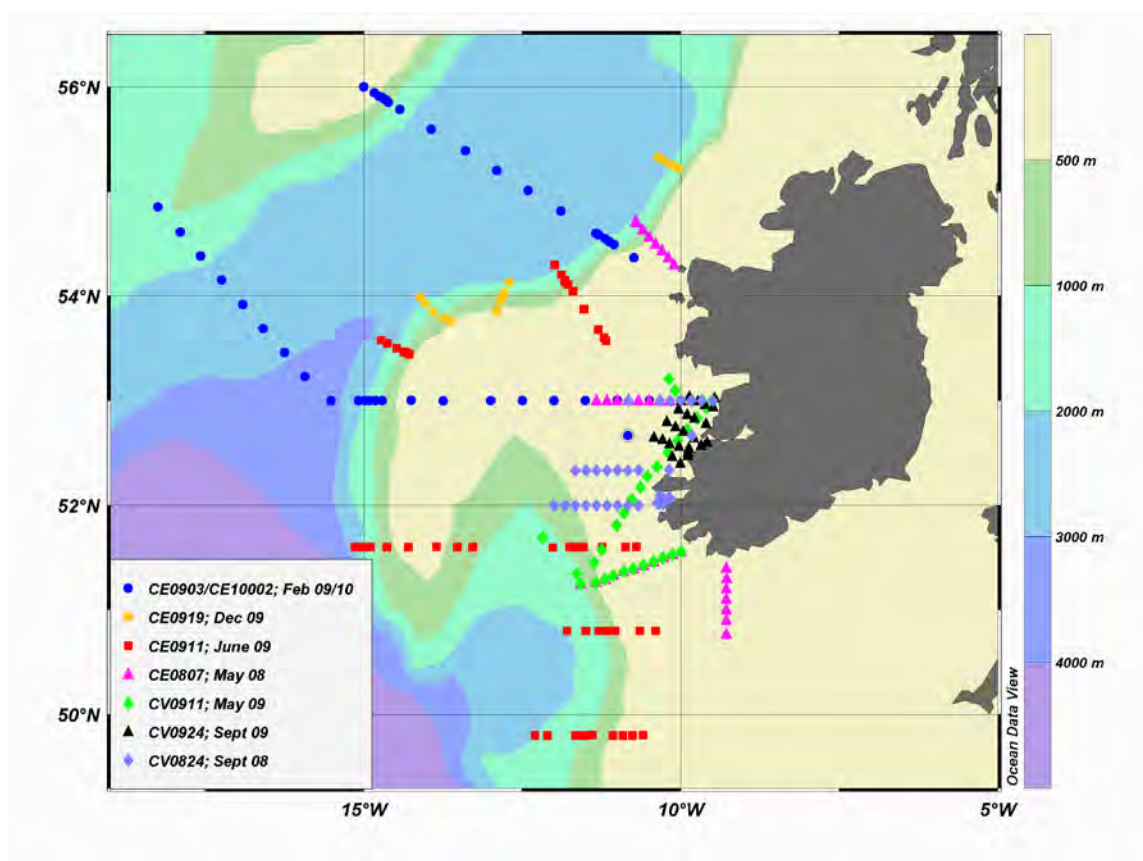
The deep sea data from the Rockall Trough and Goban Spur areas have been compared with data from WOCE (World Ocean Circulation Experiment) cruises AR24 and A24, from 1996/7. Sampling of Irish inner shelf and coastal waters for carbonate parameters has been



carried out for the first time - no prior data for carbonate parameters exist for Irish coastal waters.

**Table 3.1:** Water masses targeted for sampling. SML = Surface Mixed Layer; ENAW = Eastern N. Atlantic Water; MEDW = Mediterranean Water; SAIW = Sub Arctic Intermediate Water; LSW = Labrador Sea Water; LDW = Lower Deep Water.

Survey	CEO903	CEO911	CE10002
Date	Feb 2009	June 2009	Feb 2010
<b>Water Mass</b>			
<b>SML</b>	√	√	√
<b>MEDW</b>	√	√	√
<b>ENAW</b>	√	√	√
<b>SAIW</b>	√	-	√
<b>LSW</b>	√	√	√
<b>LDW</b>	√	-	√



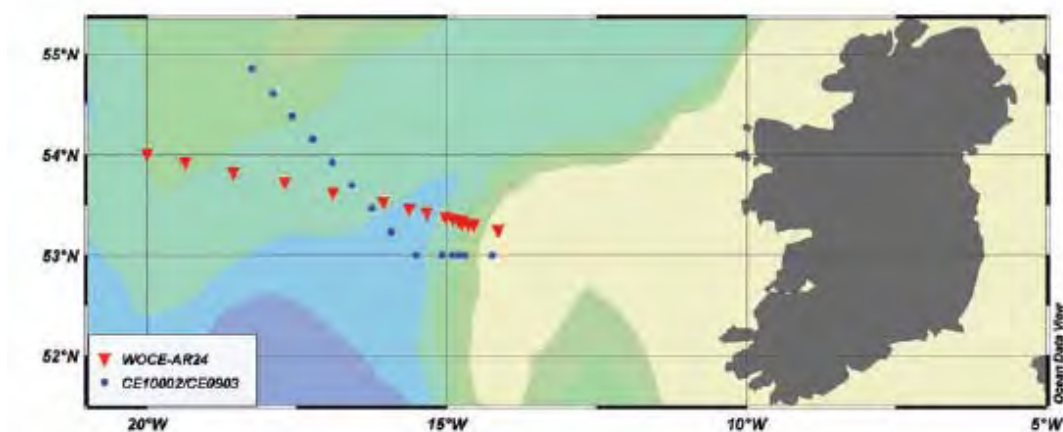
**Figure 3.1:** Coverage of Irish Shelf waters during the project. Transects running across the Rockall Trough were sampled on winter surveys in consecutive years. The transect running east-west along 53°N was sampled on one summer and two winter surveys. This plot shows the complete set of CTD stations occupied, not all of which were sampled for TA and DIC.

### 3.3 Results

The WOCE collected water samples for ocean acidification parameters in the area of the Rockall Trough in winter 1996 and summer 1997. Two of the surveys for this pilot project sampled along similar transects in the southern Rockall Trough in winter (Figure 3.2) – CE0903 (Feb 2009) and CE10002 (Feb 2010), while a further survey, CE0911 in June 2009, overlapped or was close to the summer WOCE survey. It has therefore been possible to make comparisons between the historical and recent data.

#### 3.3.1 Winter data - outer shelf and Rockall Trough

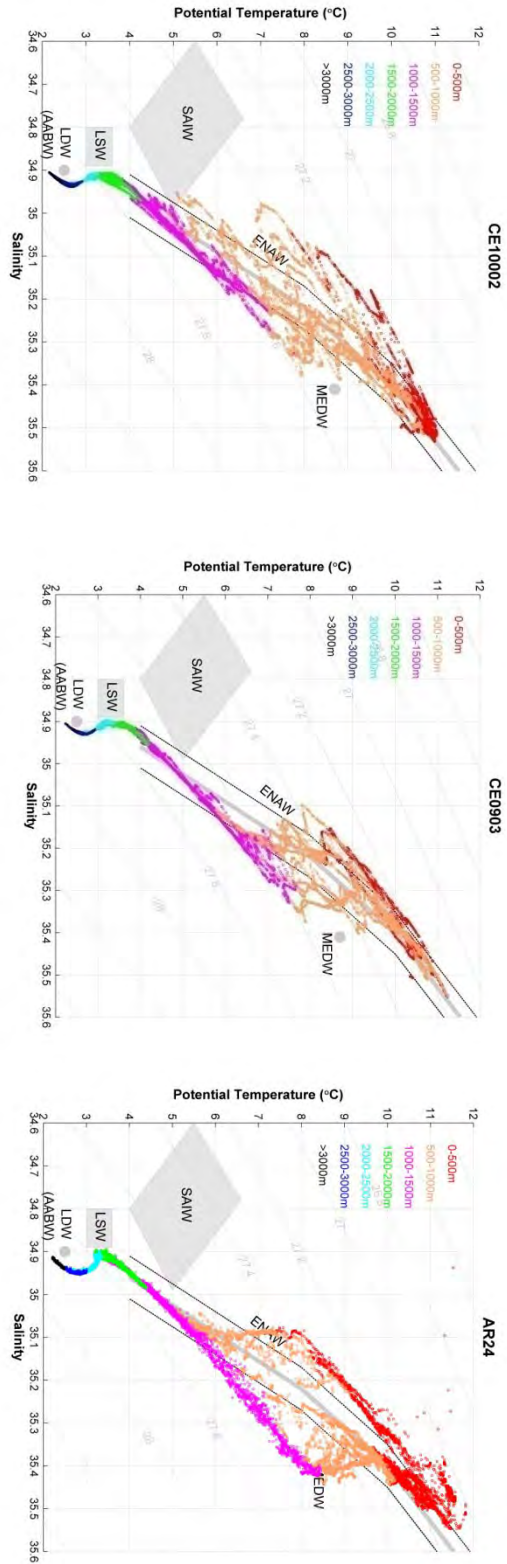
Transects across the southern Rockall Trough were sampled in February 2009 and again in February 2010 (Figure 3.2), and correspond to a similar transect sampled during WOCE AR24, on the RV Knorr in December 1996. WOCE data were sourced from the CDIAC database (<http://cdiac.ornl.gov/oceans/>).



**Figure 3.2:** A transect across the southern Rockall Trough was sampled in consecutive winters – Feb. 2009 during CE0903, and Feb. 2010 during CE10002. A similar transect in this area was sampled by WOCE AR24 in December 1996 on the RV Knorr.

#### Physics:

Potential temperature – salinity (TS) plots for 2009 and 2010 are shown in Figure 3.3, and indicate that the same series of water masses were encountered on both winter surveys. Much of the top 1000m in the region falls within the Eastern North Atlantic Water (ENAW) range. Between 500-1000m, some of the data points tend towards the warm and salty Mediterranean water (MEDW); note the MEDW limits on the TS plots in Figure 3.3 are modified water properties not source Mediterranean water properties, and the values given here are indicative of the MEDW signal seen at the southern entrance to the Rockall Trough. Also between 500-1000m, a Sub-Arctic Intermediate Water (SAIW) signal is seen, particularly in 2010.



**Figure 3.3:** Potential Temperature salinity (TS) plots for CEI10002 (Feb 2010) and CE0903 (Feb 2009) showing the water masses encountered in the southern Rockall Trough, and WOCE AR24 plot for the same region from Nov. 1996. Note MEDW limits plotted here are not source water properties, but are MEDW properties typical of those seen at the southern entrance to Rockall Trough (Harvey, 1982).  
From McGrath *et al.*, in prep.

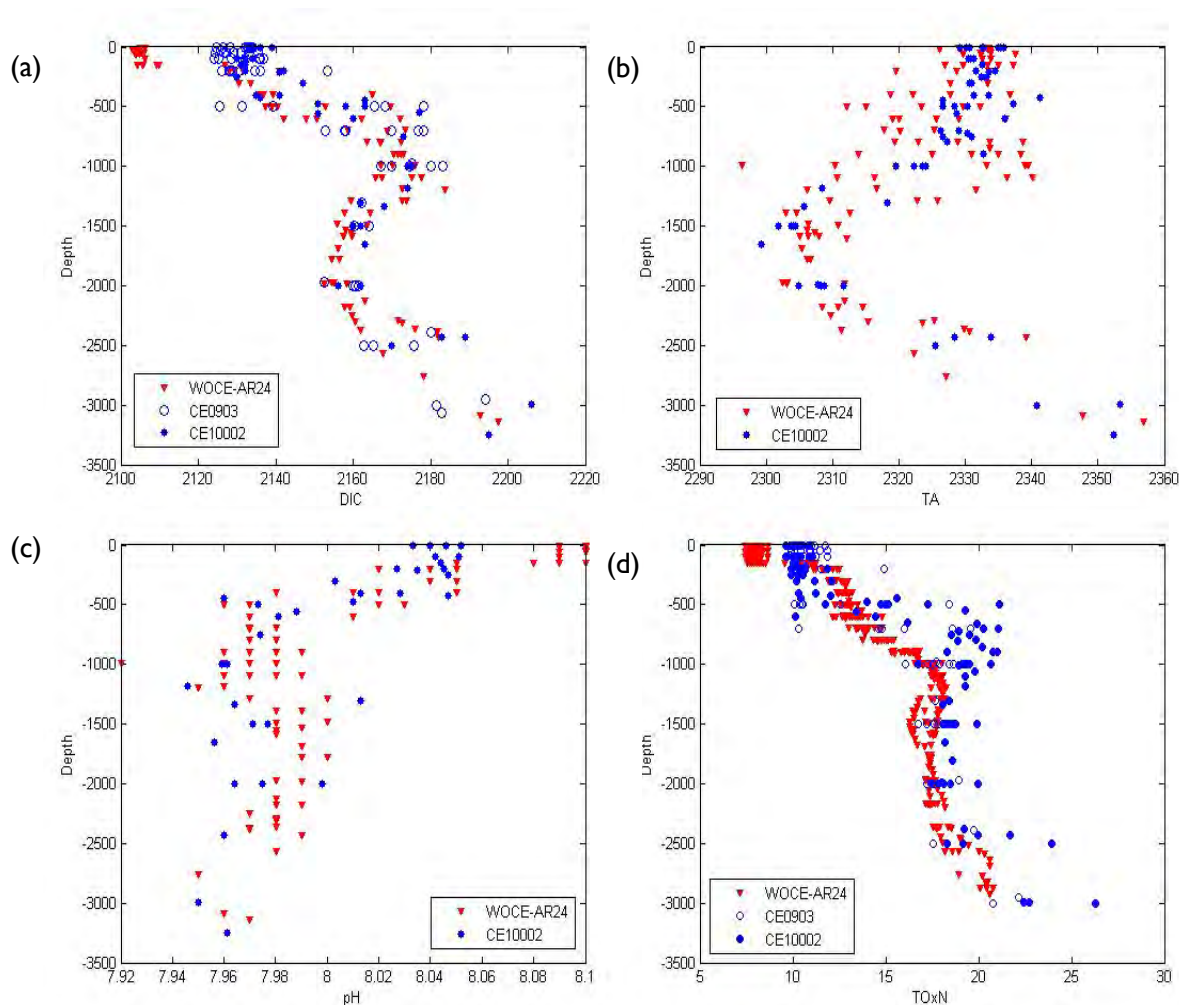
Although T-S properties of this water mass are very different from those of MEDW, both water masses have similar densities and are sometimes found within the same depth range in the Rockall Trough. Between 1500-2000m there is a very clear Labrador Sea Water (LSW) signal, with low salinity (34.9) and temperature (3.5°C), similar to source water properties. The deepest section of the Trough is composed of Lower Deep Water (LDW), with some influence from Antarctic Bottom Water (AABW) below it (depths >3000m). Vertical temperature and salinity profiles from 2009 and 2010 indicate a winter mixed layer between 400-500m deep.

Similar water masses were encountered in the 1996 WOCE-AR24 survey; however the winter mixed layer depth was only 200m. The section of the WOCE-AR24 survey compared here was sampled at the end of November 1996, while sampling in 2009 and 2010 took place in February. It is therefore possible that winter mixing was not as strong in November 1996 - at the beginning of the winter - than February 2009/10, where cooler surface temperatures and winter storms would have increased the depth of the winter mixed layer.

#### *Chemistry:*

pH was calculated for both 1996 and 2010 from the DIC and TA results (along with salinity, temperature, pressure, phosphate and silicate) using CO2SYS (van Heuven *et al.*, 2009). 1996 WOCE-AR24 data were taken from the CDIAC database. In the calculations, the seawater pH scale was used, along with constants  $K_1$  &  $K_2$  taken from Mehrback *et al.* (1973), refit by Dickson & Millero (1987), and  $K_{SO_4}$  by Dickson (1993). Note it is important that if comparisons are being made of pH data (and any other calculated parameters) from different sources, that they are calculated using the same methodology (i.e. pH scale and constants).

The overall trend for the DIC profiles is relatively low in surface waters, with a sharp increase below the winter mixed layer down to about 1000m (Figure 3.4a). Values decrease again between 1500 and 2000m, below which they increase to maximum values in the deepest part of Trough. DIC profiles are similar between 1996, 2009 and 2010 surveys below 200m, however the 2009 and 2010 surveys show higher values of DIC in the upper 200m of the water column (Figure 3.4). Vertical TA profiles were also similar in 1996 and 2010, however unlike DIC, surface TA had similar concentrations in both years, with values of 2330  $\mu\text{mol/kg}$  in surface waters down to about 500m (Figure 3.4b). Other than a high TA signal about 1000m in part of the transect, TA decreases with depth, with a TA minimum seen between 1500 and 2000m. Values increase again steadily to 2356  $\mu\text{mol/kg}$  below 3000m. There are many more data points, with more scatter in the WOCE AR24 data than in CE10001 (from 2010).



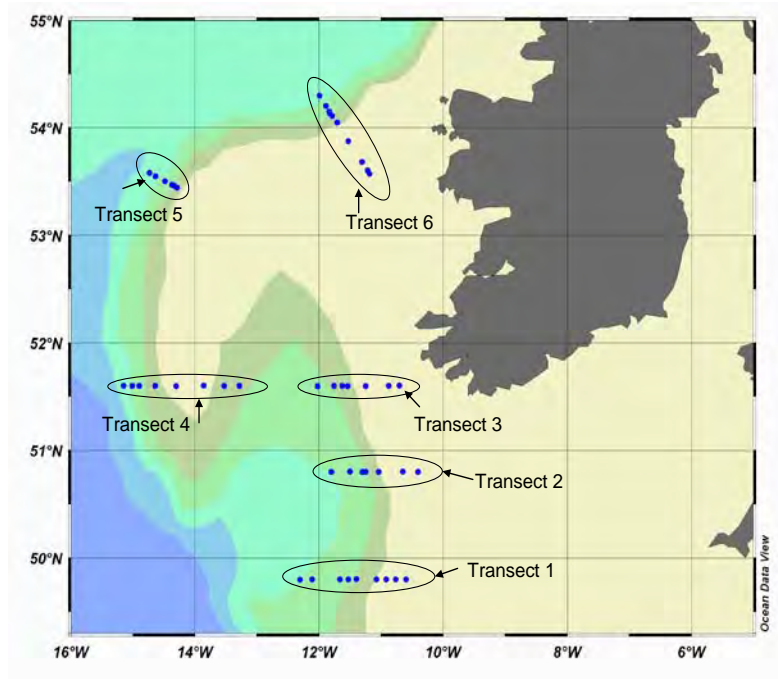
**Figure 3.4:** Vertical profiles of (a) DIC and (b)TA ( $\mu\text{mol/kg}$ ) for winter surveys in southern Rockall Trough in Feb 2009 and 2010, compared with data from WOCE AR24 in Nov 1996. There is considerable scatter in the TA WOCE data compared to the CE10002 data. Comparison of calculated seawater pH (c) and TOxN ( $\mu\text{mol/kg}$ ) (d) from CE10002 with WOCE-AR24. DIC data from the winter surveys in 2009/10 from the southern Rockall Trough are slightly higher than the WOCE data, and the calculated seawater pH is somewhat lower. From McGrath *et al.*, in prep.

The sharp increase in DIC below the winter mixed layer is likely due to remineralisation of organic material below the surface. This increase is also mirrored in the nutrient profiles, particularly TOxN, suggesting biological processes are responsible for this increase. The high TA and DIC signal seen about 1000m is due to the presence of MEDW, which is characteristically high in both TA and DIC. Without the influence of water mass mixing, DIC concentrations should increase down through the water column due to remineralisation. The reduction in DIC (and TA) concentrations between 1500-2000m is due to the presence of LSW, a relatively young water mass that was recently in contact with the atmosphere, and therefore has not been subjected to high levels of remineralisation. On the other hand, the deepest waters of the Trough have very high levels of DIC and TA, due to ageing of these water masses.

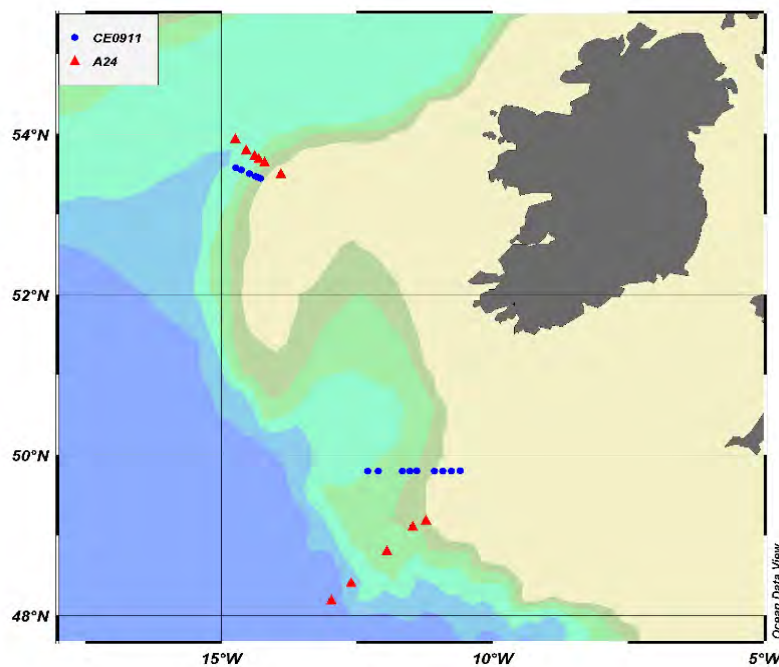
Vertical pH profiles were similar between 1996 and 2010, apart from the top 200m where the pH is very clearly higher in 1996 than in 2010, by up to 0.04 pH units (Figure 3.4c). This higher pH in surface waters in 1996 is most likely due to the lower DIC in those waters (Figure 3.4), since the pH is calculated from the DIC and TA data (and surface TA values are similar in both years). Ocean acidification in surface waters, due to increasing atmospheric CO<sub>2</sub>, acts to increase DIC in surface waters of the ocean, with a subsequent decrease in surface pH. The reduction in ocean pH of up to 0.04 pH units in 2010 relative to 1996 is in line with the IPCC's observed decline of 0.02 pH units per decade (IPCC 2010). However, the vertical profile of TOxN with depth between 1996 and 2009/10 (Figure 3.4d) indicates that TOxN was also lower in 1996 in the top 200m relative to 2009/10, which would suggest that there was more biological activity in the surface waters in 1996 relative to 2009/10. As mentioned previously, the winter mixed layer in 1996 was only down to 200m, much shallower than the winter mixed layer of 2009/10 (400-500m), which is likely due to the difference in time of sampling between cruises. The lower DIC and TOxN in surface waters of WOCE-AR24 suggests that early stages of winter mixing had only begun to break down the seasonal thermocline, and so there may still be some biological activity in 1996 relative to 2009/10. It is therefore difficult to determine any strong evidence of ocean acidification in surface waters due to the sampling dates being at either end of the winter season and the consequent difference in mixed layer depths.

### **3.3.2 Summer data - outer shelf and Rockall Trough**

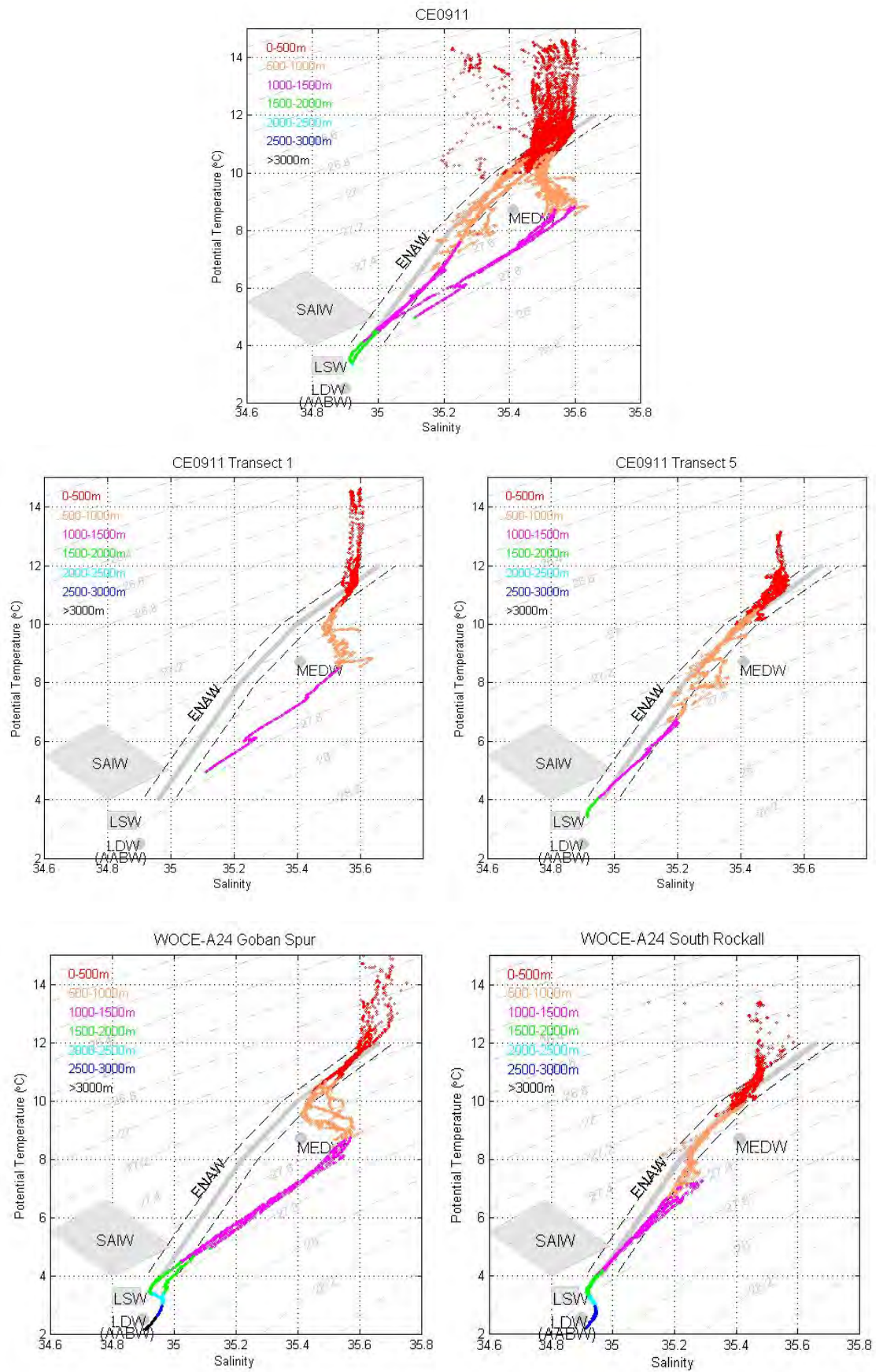
Survey CE0911 was carried out in June 2009, and sampled the western Irish shelf along the edges of both the Porcupine Sea Bight and the Rockall Trough (Figure 3.5), reaching depths of 2000m. WOCE carried out a survey in the same area in May 1997. In this report Transect 1 from CE0911 is compared to the eastern edge of A24's Goban Spur transect, while transect 5 from CE0911 is compared to the eastern edge of A24's South Rockall transect (Figure 3.6). It is important to remember when comparing the transects in the Goban Spur region, that they cover different geographical areas, and may therefore be subjected to different physical conditions. Figure 3.7 shows the TS profiles for the entire CE0911 survey and also for the sections of CE0911 and WOCE A24 transects that have been compared here.



**Figure 3.5:** Transects across the shelf carried out in June 2009, during CE0911. This survey did not cross the Rockall Trough, but sampled along its eastern edge, reaching maximum depths of 2000m.



**Figure 3.6:** Transect 1 (south) and 5 (north) from CE0911, with the corresponding stations from WOCE A24. The WOCE transects carried on across the Goban Spur and Rockall Trough.



**Figure 3.7:** TS profiles for CE0911 (June 2009, all transects), and sections of transects from CE0911 and WOCE A24 (May 1997) for S. Rockall and Goban Spur that are discussed in this section.. From McGrath *et al.*, in prep.

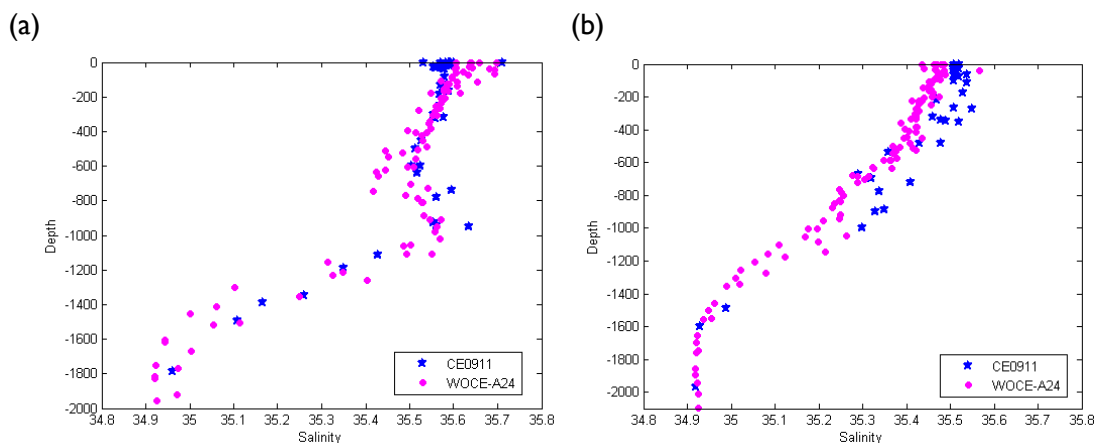


*Physics:*

During CE0911, most of the top 500m have temperatures above the ENAW limits. The data between 500 and 1000m either falls within the ENAW range, or tends towards MEDW (Figure 3.7). A strong MEDW signal at about 1000m is seen in the southern transects, with properties closer to the source water (salinity 36.5, temperature 11-12°C) than the MEDW seen at the southern entrance to the Rockall Trough. Farther north along the shelf edge, the deeper waters (to 2000m) are composed of mostly LSW, with low salinity (34.9) and temperature (3.5°C). There are no points below 2000m in CE0911. The dissolved oxygen profile supports the  $\theta$ -S diagram, with high oxygen in surface waters in contact with the atmosphere, low oxygen concentration in the MEDW, and very high oxygen content of the LSW.

In the South Rockall transect of WOCE A24, apart from high temperature surface waters, much of the top 1000m is made up of ENAW (Figure 3.7). Salinity and temperature decrease down to 1500m, where there is a strong LSW signal between 1500 and 2000m, while the bottom water is comprised of LDW and AABW. There is a similar profile in the WOCE-A24 Goban Spur transect, except that there is also a very strong MEDW signal about 1000m. It is clear that the WOCE-A24 Goban Spur transect covers a different geographical area, as the deeper water masses (LSW and LDW) are seen, there is also more variability in the profile, particularly in the 500-1000m depth range. It is important to remember this when comparing the chemistry of these transects. The southern Rockall transects are more comparable geographically, however there are still some differences in the 500-1000m depth range.

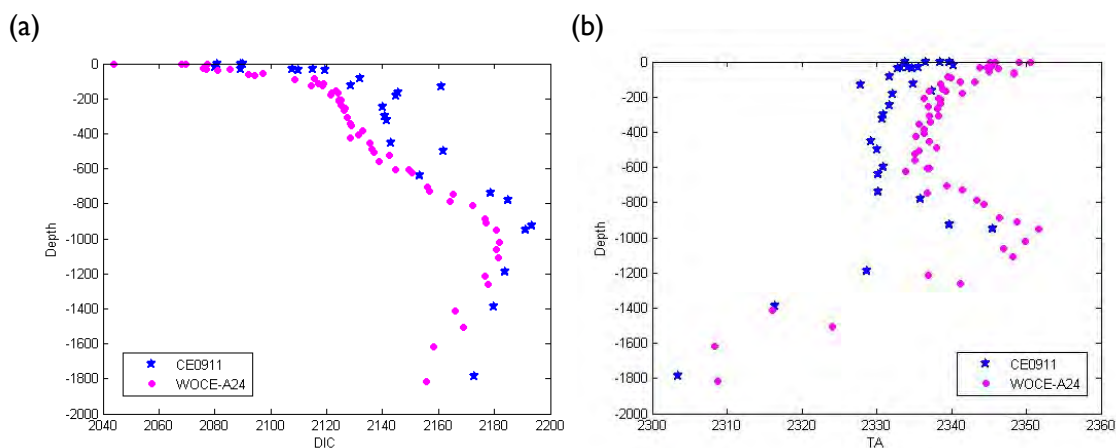
A comparison of the salinity–depth profiles for the CE0911 and WOCE A24 surveys is shown in Figure 3.8. Higher salinities were seen in surface waters of the southern (Goban Spur, Figure 3.8a) transect in 1997. There is a larger scatter of salinity in the WOCE A24 profile as it covers a larger geographical area and has more data points than transect 1 of CE0911. In the southern Rockall Trough region, the salinity is very clearly lower in 2009 relative to 1997, all the way down to 1000m. This is most likely due to differences in physical mixing between the years. This should be kept in mind when comparing the chemistry profiles of these 2 transects.



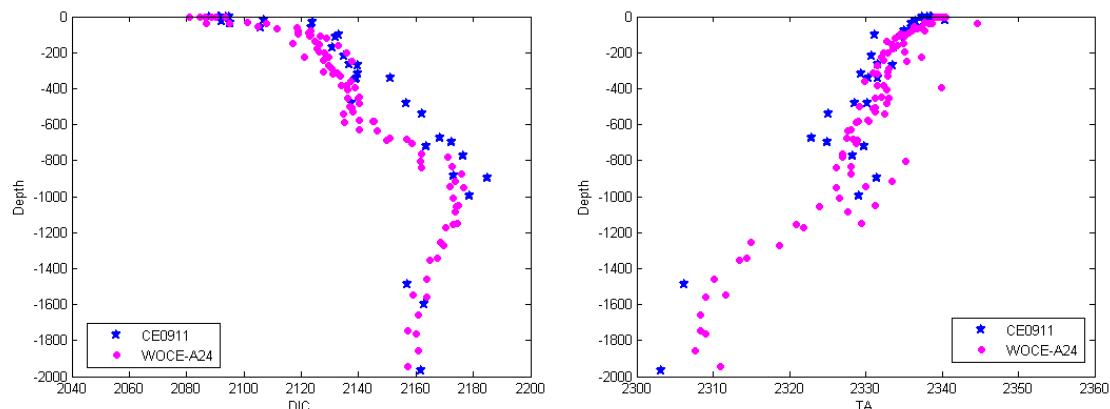
**Figure 3.8:** Comparison of salinity with depth for (a) the southern transects (Goban Spur area), and (b) the northern transects (southern Rockall Trough area), for CE0911 and WOCE A24. Mediterranean water can be clearly seen around 1000m in the southern transect in both surveys, but is not observed further north.

**Chemistry:**

The DIC and TA from the two summer surveys (CE0911 in June 2009, A24 in May 1997) are shown in Figure 3.9 and 3.10. The overall profile shows that DIC is very low in surface waters in both CE0911 and WOCE A24, reaching nearly 2060  $\mu\text{mol/kg}$ . Concentrations increase below the summer thermocline ( $\sim 30\text{m}$ ), and have an average concentration of 2145  $\mu\text{mol/kg}$  between 100 and 500m in 2009. DIC generally increases with depth, with a spike in the profile about 1000m in the MEDW region, where DIC is higher than the surrounding water column. TA on the other hand is high in surface waters and decreases with depth, apart from a sharp increase in TA in the MEDW region reaching 2346  $\mu\text{mol/kg}$ .



**Figure 3.9:** (a) DIC and (b) TA with depth for the southern transects (Goban Spur area), for CE0911 and WOCE A24.



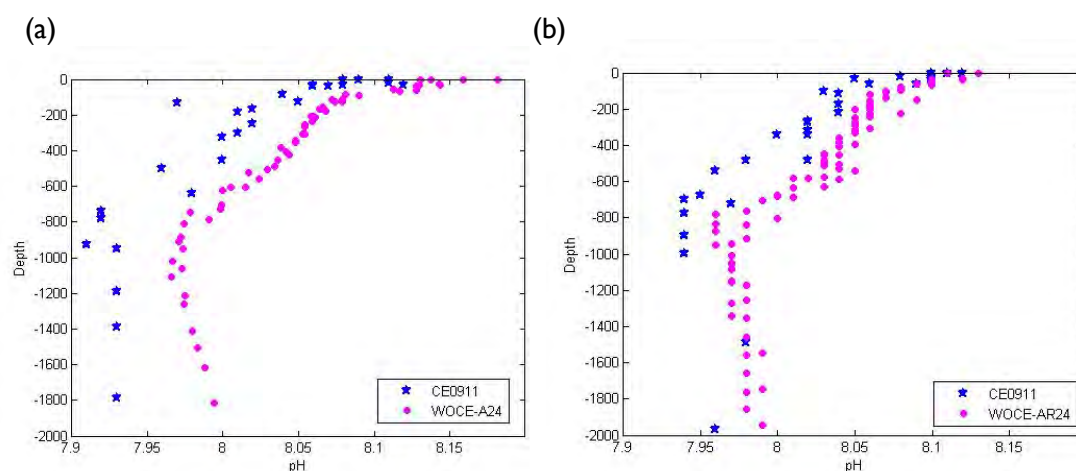
**Figure 3.10:** (a) DIC and (b) TA with depth for the northern transects (southern Rockall Trough area), for CE0911 and WOCE A24.

In the Goban Spur area, while the patterns of changing DIC and TA with depth are very similar, it is clear that, apart from water right at the surface, in waters above 1000m, the DIC from June 2009 is noticeably higher than in May 1997, and the TA is lower. Below this depth, although the difference is less marked there are very few CE0911 data points to compare with the WOCE transect. In the southern Rockall Trough region, DIC is higher in 2009 than in 1997 between 400m and 1000m, however the difference is less obvious than in the Goban Spur region. The TA of 2009 appears slightly lower between 400 and 700m, however this is only for a few data points.

The low DIC in surface waters in 1997 and 2009 is likely due to biological activity in the summer months, which acts to decrease DIC (and dissolved inorganic nutrients) in the surface sunlit layer of the ocean. Below the summer thermocline (~30m), DIC increases rapidly due to remineralisation of falling detritus or organic matter out of the euphotic zone. The sharp increase in TA and DIC, particularly seen in the Goban Spur region is due to the presence of MEDW, which is typically high in both DIC and TA.

In the Goban spur region, the higher DIC and lower TA seen in 2009 from below the thermocline down to 1000m could be due to physical factors since there were some differences in temperature and salinity profiles in the top 1000m. Likewise, in the southern Rockall Trough region, although less marked than the Goban spur area, the higher DIC and lower TA between 400 and 1000m may also be due to physical factors, since the vertical profile of salinity with depth for these transects, indicates that salinity is clearly lower right down to 1000m in 2009 relative to 1997. As seen in winter, there is a decrease in DIC and TA in both cruises due to the presence of LSW, however there are few data points below 1500m to compare this water mass between years.

Measurable differences are seen in the pH, calculated from the DIC and TA, for the 1997 and 2009 summer surveys, with pH consistently lower by about 0.04 pH units in 2009 in the Goban Spur area, and lower by about 0.02 pH units in the southern Rockall Trough.



**Figure 3.11:** Comparison of pH (calculated from TA and DIC) with depth, for (a) the southern transects (Goban Spur area), and (b) the northern transects (southern Rockall Trough area), for CE0911 and WOCE A24.

In the winter comparison, any clear evidence of ocean acidification is difficult to determine due to other processes affecting DIC in the water column (i.e. the degree of winter mixing). We cannot compare the surface waters of the summer cruises either due to strong biological activity during this time of year, which alters the carbon chemistry in the surface layer. If the decrease in pH down to 1000m seen in the summer transects was simply due to ocean acidification, we would only expect to see higher levels of DIC while the TA concentration would not be affected. However, the lower pH in 2009 is due to both higher DIC AND lower TA suggesting other processes are the primary cause for this difference. Here, the lower pH is most likely due in part to physical factors – indicated by some differences in the TS profiles of the 2 surveys.

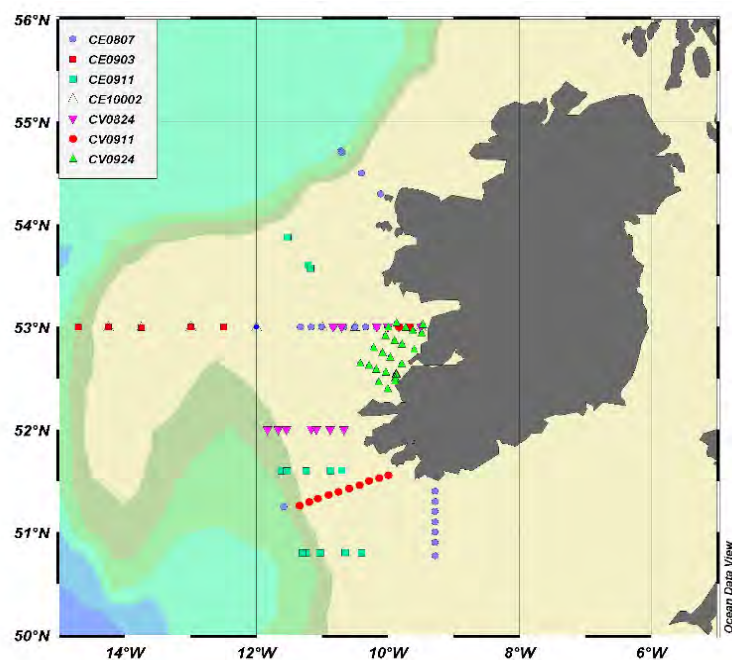
### 3.3.3 Comparison between winter and summer data

Although the areas sampled in summer and winter are not directly comparable – they have very different geographical spread, with much more localised shelf edge sampling in summer – strong seasonal variation can be seen between the surveys. There are large differences between surface waters of the winter and summer surveys, particularly in DIC profiles. Average DIC concentration in the top 5m across the Rockall Trough in Feb 2009 was 2131  $\mu\text{mol}/\text{kg}$ , while average surface values (top 5m) for the June CE0911 cruise was 2089  $\mu\text{mol}/\text{kg}$ . This is most likely due to biological activity during the spring and summer months, which takes up dissolved inorganic carbon and nutrients from the surface layer. In June, CTD measurements show a shallow summer thermocline (30-50m), which is reflected in a sharp increase in DIC below this layer. In February, winter mixing has broken down any seasonal

thermocline, and so DIC remains almost constant down to the base of the winter mixed layer, which can be over 500m in the Rockall Trough.

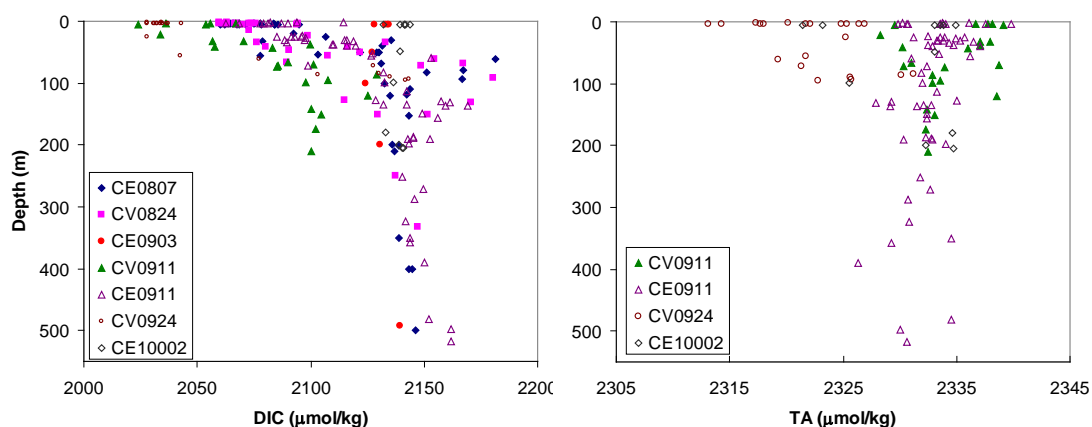
### 3.3.4 Coastal and inner shelf data

Seven of the 8 surveys took samples on the inner shelf and in coastal waters (Figure 3.12). Inner shelf and coastal surveys were carried out in May and September, during the main phytoplankton growth seasons, however stations along the 53°N line were also sampled in winter.



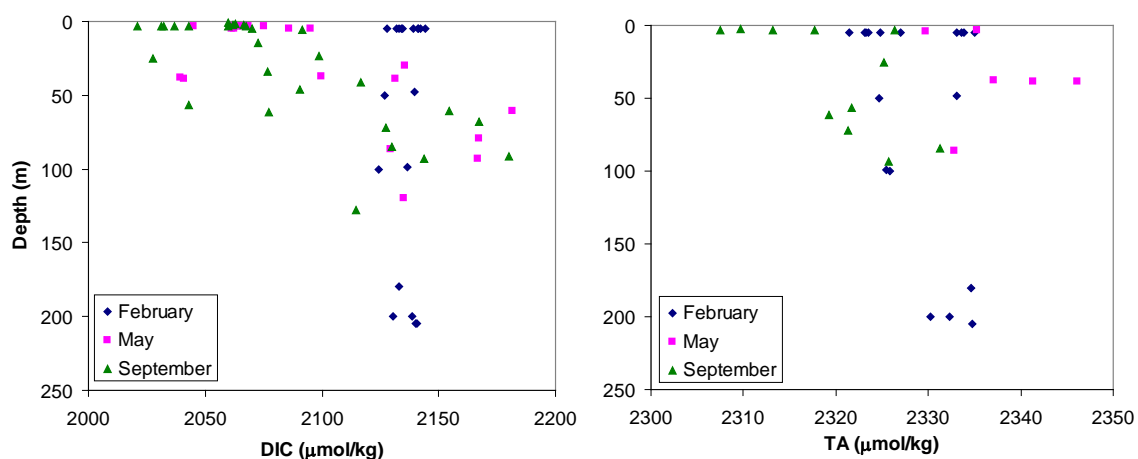
**Figure 3.12:** Map of inner shelf and coastal stations occupied. Not all of these were sampled for TA / DIC.

The full range of TA and DIC values encountered in coastal and inner shelf waters can be seen in Figure 3.13. DIC in surface waters varies from 2030 to 2150  $\mu\text{mol/kg}$ , with the highest values in winter and the lowest in early Autumn, around the period of the Autumn bloom. Surface TA ranges from 2315 to 2340  $\mu\text{mol/kg}$ .



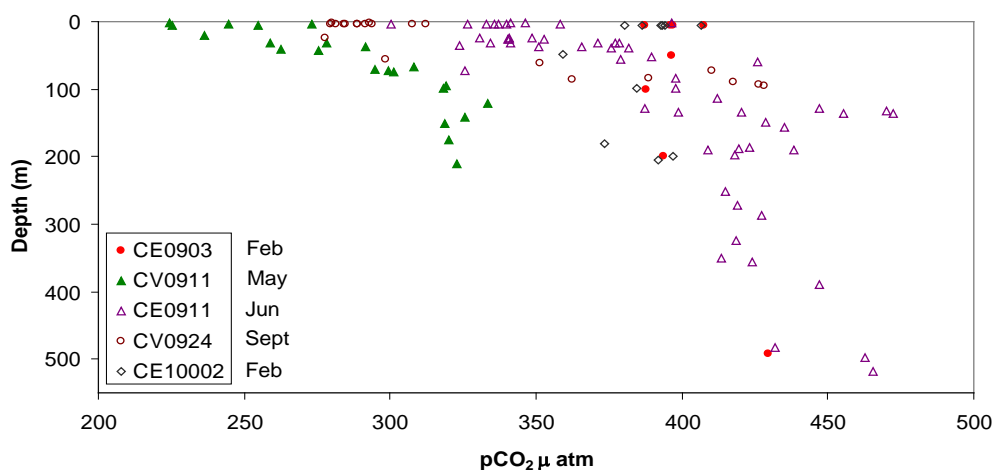
**Figure 3.13:** DIC and TA for all coastal stations with salinity > 34.5, showing the range encountered in coastal waters at different seasons. From Kivimäe *et al.*, in prep.

The seasonal variability of DIC and TA in inner shelf waters can be seen in Figure 3.14. The water column is well mixed for these parameters, particularly for DIC, in February, but shows low DIC at the surface in Spring and early Autumn, increasing down through the mixed layer and reaching a maximum below the mixed layer, between 50m and 100m.



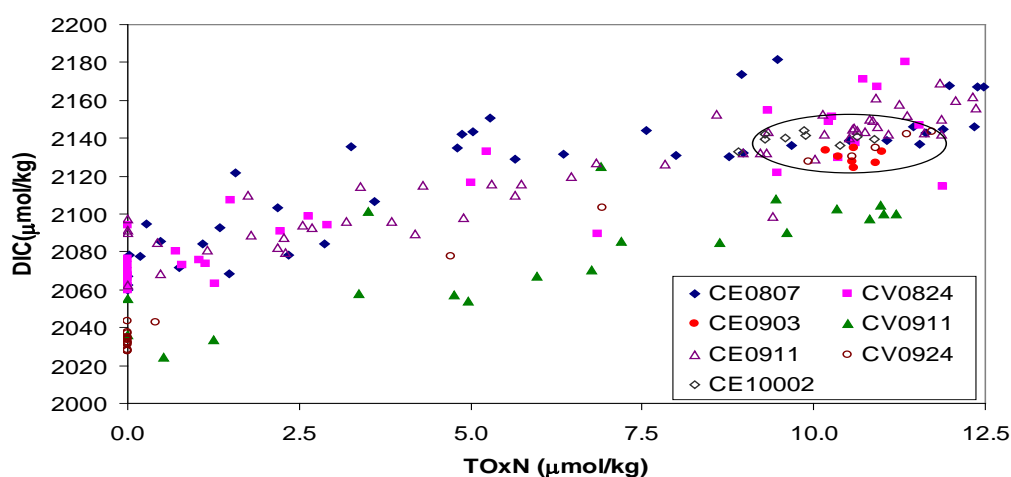
**Figure 3.14:** Seasonal data for the inner shelf, 53°N line. The deep mixing of the water column can be clearly seen in the February data for DIC, compared to the May and September data, but is less obvious for TA. February samples are from CE10002 and CE0903, May samples are from CE0807 and CV0911, and September samples are from CV0824 and CV0924. From Kivimäe *et al.*, in prep.

pCO<sub>2</sub> has been calculated using CO2SYS for the inner shelf stations where both TA and DIC data are available (Figure 3.15). The lowest surface pCO<sub>2</sub> is observed in early May (CV0911), likely associated with the Spring bloom, and the highest in Feb. 2009 and 2010 (CE0903 and CE10002). The June (CE0911) and September (CV0924) data sets fall between these two, and again the low surface values are associated with phytoplankton activity. For the May, June and September data, the pCO<sub>2</sub> increases rapidly down through the water column, reaching a maximum below the surface mixed layer, at about 150m, associated with respiration/decomposition.



**Figure 3.15:**  $p\text{CO}_2$  on the inner shelf calculated from TA and DIC measurements. From Kivimae *et al.*, in prep.

The relationships between DIC and dissolved inorganic nitrogen, in the form of nitrite+nitrate or ToxN, are plotted in Figure 3.16. Data from the two winter surveys, CE0903 (Feb 2009) and CE10002 (Feb 2010), are closely clustered, showing the well mixed nature of the water column in winter, with high nutrients throughout (samples go from surface to > 200m) and a small range of DIC. Late Spring /early summer samples (CE0807, late May 2008 and CV0911, early May 2009) represent depths from surface to 120m, and show nutrient concentrations generally increasing with DIC. Nutrients tend to be depleted at the surface in May and also tend to increase with depth and salinity. The trend for early September samples (CV0824 and CV0924, from surface to 130m), when productivity is expected to be increasing after the summer, is similar to this, and lies between the two sets of May data.



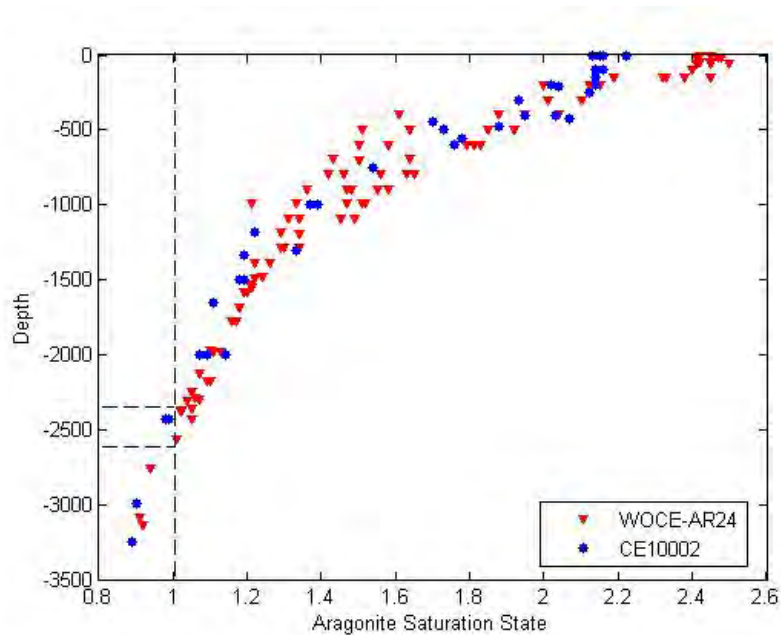
**Figure 3.16:** Relationships between DIC and nitrite+nitrate (ToxN) on the inner shelf and coastal regions. The ellipse encompasses all the winter data from CE0903 (Feb 2009) and CE10002 (Feb 2010). CE0807 (late May 2008) and CV0911 (early May 2009) form the upper and lower limits of the plot, with data from Sept 2008 (CV0824) and Sept 2009 (CV0924) falling between the two May trends. From Kivimae *et al.*, in prep.

### 3.4 Calcite and Aragonite Saturation State

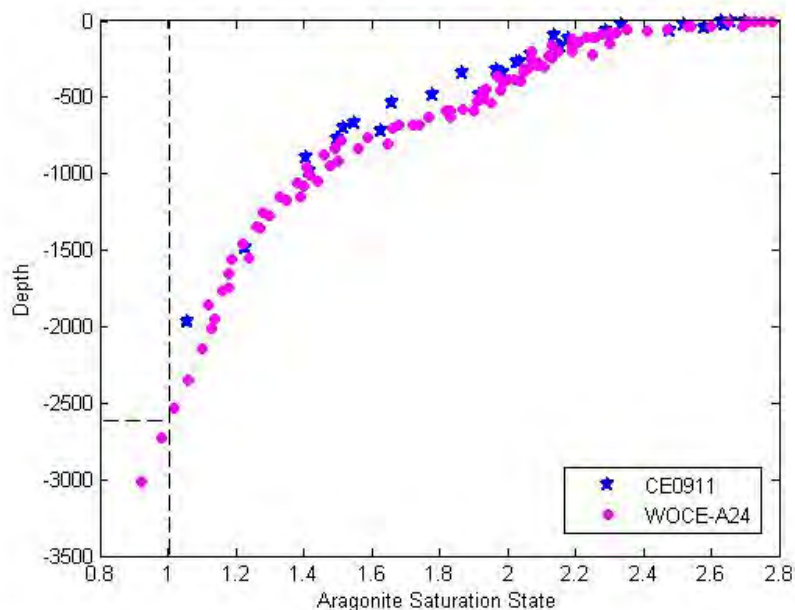
A key indicator of climate-change induced stress in ocean systems is a change in the calcite and/or aragonite saturation state. Many organisms depend on calcium carbonate to generate their hard parts, and secrete either the aragonite or calcite form, depending on the species. Any decrease in the saturation state will have implications for the amount of energy a given organism has to expend in order to produce its hard parts. The Saturation Horizon refers to the water depth below which calcite (CSH) or aragonite (ASH) is under-saturated, meaning that the hard parts of organisms which secrete calcite or aragonite will begin to dissolve (if the organism is dead) or will require very high energy expenditure to maintain (if the organism is living). The N. Atlantic is generally saturated with calcite throughout the water column, with few regions deep enough to be below the CSH, which reaches > 4000m. The ASH is generally much shallower than the CSH and many organisms which depend on calcium carbonate to generate their hard parts choose the aragonite form, including the cold water corals whose mounds dominate the slopes of the Irish continental shelf (de Mol *et al.*, 2002).

The area below the ASH is known as the lysocline, and the base of the lysocline is the aragonite compensation depth (ACD), at which depth all aragonite will be dissolved. Calculation of the ACD is not straightforward, so oceanographers tend to use the ASH (saturation state = 1) instead. Below the ASH aragonite is under-saturated and will begin to dissolve. The calcite and aragonite saturation states were calculated using CO2SYS (van Heuven *et al.*, 2009) for samples from the deep water surveys collected during the project, and compared with data from WOCE cruises A24 and AR24. The CSH as expected was not reached on any of the cruises, with calcite saturation values of 4 to 5 in surface waters going down to ~1.5 at 3000m. The ASH however was found at depths of ~2500m and is illustrated here. The winter data from the southern Rockall Trough is shown in Figure 3.17, and indicates an ASH of around 2500m, with similar values in both 1996 and 2010. The WOCE summer data from the same area, shown in Figure 3.18, indicate a similar ASH to the winter depth. Samples from the summer of 2009 do not go deeper than 2000m and do not reach the ASH.





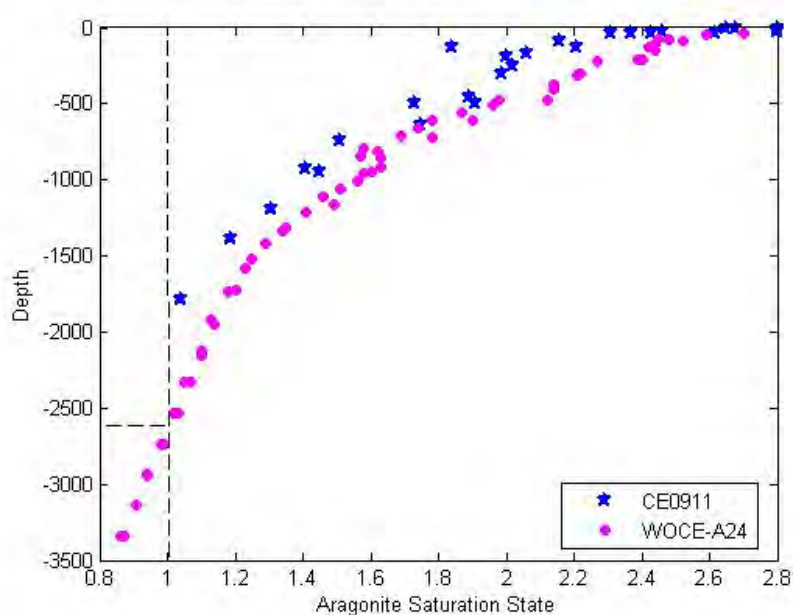
**Figure 3.17:** The aragonite saturation state for the water column sampled during CE10002 (Feb. 2010) and WOCE AR24 (Nov. 1996) in the southern Rockall Trough. The ASH occurs at saturation state =1, shown by the vertical dashed line, and appears to occur around 2500m in both surveys. See Figure 3.2 for the location of these transects. From McGrath *et al.*, in prep.



**Figure 3.18:** The aragonite saturation state for the water column sampled during CE0911 (summer 2009) and WOCE A24 (summer 1997) in the southern Rockall Trough. The WOCE data indicate an ASH (saturation state =1) in 1997 of just below 2500m, similar to the winter data. The samples from CE0911 do not reach the ASH. See Figure 3.6 for the location of these transects. From McGrath *et al.*, in prep.

Data from the Goban Spur region from summer 2009 and summer 1997 are shown in Figure 3.19. Here the ASH is just below 2500m in 1997, similar to the ASH calculated for the southern Rockall Trough sampled on the same survey. However, while the summer 2009

samples for this area do not go below 1800m, there is a clear trend in the samples above this depth which indicates the ASH may now be at or above 2000m, some 500-600m shallower than in 1997. Although the saturation state for most of the water column in this area is lower in 2009 than in 1997, it is important to remember that the geographical area differs for these two transects, and as was mentioned previously, temperature and salinity profiles differ between 1997 and 2009 suggesting this lower saturation state is likely related in part to changes in water mass mixing. It is therefore very important that the physical oceanography is well understood before drawing conclusions from differences between surveys.



**Figure 3.19:** The aragonite saturation state for the water column sampled during CE0911 (summer 2009) and WOCE A24 (summer 1997) in the Porcupine Sea Bight north of the Goban Spur. Samples from 1997 indicate an ASH (saturation state = 1) just below 2500m, similar to that found in the southern Rockall Trough on the same survey. However, the trend in the 2009 data indicate the present-day ASH is above 2000m, possibly as shallow as 1800m, in this area. See Figure 3.6 for the location of these transects. From McGrath *et al.*, in prep.

The main cold water coral occurrences in the N. Atlantic are at depths shallower than 1000m (e.g. de Mol *et al.*, 2002). Coral mounds are found at depths down to 1000m in the southern Rockall Trough (e.g. Guinan *et al.*, 2009) and the Porcupine Sea Bight north of the Goban Spur (e.g. Dolan *et al.*, 2008). This is some 1500m above the present depth calculated for the ASH in the southern Rockall Trough, and ~1000m above the ASH in the Porcupine Sea Bight. These results merit further investigation to establish if the conditions seen in June 2009 were only short term, or whether the habitats along the Porcupine Sea Bight will be subjected to a lower aragonite saturation state in the long-term. This emphasises the importance of continued monitoring of the carbonate system off the Irish continental shelf.

### 3.5 Activity synthesis

Surveys covering the waters off western Ireland from coast to the outer shelf and into the Rockall Trough have been carried out, with sampling and analysis of surface and deeper waters across seasons and years. Baseline data for ocean acidification parameters have been produced and assessed, providing a yardstick against which future measurements for carbonate parameters in Irish waters may be compared. This dataset will also provide the wider oceanographic and climate research community with valuable information on the status of surface and deep water masses off the Irish shelf. Samples collected in the Rockall Trough and Goban Spur areas have been compared with data gathered in 1996/97 on WOCE surveys. A first glance at the carbonate results indicates that waters down to 200m on the outer shelf and Rockall Trough in winter are more acidic than those sampled during a WOCE survey in 1996, by 0.02 to 0.04 pH units. However, salinity and TOxN profiles suggest that the lower DIC seen in 1996 relative to 2009/10 (which has resulted in the lower pH) is at least in part due to higher levels of biological activity in November 1996, where winter mixing has not yet fully broken down the seasonal thermocline. Likewise, a comparison of summer data has indicated differences in DIC, TA and consequently pH that may be attributable in part to differences in physical oceanographic conditions of the water sampled. Calculations of the aragonite saturation state indicate that the ASH was found at depths of ~2500m, with little or no change observed between 1996 and 2010 in the southern Rockall Trough. However, the saturation state in the Porcupine Sea Bight north of the Goban Spur is lower throughout the water column in 2009 than in 1997, and the aragonite saturation horizon (ASH) appears to be shallower by several hundred metres. This may, however be due to physical factors, such as difference in geographical spread of sampling points and water mass mixing. Overall, the results illustrate the complexity of the carbonate system, and highlight the importance of a clear understanding of the physical and biological processes occurring in the study region. The results emphasise the importance of continued, integrated monitoring of the carbonate system alongside other oceanographic parameters in Irish coastal and deep waters.

## 4. CO<sub>2</sub> FLUX QUANTIFICATION AND SEASONAL PROCESSES IN IRISH SHELF WATERS

### 4.1 Aims and Overview of Outcomes

This activity centered on three elements: (1) to analyze the coastal buoy pCO<sub>2</sub> data for seasonal trends; (2) to integrate year-long buoy pCO<sub>2</sub> data at Mace Head with the Mace Head CO<sub>2</sub> flux data and to explore the seasonality in both CO<sub>2</sub> flux and the gas transfer coefficient; and (3) to develop and apply techniques to derive CO<sub>2</sub> fluxes from instruments mounted on the Celtic Explorer. Seasonal trends were observed in both pCO<sub>2</sub> trends from the Mace Head buoy along with seasonal trends in CO<sub>2</sub> flux with a maximum occurring in the winter season. The peak in CO<sub>2</sub> flux during winter was surprising as it was expected to occur during spring/summer periods when marine productivity was highest. However, the pattern can be also be explained by higher wind speeds and lower water temperatures combined with increased shoaling effects in the shallow coastal waters, all of which increase the air-to-sea flux of CO<sub>2</sub>. There were insufficient data, due to extensive quality control procedures, combined with a low occurrence of overlapping pCO<sub>2</sub> data with tower flux data, to build up an extensive gas-transfer velocity – wind speed relationship let alone explore the seasonality in this relationship. In any event, the data gathered illustrated that coastal CO<sub>2</sub> fluxes, and the associated transfer velocity, were significantly higher than those previously reported over the open ocean.

#### 4.1.1 Seasonality in Coastal pCO<sub>2</sub>

The seasonality in pCO<sub>2</sub> concentrations was shown in Figure 4.1 from November 10<sup>th</sup> 2008 to November 30<sup>th</sup> 2009. Minimum concentrations are seen in wintertime while peak concentrations are seen in summer. It was, however, difficult to see a clear seasonal pattern as there were periods during which large spikes in concentration were observed as discussed in Chapter 1.

The inter-relationship between seawater pCO<sub>2</sub> levels and seawater temperature was also explored and is shown in Figure 4.1. A relationship in the form of  $Seawater\ pCO_2\ Level = 276 + 14.4(SST)$ , with a correlation coefficient of 0.298 was found. While the general trend of increasing pCO<sub>2</sub> with sea surface temperatures is seen for the year long dataset, there are many periods where pCO<sub>2</sub> appears independent of sea surface temperature.

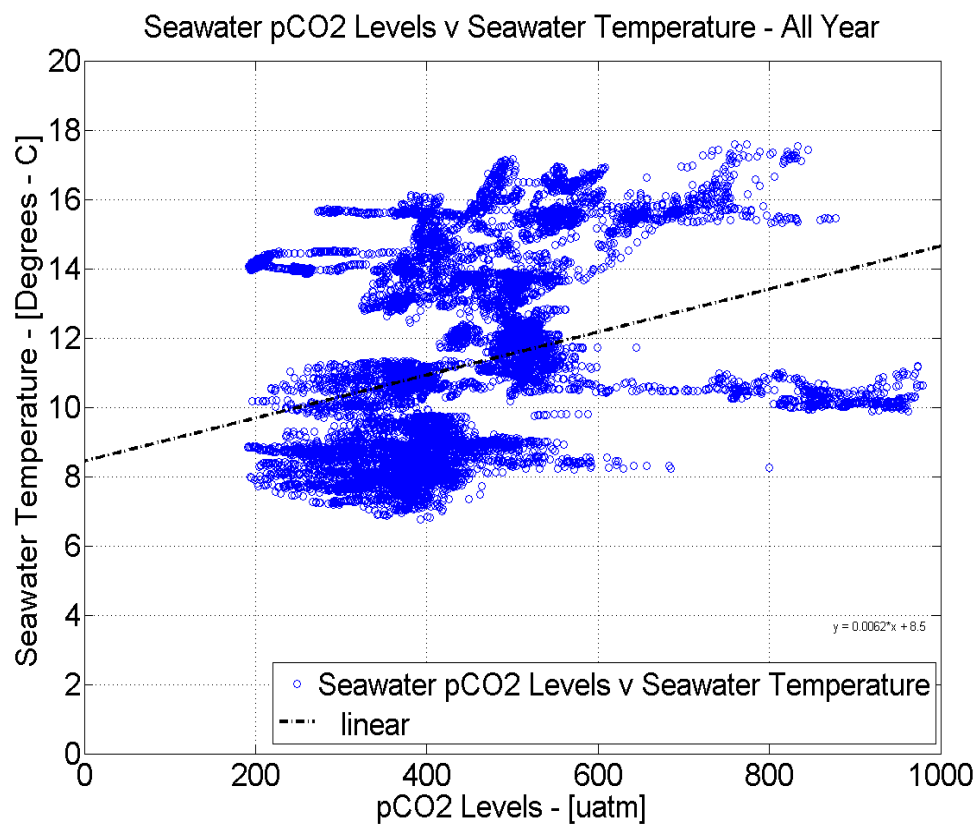
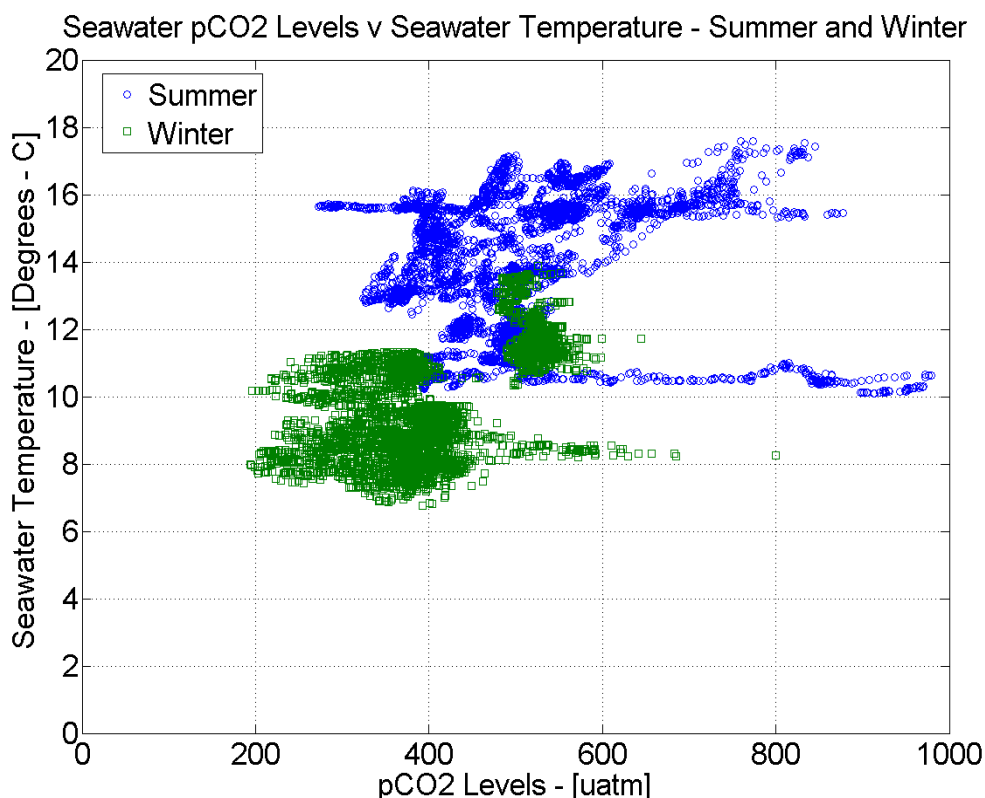


Figure 4.1: Seawater pCO<sub>2</sub> Levels v Sea Surface Temperature

There is a weak positive correlation between each of the two variables. The high pCO<sub>2</sub> levels observed between 10 – 11°C occurred during one of the “spikes” in seawater pCO<sub>2</sub> levels.

In Figure 4.2, the relationship between seawater pCO<sub>2</sub> levels and sea surface temperature, separated by summer and winter seasons, is plotted.



**Figure 4.2:** Seawater pCO<sub>2</sub> Levels v Sea Surface Temperature – Summer and Winter

For summer, the following regression equation was found:  $\text{Seawater } p\text{CO}_2 \text{ Level} = 478 + 2.35(\text{SST})$  with a correlation coefficient of 0.03 and for winter, the following regression equation was found:  $\text{Seawater } p\text{CO}_2 \text{ Level} = 139 + 27(\text{SST})$  with a correlation coefficient of 0.514. There is virtually no correlation between seawater pCO<sub>2</sub> levels and sea surface temperature during the summer months. This is no surprise, as seawater pCO<sub>2</sub> levels were highly variable during the summer months. A better correlation exists between the two variables during the winter months.

From Figure 4.2, it is clear that during the winter months, the majority of lower seawater pCO<sub>2</sub> levels were observed with lower seawater temperatures. The opposite occurs during the summer months: higher seawater pCO<sub>2</sub> levels accompanied by higher water temperatures.

## 4.2 Coastal CO<sub>2</sub> Fluxes

### 4.2.1 Experimental

From August 2006 until February 2009, a CO<sub>2</sub> flux package was deployed on a 22 m tower at the Mace Head atmospheric research station, on the west coast of Ireland adjacent to the N.E. Atlantic (53°20'N, 9°54'W). The local climate at the station is temperate, and is subjected to clean marine air for approximately 60 % of the time (Jennings *et al.*, 2003) due to prevailing westerly winds at an average speed of ~7-8 ms<sup>-1</sup>. The shoreline in front of the 22 m tower is inhomogeneous, rocky and slanted, with a tidal region that extends from 80 m to 180 m away from base of the tower.

Previous flux-footprint (Geever *et al.*, 2005) and micro-meteorological analysis (Kunz *et al.*, 2000) under clean air mass conditions indicated that fluxes representative of open ocean conditions could be derived from the 22 m tower. Analysis indicated that the peak of the flux-footprint occurred around 1 - 1.5 km away, with contributions extending to 5 km, and that the tidal area contributed to only a minor percentage of the total flux signal (McVeigh, 2010). Water depths within the flux footprint varied between 10 - 33 m, being 18 m where an ocean chemistry data buoy was moored 2 km west of the flux tower. This buoy was deployed in July 2008, and housed a suite of instruments including a Pro-Oceanus system, which provided measurements of water partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>).

The flux package comprised a Gill R3 sonic anemometer and a Li-COR LI-7500 open path CO<sub>2</sub>/H<sub>2</sub>O sensor, which were logged at 10 Hz. The LI-7500 head was tilted at a slight angle to prevent water build-up on the optical windows, and was co-located with the sonic head on a 3 m pole extending westward into the prevailing wind in order to minimize flow distortion. The sonic anemometer was regularly validated through a range of other meteorological sensors at Mace Head, while the LI-7500 was regularly calibrated with a hydrometer and NOAA CO<sub>2</sub> standards at three different concentrations. Tidal and wave forecast data were obtained online. Disruptions to measurements resulted mainly from power cuts or corrosion, and only fluxes for the clean marine air sector combined with periods of no precipitation are reported.

### 4.2.2 Data Analysis

A significant amount of data quality control and filtering was conducted, resulting in a relatively small number of accepted flux values in the database. The data set was initially filtered for clean marine air and then for rainfall – the latter resulting in the single most important factor leading to data rejection. Spikes were removed, time delays from data acquisition were alleviated, and sonic temperatures were corrected for the effects of water vapour fluctuations. Two-

dimensional co-ordinate rotations were performed on sonic data, and running means with a time constant of 5 minutes were calculated over all variables for the purposes of detrending. Covariances were computed and block averaged over 30 minute intervals to produce raw fluxes, from which micrometeorological flux parameters such as Drag Coefficient ( $CD10$ ) and Friction Velocity ( $u^*$ ) could be determined. These were regularly checked to ensure open ocean values and zero land surface contamination. For filtered data,  $u^*$  correlated to a wind speed relation ( $u^* = 0.018 \times U10^{1.32}$ ) with a high correlation coefficient of  $r^2 = 0.97$ .  $CD10$  was linearly correlated to  $u^*$  reaching a maximum of 0.0025 at a wind speed of 18 m s<sup>-1</sup>. Due to instrumental limitations and signal processing techniques, frequency response corrections outlined by Moore, (1986) had to be applied to fluxes of momentum, CO<sub>2</sub> as well as sensible and latent heat. Sensor size, separation, response time and path averaging were mostly responsible for high frequency losses, whereas high pass filtering (detrending) contributed to low frequency losses. The magnitude of frequency response corrections typically amounted to less than 20 % of fluxes.

Data were filtered for an oceanic footprint, near neutral stability, low wind speed variability and proximity to measurements from other instruments. Periods with relative humidities greater than 95 % were also removed as they were too strongly affected by the presence of water vapour (Jacobs *et al.*, 1999). Finally, using forecast wave data (significant wave heights and wave periods at the peak of the wave spectrum), certain wave parameters such as the wavelength, phase velocity, wave age and wave slope were determined for further analysis.

#### 4.2.3 Cross-Sensitivity

Cross-sensitivity (CS) between H<sub>2</sub>O and CO<sub>2</sub> readings from the use of open-path analysers over the ocean have been reported in a number of cases, and arises from the fact that H<sub>2</sub>O fluctuations are much larger than CO<sub>2</sub> fluctuations over the ocean, which has not been accounted for by instrument manufacturers. In the 1996 ASGAMAGE experiment (Jacobs *et al.*, 1999), two types of open-path sensor were used; the Infra-red Fluctuation Meter (IFM-heated optics), and the Oak Ridge sensor (ORS – unheated optics). Both instruments gave  $kCO_2$  values larger than indirect methods, but higher values from the ORS were attributed to humidity effects after Kohsiek (2000) noted a cross-sensitivity to relative humidity in laboratory experiments. Despite heating of the optics,  $kCO_2$  values from the IFM sensor were still a factor of 2 - 3 times larger than indirect techniques. Such effects were inconsistent though, and reasons for its high variability were not clear.



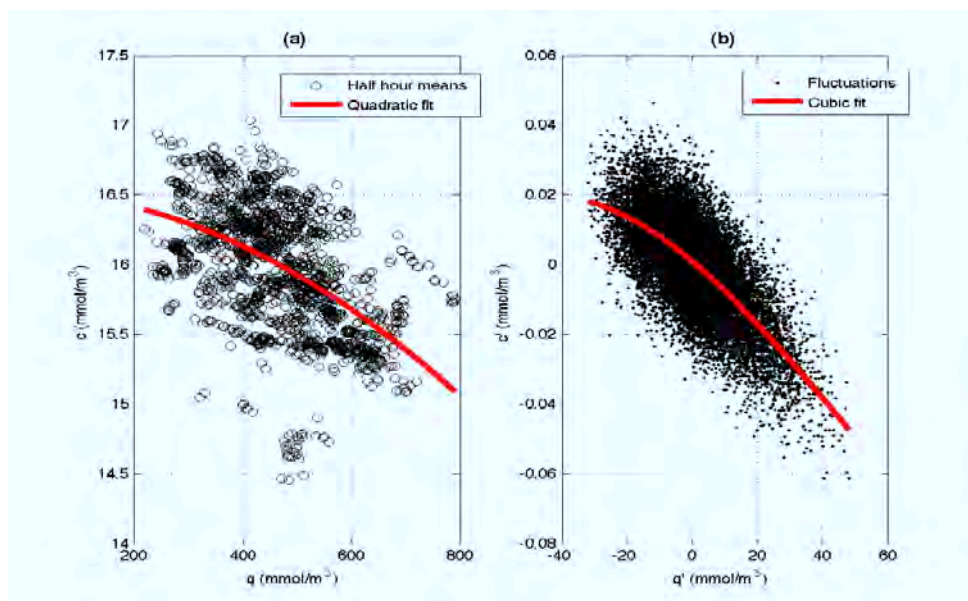
Various possible explanations for CS included; (1) Absorption of light by water vapour in the absorption and/or reference band of CO<sub>2</sub>, (2) Absorption of light at wavelengths well outside the passband of the optical interference filter, (3) Presence of water dimers, and (4) Pressure Broadening. A more plausible reason for the observed interference with CO<sub>2</sub> fluctuations was the presence of liquid water in the optical path, either in the form of small droplets or a film of absorbed water on the optics. Such very thin layers respond quickly to changes in ambient humidity, and were likely to be present on the optics, even if the air wasn't close to saturation. This cross-sensitivity correlation between H<sub>2</sub>O and CO<sub>2</sub> was found to be negative, but hard to quantify.

Similar findings have been reported by Prytherch *et al.* (2010), who suggested that the effect was due to hygroscopic particles, or salt, on the optics of the LI-COR LI-7500. Their CO<sub>2</sub> fluxes were typically 10 times higher than would be expected using accepted values for transfer velocities. A method to correct for such effects was developed (termed the “PKT method”), which involved removing the trend between the negatively correlated relative humidity and CO<sub>2</sub> mixing ratios using a 3rd order polynomial fit. The resulting CO<sub>2</sub> fluxes were then adjusted to expected values based on the assumption that the dimensionless vertical profiles of relative humidity and CO<sub>2</sub> are equal.

In this investigation, a similar unpredictable cross-sensitivity between H<sub>2</sub>O ( $q$ ) and CO<sub>2</sub> ( $c$ ) with a negative correlation was observed, as shown in Figure 4.3(a), which displays all half hour periods recorded from an oceanic wind sector. Operation of the LI-7500 is based on the principle that CO<sub>2</sub> and H<sub>2</sub>O have different infra-red absorption bands, which are centered at 4.26 $\mu$ m and 2.59 $\mu$ m respectively. However, it suffers from CS due to imperfections in the frequency response of the detector, as well as band broadening effects, which are corrected for by internal software (LI-COR Biosciences, 2004). Thin films of water on the optics, as in the case of Kohsiek (2000), were most likely responsible for these additional variable CS effects, whereas unlike ship borne applications, sea salt was unlikely to have been a major problem, given the distance of the LI-7500 from the sea surface. The negative correlation between  $q$  and  $c$  support this notion, whereby  $c$  responds to changes in  $q$ .

An adaptation of the approach outlined by Prytherch *et al.* (2010) was used to correct for such effects, with the main difference being that the relationship between fluctuations of H<sub>2</sub>O ( $q'$ ) and CO<sub>2</sub> ( $c'$ ) was determined instead of the relationship between relative humidity and CO<sub>2</sub> mixing ratios. This is because the relationship between  $q$  and relative humidity over the ocean is virtually linear (Prytherch *et al.*, 2010), and these fluctuations could be calculated directly

from raw LI-7500 data, which was desirable seeing as the effect was primarily instrumental. Fluctuations obtained from a running mean as opposed to a fixed mean for  $q$  were used to calculate the response of  $c$  to  $q$  so as not to introduce low frequency trends into subsequent calculations, and is also an assumption of the EC method. Finally, the iterative procedure to adjust  $\text{CO}_2$  fluxes to their expected values was not used in order to minimise the amount of calculations to which the  $\text{CO}_2$  data was subjected (given its highly sensitive nature), and to ensure that results were more representative of actual measurements.



**Figure 4.3:**  $\text{CO}_2$  against water vapour. (a) Half hour mean concentrations for the oceanic wind sector ( $220\text{-}320^\circ$ ). (b) Fluctuations from the first half hour period recorded in August 2006

To demonstrate this correction procedure, the first half hour period of data recorded was selected (3rd August, 2006), when the LI-7500 windows were clean (e.g. free from salt) and the instrument had been recently calibrated. The average wind speed was  $5 \text{ ms}^{-1}$  from a westerly direction ( $286^\circ$ ), the relative humidity was 70 %, and latent and sensible heat fluxes were positive. As shown in Figure 4.3(b), a cubic fit was applied to the correlation between ( $q'$ ) and ( $c'$ ). Water vapour fluctuations were then made dimensionless:

$$\hat{q} = \frac{q'}{\sigma_{q'}} \quad (1)$$

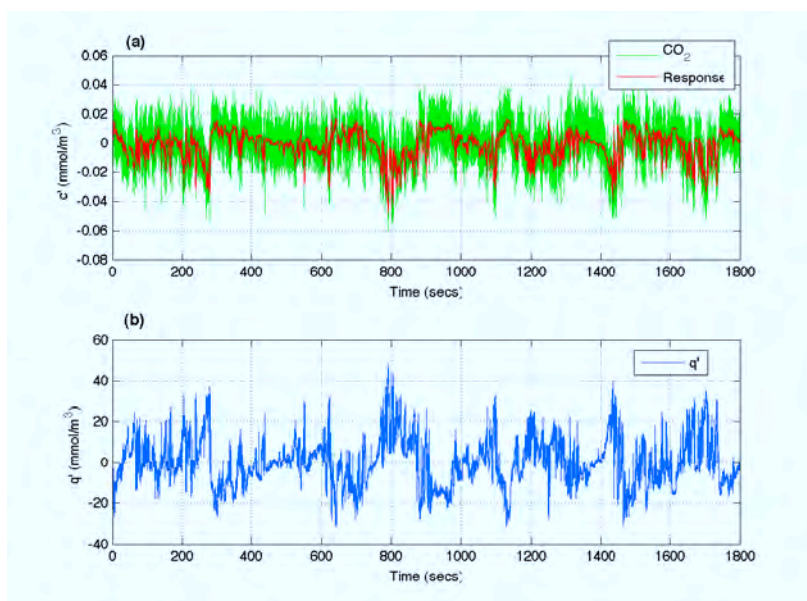
$\sigma_{q'}$  represents the standard deviation of water vapour fluctuations. Using the three coefficients, X, Y and Z that described the cubic fit in Figure 4.3(b), along with the dimensionless water vapour fluctuations, the response, R, of  $c'$  to  $q'$  could be calculated:

$$R = X\hat{q}^3 + Y\hat{q}^2 + Z\hat{q} \quad (2)$$

This response is shown in Figure 4.4(a) as a component of  $c'$ , where the effect of  $q'$  on  $c'$  is visibly evident. When this response is compared to Figure 4.4(b), it is very similar in shape, but in the opposite direction to  $q'$ , clearly exhibiting the effect of water vapour on  $\text{CO}_2$  measurements. To correct for cross-sensitivity, the response was simply subtracted from  $c'$ :

$$c'_C = c'_U - R \quad (3)$$

The subscripts C and U denote corrected and uncorrected respectively. Equation (3) was found to be of the same form as Equation (2) by Jacobs *et al.* (1999), whereby the cross-talk factor of the  $\text{H}_2\text{O}$  flux was subtracted from the uncorrected  $\text{CO}_2$  flux, having the same outcome. This correction removed the negative correlation between  $q'$  and  $c'$ , and for this half hour example, the  $\text{CO}_2$  flux was reduced from  $-38 \text{ mol m}^{-2} \text{ yr}^{-1}$  to only  $-3.8 \text{ mol m}^{-2} \text{ yr}^{-1}$ , an order of magnitude smaller. Correcting for CS dramatically changed the magnitude of fluxes, but only changed the direction if the response flux was greater than the initial  $\text{CO}_2$  flux.



**Figure 4.4:** The response of  $\text{CO}_2$  fluctuations to water vapour fluctuations. (a) Time series for  $\text{CO}_2$  fluctuations showing the effect of water vapour, again from the first half hour period recorded in August 2006. (b) The water vapour fluctuations used to calculate the response.

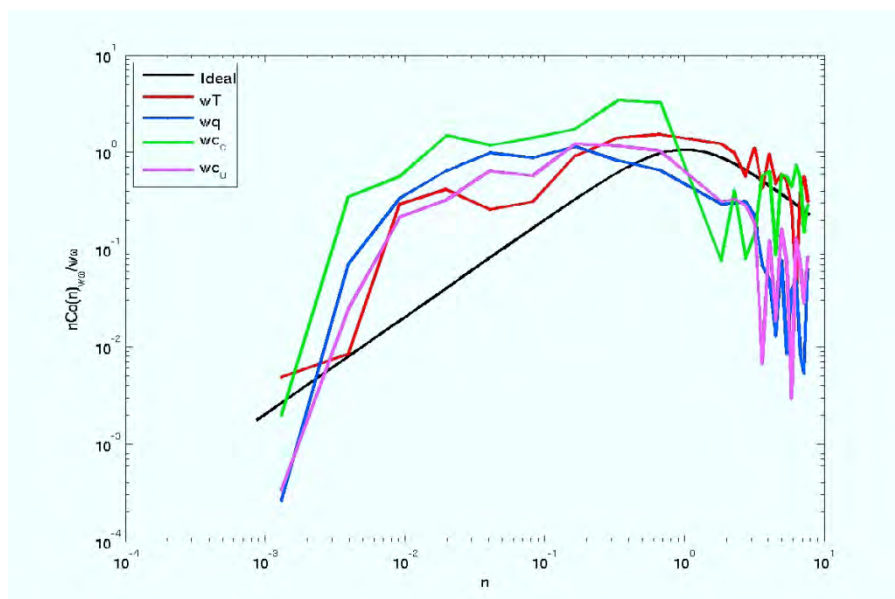
A procedure similar to that performed by Prytherch *et al.* (2010), was carried out to test the validity of this correction. This test involved correcting the sensible heat flux (FSH) data for any CS effects of water vapour using a fixed or running mean, then correcting the latent heat flux (FLH) for any CS effects of FSH. Corrected FSH values diverged slightly from uncorrected FSH values above  $0 \text{ Wm}^{-2}$ , and corrected values calculated using a running mean displayed less scatter overall.

Divergence was smaller for corrected latent heat flux (FLH) data, being very similar from using a running or fixed mean. This similarity and lack of divergence are most likely due to the fact that latent heat fluxes are much larger than sensible heat fluxes over the ocean. Although interesting, this test wasn't entirely relevant to the CS correction for CO<sub>2</sub>, as temperature and water vapour fluctuations were measured by two different instruments, using different measurement principles. However, it did demonstrate the potential for introducing errors into calculations, especially for CO<sub>2</sub> fluxes, which are extremely small in comparison.

#### 4.2.4 Density Correction

Gas fluxes calculated from mass density measurements must be corrected for air density changes due to fluctuations of water vapour and temperature, better known as the Webb correction (Webb *et al.*, 1980). Latent heat fluxes only need to be corrected for temperature, but CO<sub>2</sub> fluxes need to be corrected for temperature and water vapour. Given that CO<sub>2</sub> fluctuations had already been corrected for fluctuations of water vapour in the CS correction, its density effects were considered to be accounted for already. Therefore, to avoid a double correction (or over correction), only the temperature part of the Webb correction was used on the final CO<sub>2</sub> flux (termed the 'half Webb' correction), also conserving the number of calculations applied to CO<sub>2</sub> data.

The half Webb was applied since the direction of both the CS and Webb correction due to water vapour on CO<sub>2</sub> fluxes were the same. Using the full Webb correction resulted in an average upward flux of +8.06 mol m<sup>-2</sup> yr<sup>-1</sup> whilst use of the half Webb correction gave an average downward flux of -11.6 mol m<sup>-2</sup> yr<sup>-1</sup>. pCO<sub>2</sub> measurements showed an average difference of around -13.8 ppm in the air-sea concentration of CO<sub>2</sub>, so when the full Webb correction was used, the resultant flux was against the concentration gradient, confirming a possible double water vapour correction. The order in which both corrections (CS and half Webb) were applied had the same outcome in either case. The impact of these two primary stages of correction are shown in Figure 4.5, where the raw fluxes, the cross-sensitivity corrected fluxes and the combined full and half Webb corrected fluxes are illustrated. It can be seen that the Webb corrections can have significant impacts on the magnitude and sign of the fluxes. This is reminiscent of previous issues with the density correction that were initially highlighted by Ohtaki *et al.* (1989), which was found to be larger than the raw CO<sub>2</sub> flux, and could even change the transportation direction, with similar findings having been confirmed by Jacobs *et al.* (1999), Weiss *et al.* (2007), and Kondo and Tsukamoto (2007).

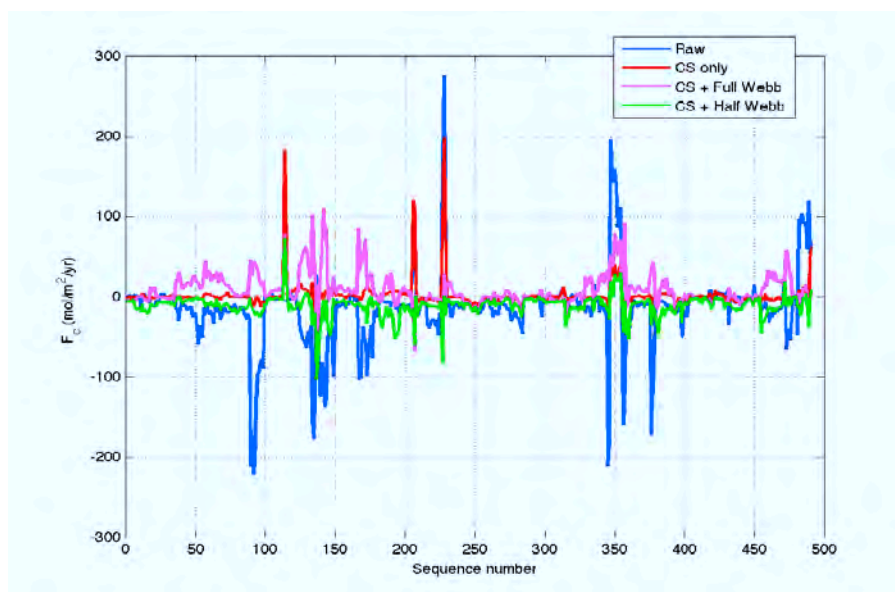


**Figure 4.5:** Normalised scalar co-spectra plotted as a function of frequency. Ideal (Kaimal *et al.*, 1972), wT (temperature), wq (H<sub>2</sub>O), wc<sub>c</sub> (CO<sub>2</sub> corrected for CS), wc<sub>u</sub> (CO<sub>2</sub> uncorrected).

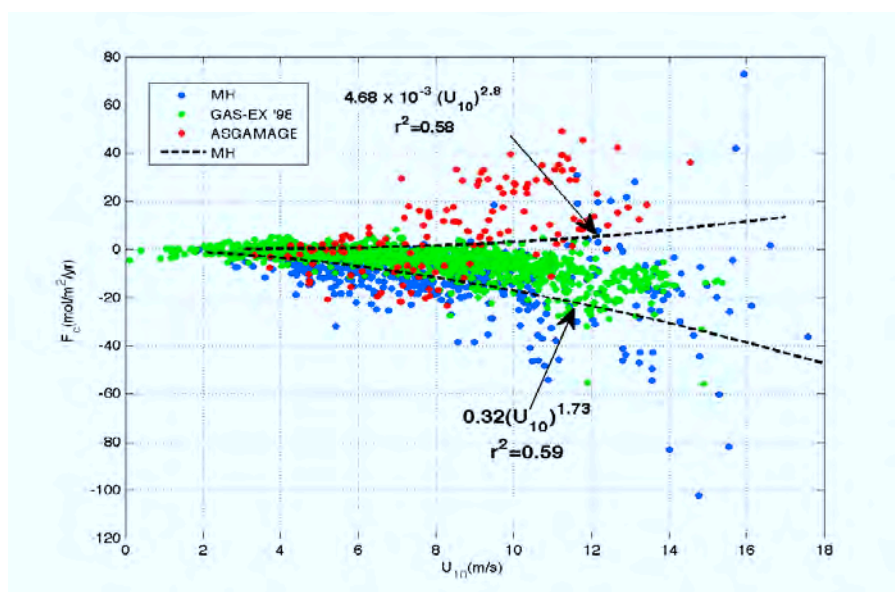
#### 4.2.5 Coastal CO<sub>2</sub> Flux Results

Scalar co-spectra give a good indication of data quality, and can highlight instrumental problems. Co-spectra from all half hour periods were inspected. Figure 4.6 shows the co-spectra as a function of frequency ( $n$ ) from one such half hour period, along with the ideal co-spectra proposed by Kaimal *et al.* (1972). wT represents temperature flux, wq represents water vapour flux, and wcc and wcu represent the cross-sensitivity corrected and uncorrected CO<sub>2</sub> flux respectively. Higher frequency eddies transport scalars more effectively than lower frequency eddies, associated with the dissipation of turbulent kinetic energy into heat through viscous effects (Stull, 1988). These are of most interest here, and it can be seen that the CO<sub>2</sub> co-spectrum is less similar to the water vapour co-spectrum after correcting for cross-sensitivity, but maintains its overall shape. The CO<sub>2</sub> flux ( $F_c$ ), whether positive or negative, was found to increase with wind speed, as shown in Figure 4.7. Fluxes over different seasons did not exhibit any clear seasonal signal. This was surprising given an expected biogenic influence on CO<sub>2</sub> uptake. The biological uptake signal in summer may have been surpassed by higher wind and wave energy in winter, combined with lower temperatures (solubility is an inverse function of temperature). Although there is a considerable scatter present in the data, presumably resulting from the wide range of conditions in biological activity and temperature associated with seasonality, both the upward and downward fluxes exhibit a power-law dependence on wind speed. The upward flux was parameterised by  $F_c = 4.68 \times 10^{-3} (U102.8)$  ( $r^2=0.58$ ) and the downward flux was parameterised by  $F_c = -0.32 (U101.73)$  ( $r^2=0.59$ ). The Mace Head coastal fluxes are compared in the same figure to the open ocean N. Atlantic fluxes from GAS-EX '98 (McGillis *et al.*, 2001) and North Sea fluxes from ASGAMAGE (Jacobs

et al., 1999). The absolute CO<sub>2</sub> fluxes in the Mace Head coastal zone are a factor of 3.56 higher than those observed during GAS-EX '98, but are comparable in magnitude with other shallow waters such as the North Sea.



**Figure 4.6:** CO<sub>2</sub> fluxes at various stages of the correction process; raw fluxes, CS (cross-sensitivity) corrected, and CS corrected along with the full and half Webb corrections. Sequence number denotes the order of data in the final data series (after all filtering and correcting).



**Figure 4.7:** CO<sub>2</sub> fluxes ( $F_c$ ) plotted against 10 m wind speeds. MH represents Mace Head. GAS-EX '98 (McGillis et al., 2001) and ASGAMAGE (Jacobs et al., 1999) data are shown for comparison.

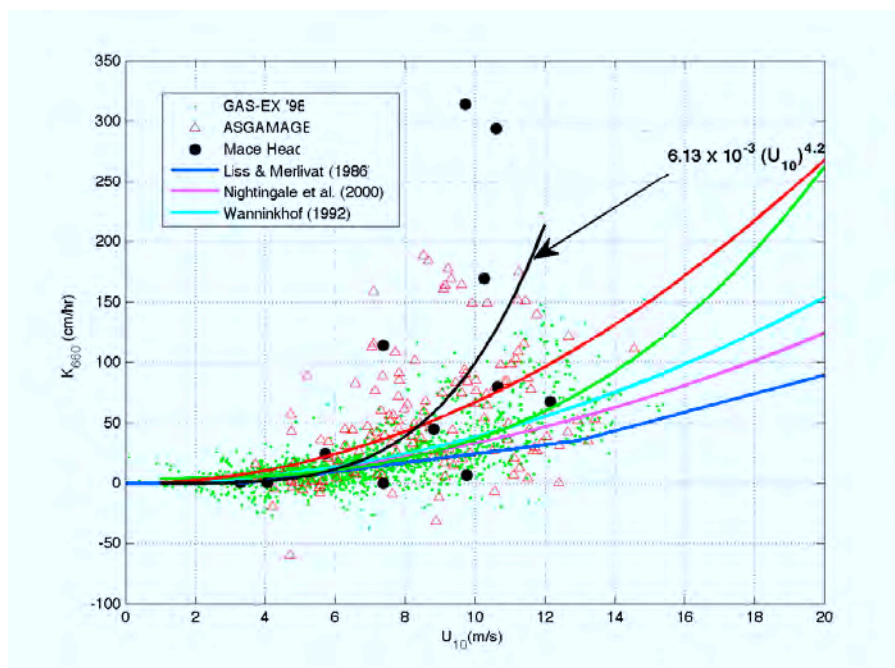
The air-sea transfer velocity of CO<sub>2</sub>,  $kCO_2$ , was normalised to waters at 20°C to compute  $k660$ , illustrated by Wanninkhof (1992).  $kCO_2$  is usually parameterised as a function of wind speed, and a proposed cubic fit to such parameterisations was made by Wanninkhof & McGillis (1999). There was not enough overlapping pCO<sub>2</sub> and  $F_c$  data here to get an accurate parameterisation, but an approximate power law was deduced of the form:

$k_{660}=6.13 \times 10^{-3}(U_{10})^{4.2}$ , as shown in Figure 4.8.

Two of the points from Mace Head are notably higher than the other studies, suggesting that  $k_{CO_2}$  is not a function of wind speed alone, most likely because it does not influence gas exchange directly.

However, using the data available, no reason could be found for their high values. The coastal ocean is a much more dynamic environment than the open ocean, and there are many factors that can affect gas exchange due to shallow water depths and their proximity to land. Some of these factors are likely to vary independently of wind speed, and may even have varying combined effects.

Water depths at Mace Head scale with wavelengths associated with the effects of shoaling. As described by Jähne *et al.*, (1987), shoaling causes the orbital motions of groundswell to flatten on interaction with the seabed, giving bottom driven turbulence in addition to any near surface turbulence, increasing vertical mixing as well helping to break down resistance to transfer. Analysis by Taylor & Yelland (2001) for coastal waters predicted higher values for  $k_{CO_2}$  close to shore due to the effects of shoaling and may explain why some of the transfer velocities are higher. Groundswell can be present in the absence of wind, and so is an example of a wind speed independent influence. The shallowness of coastal waters also restricts convection of cooling water, giving relatively cool and dense waters, promoting the solubility pump and leading to increased storage of inorganic carbon (Tsunogai *et al.*, 1999). This is augmented by increased biological production due to improved sunlight exposure and mixture of nutrients through shoaling and/or tidal movements.



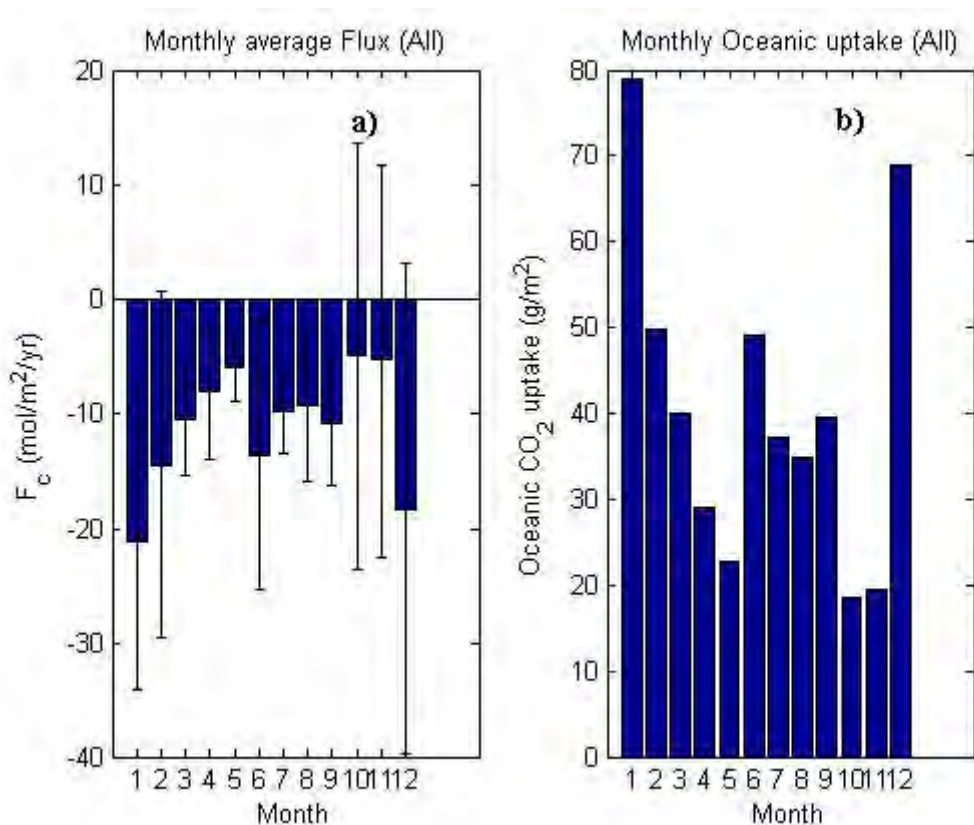
**Figure 4.8:** Air-sea transfer velocity normalised to water at a temperature of 20°C ( $k_{660}$ ) plotted against 10 m wind speed. GAS-EX '98 (McGillis *et al.*, 2001a) and ASGAMAGE (Jacobs *et al.*, 1999) data are also shown for comparison.

#### 4.2.6 Seasonality in Coastal CO<sub>2</sub> Flux

Integrated average monthly fluxes were computed by summing the total fluxes in a given month, then dividing by the number of half hour periods. Monthly oceanic CO<sub>2</sub> uptakes were computed by multiplying the average monthly CO<sub>2</sub> flux by the number of half periods in a month (not the number recorded) as a fraction of a year, to give an estimate on the amount of CO<sub>2</sub> absorbed by the ocean. It should be noted here, to avoid confusion, that uptakes are in the opposite direction to the fluxes, e.g., positive upward fluxes represent a release of CO<sub>2</sub> to the atmosphere, and so the oceanic uptake would be negative.

A seasonal signal based on biological activity, or the biological pump might have been expected to give larger fluxes from March-October than from November-February. However, it seemed (from Figure 4.9) that this may not have been the case.





**Figure 4.9:** (a) Averaged monthly Positive & Negative (All) CO<sub>2</sub> fluxes at Mace Head, along with standard deviations for each month & (b) Estimated monthly oceanic uptake of CO<sub>2</sub>

The bar chart in the figure gives a clearer picture of seasonal flux trends, displaying larger downward fluxes during winter months than during summer months. However, the months of June to September displayed relatively large downward fluxes, which may be a biological signal. The graph also shows that fluxes of CO<sub>2</sub> during the months of January, June, September and December were significant. However, to get a better idea of what was happening, we need to inspect the upward and downward fluxes for each month.

These trends suggest that there is biological activity from May into June, which is a period associated with phytoplankton blooms and the rapid growth of other marine organisms, such as algae or macroalgae, and hence the large increase in flux of CO<sub>2</sub> during this time. The month of June then shows a high CO<sub>2</sub> flux, which is a period associated with proliferation, and the growth of fish such as jellyfish and other sea life. The month of July displays a decline in the uptake of CO<sub>2</sub>, most likely because the water had a higher content of CO<sub>2</sub>, and less rapid growth occurred due to a decrease in nutrient availability.

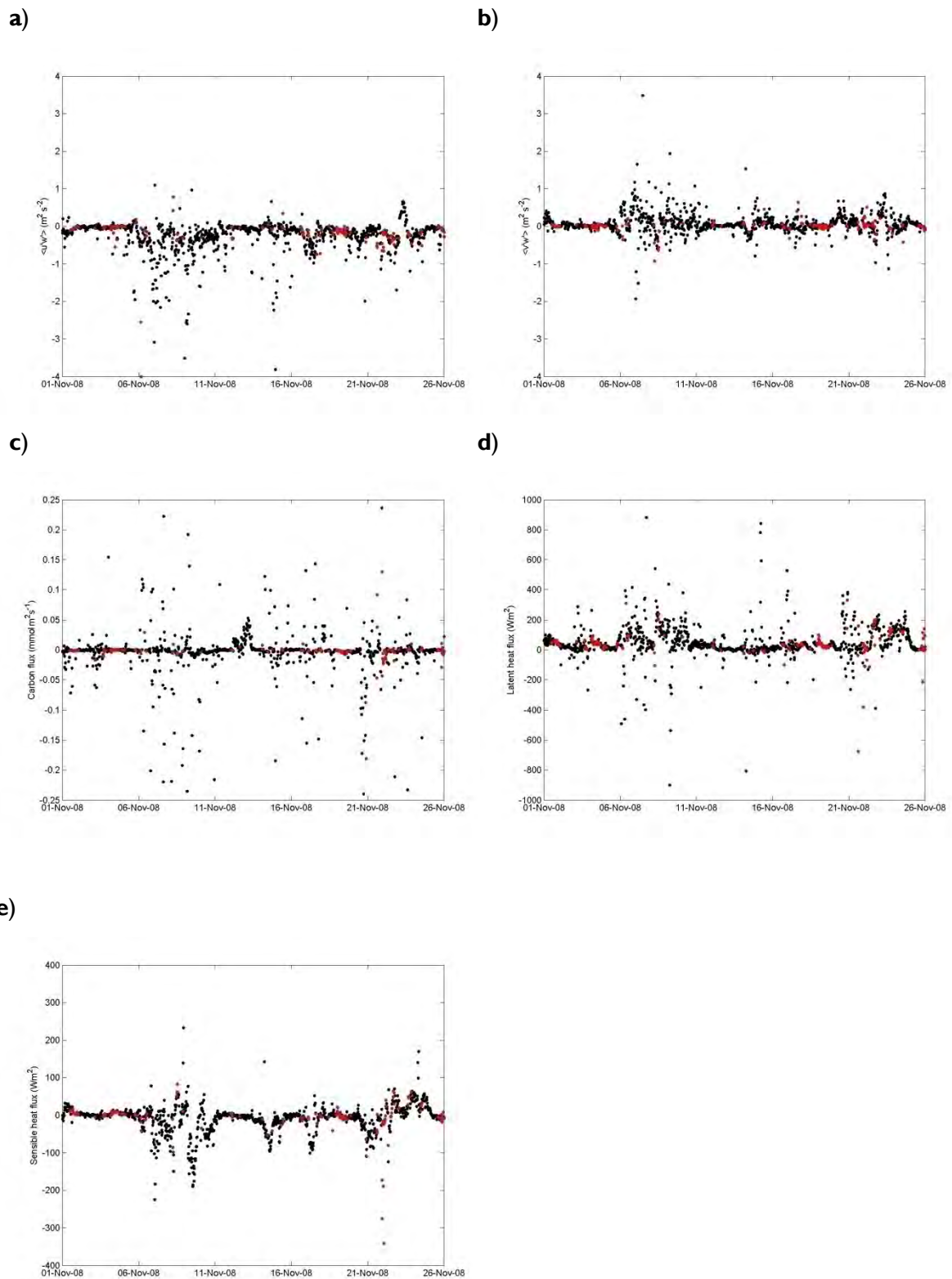
This activity slowed down again in August, and then increased through the months of September and October during which period micro blooms may have occurred, and equilibrium in biological activity was reached. Eventually biomass starts to die off coming into

autumn, giving a net release of CO<sub>2</sub>, and a sharp decline in uptake toward winter occurs. However, the fluxes for October and November in both directions show an increase after positive fluxes were removed, suggesting a hidden upward signal during these months that was not detectable. The overall trend is explained with the reasoning that biotic factors would be expected to dominate during the summer months, whereas abiotic factors would be expected to dominate during winter, and the middle month of June is the turning point of this annual cycle, when both positive and negative fluxes were more balanced. Abiotic and biotic factors obviously have a combined effect as well, but their relative importance must vary, having the potential to cancel each other out.

## **4.3 Shipborne CO<sub>2</sub> Fluxes**

### *4.3.1 Results*

Eddy covariance CO<sub>2</sub> flux measurements were conducted onboard the R.V. Celtic Explorer during the project. In addition to standard analysis procedures required for flux calculations from ground-based (i.e. stationary platforms), additional analysis is required to remove the ship's motion (i.e. a motion correction). Typical momentum, sensible heat, latent heat and CO<sub>2</sub> fluxes are illustrated in Figure 4.10 for cruise CE0814.



**Figure 4.10:** Fluxes measured by Eddy Covariance for the cruise CE0814. The longitudinal and transversal momentum fluxes, the CO<sub>2</sub> flux, the latent and sensible heat fluxes are shown in **a**, **b**, **c**, **d**, **e**, respectively.

Edson *et al.* (1998), have calculated  $\langle u'w' \rangle$  values of between -0.13 and 0.01 m<sup>2</sup>s<sup>-2</sup>, which is of the same order of magnitude as the mean value of -0.20 m<sup>2</sup>s<sup>-2</sup> for the cruise CE0814. Note

that the maximum wind speed recorded by Edson was around  $8.5 \text{ ms}^{-1}$ , while there were winds up to  $24 \text{ ms}^{-1}$  during CE0814. For  $\langle v'w' \rangle$ , Edson found values between  $-0.08$  and  $0.06 \text{ m}^2\text{s}^{-2}$ , while it was around  $0.01 \text{ m}^2\text{s}^{-2}$  during CE0814, which is here also of the same order of magnitude.

From annual estimates recorded in various continental margins, Chen and Borges (2009), report  $\text{CO}_2$  fluxes from  $-5.5 \times 10^{-4}$  to  $8.2 \times 10^{-4} \text{ mmol m}^{-2}\text{s}^{-1}$  (the conversion from  $\text{mol C m}^{-2}\text{yr}^{-1}$  to  $\text{mmol CO}_2 \text{ m}^{-2}\text{s}^{-1}$  has been made here), while the mean value during CE0814 was  $3 \times 10^{-4} \text{ mmol m}^{-2}\text{s}^{-1}$ , which is of the same order of magnitude.

Miller *et al.* (2010), report values of heat fluxes as a function of the latitude. For a latitude around  $52^\circ \text{ N}$  (i.e., the mean latitude of CE0814), they found sensible and latent heat fluxes around  $\pm 20$  and  $\pm 10 \text{ W m}^2$ , respectively, while during CE0814, the mean sensible and latent heat fluxes were  $-3.1$  and  $41 \text{ W m}^2$ . Here also, the order of magnitude seems reasonable. Note that for Miller's values, the corresponding winds were comprised between  $5$  and  $10 \text{ ms}^{-1}$ . These initial results are promising; however, insufficient data were available to derive a wind speed relationship for the gas transfer coefficient.

#### 4.4 Activity Synthesis

Seasonal measurements of  $\text{CO}_2$  fluxes were conducted at the Mace Head Atmospheric Research Station where maximum fluxes of the order of  $-20 \text{ mmol m}^{-2} \text{ year}^{-1}$  were observed in winter months and minimum fluxes of the order of  $-5 \text{ mmol/m}^2/\text{year}^{-1}$  were observed. A secondary peak was of  $-10 \text{ mmol m}^{-2} \text{ year}^{-1}$  were observed over summer months. The winter peak is thought to be due to the increased wind speeds and lower temperatures promoting a higher flux, while in summer, biological activity is thought to account for the secondary peak. Overall, coastal fluxes were higher than those previously reported over open oceans.

A first attempt was made to derive shipborne fluxes. Reasonable success was achieved in applying the motion correction to the raw data and subsequently deriving  $\text{CO}_2$  and micrometeorological fluxes. Quantitative relationships between wind speed and the gas transfer velocity coefficient were not achieved within the duration of the work programme for the ship/open ocean data.

## 5. POTENTIAL ECOLOGICAL IMPACTS AND INDICATORS OF OCEAN ACIDIFICATION FOR IRISH MARITIME AREA AND RECOMMENDATIONS FOR THE FUTURE

### 5.1 Aims and overview of outcomes

The aim of this work package was to complete a short desk study review of potential ecological impacts and identify indicators of ocean acidification relevant to Irish waters; and to develop and communicate to policy-makers recommendations for an Irish long-term research and monitoring programme with respect to ocean carbon cycling/acidification and associated ecological impacts. A comprehensive report was produced and published as a Marine Institute Foresight report in May 2010 (Ní Longphuirt *et al.*, 2010). That report summarised current scientific information in the field of ocean carbon chemistry and reviewed research outcomes relating to biological effects and ecological consequences. The report also addressed the potential socio-economic consequences and broader policy considerations. Recommendations concerning research and monitoring needs were elaborated in chapter 5. The report was reviewed by the project's external advisory group prior to publication. A short information leaflet was also produced summarising the issues in an accessible format for high level policy makers and the general public.

### 5.2 Background

Although ocean acidification can be anticipated with a high degree of certainty (Orr *et al.*, 2005) there is significant uncertainty as to how increasing CO<sub>2</sub> and decreasing ocean pH will affect marine organisms and ecosystems. Laboratory, mesocosm and especially field research is at an early stage. Many marine calcifying organisms have shown a negative response to decreasing carbonate saturation although there is a broad variability in the response of different organisms (Ries, *et al.*, 2009). Observations at naturally high CO<sub>2</sub> environments in the Mediterranean Sea suggest that some ecosystems may not be able to readily adapt (Hall-Spencer *et al.*, 2008). Many of the marine calcifiers that may be affected occupy the base of the marine food web but the potential consequences for marine ecosystems are poorly understood. Important habitats that may be at risk include the deep-sea cold water corals (e.g. *Lophelia pertusa*) such as those to the west of Ireland. Although the aragonite saturation horizon is deep in the North Atlantic even modest changes in the saturation state may affect calcification rates (Guinotte *et al.*, 2006). Several reports have reviewed the evidence for

impacts (Raven *et al.*, 2005, OSPAR 2006, Secretariat of the Convention on Biological Diversity 2009, IAP 2009) reports. A number of international workshops have identified prioritised research needs including the need for laboratory and field investigations of biological and ecological responses, recognising the challenge and need for field manipulations (Kleypas *et al.*, 2006; Orr *et al.*, 2009 ; ICES, 2008 ).

### Desk Study

Ocean acidification is a relatively new although exponentially growing field of research. Indeed it is only emerging as a new concept for policy makers to consider in the broader discussions on climate change mitigation and adaptation and measures. As part of WP5, a post doctoral researcher, Dr. Sorcha Ní Longphuirt, and Work Package participants McGovern, Stengel and O'Dowd prepared the desk study. The study examined the current state of knowledge, the potential consequences and nationally relevant policy considerations including monitoring and research needs under the following themes:

- CO<sub>2</sub> emissions and changes to ocean chemistry
- Potential Ecological consequences
- Potential socio-economic consequences
- Implications for policy
- Research and information needs

The desk study was reviewed by the project's international external advisory group and comments received were incorporated. It was published in the Marine Institute's Marine Foresight Series in May 2010 and is available for download from the Marine Institute website ([www.marine.ie/publications](http://www.marine.ie/publications)). A short summary leaflet setting out the key issues and recommendations was also produced for policy makers and the general public. A one page summary for policy makers and a schematic of potential impacts are reproduced from the report.



## BOX I: OCEAN ACIDIFICATION - ESSENTIAL FACTS FOR POLICY DEVELOPMENT

**Ocean acidification** is caused by increasing anthropogenic CO<sub>2</sub> levels in the atmosphere and the subsequent uptake by the oceans. Recent research has shown that this phenomenon has resulted in a 30% increase in global surface ocean acidity since the industrial revolution. It is projected that the acidity of seawater will increase a further 120% by 2100.

**Impact on Ocean Ecosystems:** Although the overall impact of ocean acidification on marine life and ecosystems remains uncertain, there is growing international concern that key species, especially calcifying organisms, and habitats are threatened. This includes important components of the food web in Irish waters such as primary producers, cold water coral reefs, shellfish and crustaceans. This could have profound consequences for entire marine ecosystems and their functioning.

**Socio-Economic Consequences:** Marine and coastal ecosystems provide essential goods and services to mankind and play a vital part in the economy of maritime nations. The impact of ocean acidification on the ocean and its ecosystems is likely to have major consequences for climate processes, food production, biodiversity and sectors reliant on these services, such as fisheries and aquaculture.

**Policy:** Ocean acidification is essentially irreversible on practical human timescales. Mitigation can only be achieved through early commitment to a reduction of CO<sub>2</sub> emissions. Protection of the Irish marine environment, underpinned by science-based assessment, is a legal requirement under international obligations such as the OSPAR Convention and Marine Strategy Framework Directive (Dir. 2008/56/EC).

**Research Needs:** Research on ocean acidification and impacts on marine ecosystems is in its infancy. Much more information is required on the environmental change taking place and the effects on biological processes so as to better forecast the ecological impacts and socio-economic consequences. This information is essential to develop mitigation and adaptation management policies including risk analysis.

**Research Capabilities:** Ireland has a unique geographical location for conducting research into ocean acidification and its impacts in important North Atlantic margin and shelf waters. Significant expertise and infrastructure is already in place which can form the basis of an effective and cost-efficient monitoring and research programme.

### Key Recommendations:

The potential consequences of ocean acidification need to be addressed in climate change and environmental policy development, especially in relation to mitigation strategies to reduce carbon emissions.

A nationally coordinated multidisciplinary marine climate change and ecosystem monitoring and research programme should be firmly established for Irish waters with ocean acidification monitoring as a cornerstone. Priority activities should include measurements of the inorganic carbon system and monitoring of key marine species and habitats at risk. This should take place within the framework of international monitoring obligations and policy requirements. Strong links and partnership should be developed with ocean acidification programmes in other European countries.

Specialist capacity and expertise is further required and existing infrastructure needs to be further developed and maintained. This is essential in order to undertake a viable and cost-effective research and monitoring programme. It will also facilitate future involvement of Irish researchers in international projects in this field. Focussed research into impacts of ocean acidification will enable progressively better evaluations to be made of the long-term threat posed to the Irish marine environment and economy.

### **5.3 Research and monitoring needs**

A much better understanding of biological and ecosystem impacts of ocean acidification is required to predict potential socio-economic impacts. Research and monitoring are essential to underpin mitigation and adaptation policies. The requirement for a multidisciplinary ocean acidification and marine climate change monitoring programme to support policy development was emphasised in the report. This should build on complementary activities and utilise available infrastructure and resources to deliver a cost-effective programme. The desk study identified the need for monitoring of CO<sub>2</sub> uptake and changes in the carbonate chemistry of Irish marine waters. These activities should link to international activities and contribute to regional monitoring as proposed by the OSPAR Convention and under Directive 2008/56/EC - Marine Strategy Framework Directive (ICES, 2010). Key areas for research that are needed to improve our understanding of the potential impacts of ocean acidification were highlighted in the desk study. A number of potential indicators of ecological impact were identified although further work is required at international level to formulate a harmonised set of indicators that are appropriate for use on a regional basis. Nonetheless development and maintenance of critical capacity and expertise (for example in carbonate measurement) is essential to underpin any such programme. Box 2 presents the recommendations for monitoring from the desk study.



## BOX 2: KEY RECOMMENDATIONS FOR MONITORING OF OCEAN ACIDIFICATION

### The authors recommend the following:

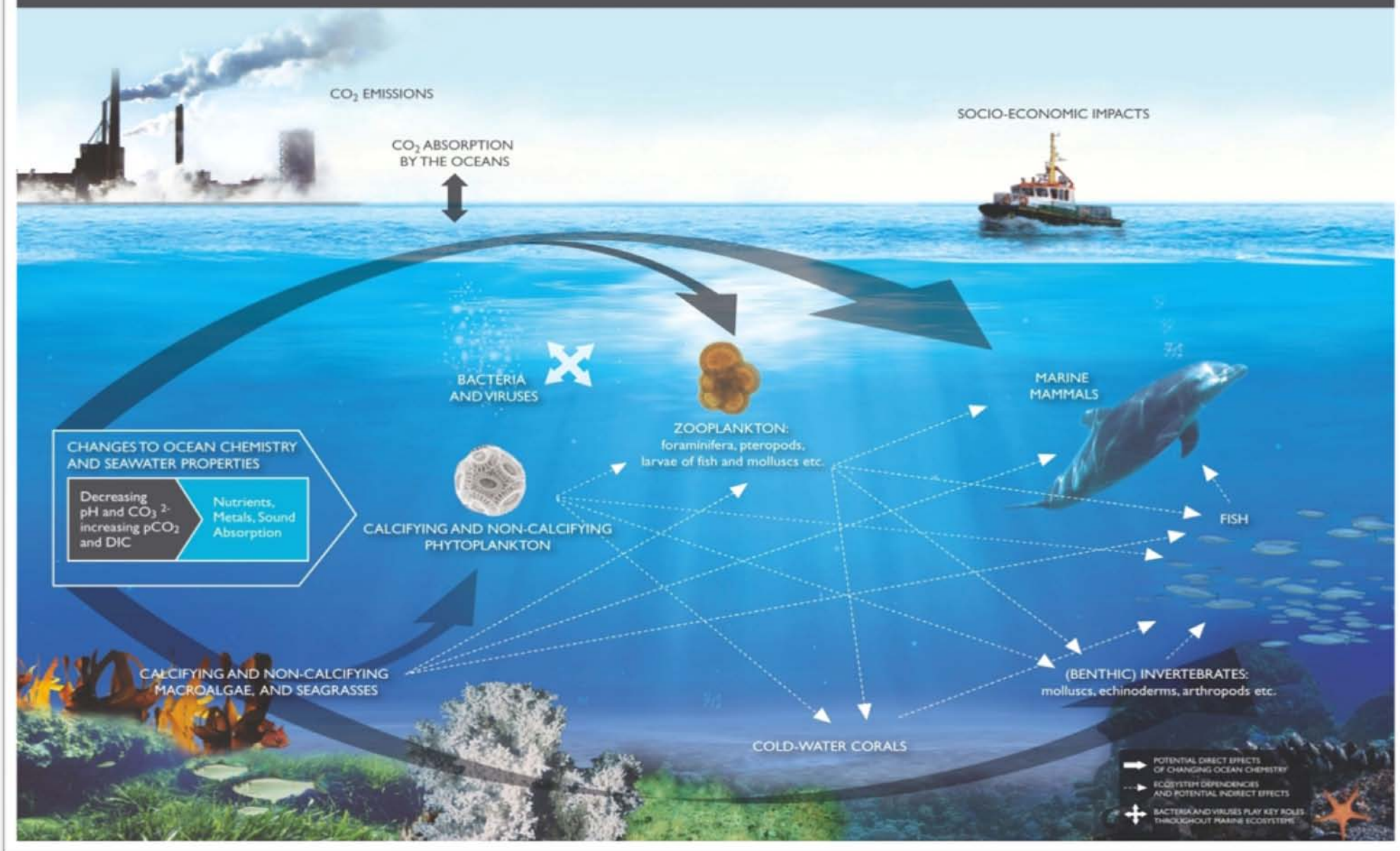
- Initiation of integrated long-term multi-disciplinary marine ocean acidification and climate change monitoring to support policy decisions for mitigation and adaptation.
- Support of studies aimed at determining the extent and rate of environmental change and ecological impact due to ocean uptake of anthropogenic CO<sub>2</sub> from the atmosphere.
- Support of activities underpinning the development and evaluation of assessment and future prediction tools (e.g. large scale coupled ocean-atmosphere climate change simulations).
- Building of capacity and expertise to deliver a viable and cost-effective research and monitoring programme.

### Monitoring should:

- meet the requirements of key statutory drivers such as the Marine Strategy Framework Directive and the Joint Assessment and Monitoring Programme of the OSPAR Convention;
- include coherent data collection for key ocean acidification parameters (carbonate system and related physico-chemical and biological parameters) ;
- include data collection into existing programmes and surveys where appropriate and deploy novel sensors on available platforms (e.g. research vessels and moorings) to facilitate a cost-effective measurement programme;
- include the use of coastal sentinel sites for high frequency climate change and ocean acidification monitoring. For example, the unique location of NUI Galway's atmospheric research facility at Mace Head could be capitalised upon for ongoing study of air-sea CO<sub>2</sub> exchange, changes to seawater chemistry and impacts on coastal organisms and ecology;
- target ecologically vulnerable areas and include seasonal off-shore transects and the mapping and monitoring of saturation horizons; and
- incorporate relevant indicators to track impacts on key ecological processes, sensitive habitats and ecologically and economically important organisms (e.g. cold-water corals, coccolithophores, molluscs and macroalgae).

**Figure 5.1: (Next page)** Simple ecosystem schematic highlighting potential direct effects of changing ocean chemistry and indirect effects arising from ecosystem dependencies (source Ní Longphuirt *et al.*, 2010).

# OCEAN ACIDIFICATION MAY HAVE DIRECT AND INDIRECT IMPACTS ON MARINE LIFE



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## 7. GLOSSARY

<b>AABW</b>	Antarctic Bottom Water	<b>kCo<sub>2</sub></b>	Gas Exchange rate
<b>ACD</b>	Aragonite Compensation Depth	<b>LDW</b>	Lower Deep Water
<b>ASGAMMAGE</b>	Air Sea Gas Exchange	<b>Li</b>	
<b>ASH</b>	Aragonite Saturation Horizon	<b>Li-COR</b>	
<b>CD10</b>	Drag Coefficient	<b>LSW</b>	Labrador Sea Water
<b>CDIAC</b>	Carbon Dioxide Information Analysis Centre	<b>MEDW</b>	Mediterranean Water
<b>CEYYXX</b>	CE-Celtic Explorer YY- Year of Sampling XX- Cruise Number	<b>NDP</b>	National Development Plan
<b>CFC</b>	Chlorofluorocarbon	<b>NE Atlantic</b>	North East Atlantic
<b>Co<sub>2</sub></b>	Carbon Dioxide	<b>NOAA</b>	National Oceanic and Atmospheric Administration
<b>CO<sub>2</sub>SYS</b>	CO <sub>2</sub> System in seawater	<b>NUIG</b>	National University of Ireland, Galway
<b>Co<sub>3</sub><sup>2-</sup></b>	Carbonate ion	<b>O<sub>2</sub></b>	Oxygen
<b>CRM</b>	Certified Reference Materials	<b>OH</b>	Hydroxide
<b>CS</b>	Cross-sensitivity	<b>ORS</b>	Oak Ridge Sensor
<b>CSH</b>	Calcite Saturation Horizon	<b>OSPAR</b>	Oslo/Paris Convention( for the protection of the Marine Environment of the North- East Atlantic
<b>CTD</b>	Conductivity Temperature Depth	<b>pCo<sub>2</sub></b>	Partial pressure of Carbon Dioxide 9in Seawater)
<b>CVYYXX</b>	CV- Celtic Voyager YY-Year of Sampling XX-Cruise Number	<b>Quasimeme</b>	Quality Assurance of Information for Marine Environmental Monitoring in Europe
<b>DIC</b>	Dissolved Inorganic Carbon	<b>R.V.</b>	Research Vessel
<b>DOC</b>	Dissolved Organic Carbon	<b>SAIW</b>	Sub Arctic Intermediate Water
<b>EC</b>	Eddy Correlation	<b>SML</b>	Surfaced Mixed Layer
<b>ENAW</b>	Eastern North Atlantic Water	<b>SSS</b>	Sea Surface Salinity
<b>fc</b>	Co2 flux	<b>SST</b>	Sea Surface Temperature
<b>fLH</b>	Latent Heat flux	<b>TA</b>	Total Alkanity
<b>fSH</b>	Sensible heat flux	<b>TCO<sub>2</sub></b>	Dissolved Inorganic Carbon
<b>GEOSECS</b>	Geochemical ocean Section Study	<b>TOC</b>	Total Organic Carbon
<b>H<sub>2</sub>O</b>	Water	<b>TO<sub>x</sub>N</b>	Total Oxidised Nitrogen
<b>HFC</b>	Hydrofluorocarbon	<b>TS</b>	Potential Temperature Salinity
<b>IAP</b>	Inter academy panel on international issues	<b>U</b>	Friction velocity
<b>ICES</b>	International Council for the Exploration at Sea	<b>UIC</b>	
<b>IFM</b>	Infra-red fluctuation meter	<b>VINDTA</b>	Versatile Instrument for the Determination of Total Inorganic Carbon and Titration Alkalinity
<b>IPCC</b>	Intergovernmental Panel on Climate Change	<b>WOCE</b>	World Ocean Circulation Experiment
<b>ISO</b>	International Organisation for Standardisation	<b>WP</b>	Work Package
<b>K<sub>1</sub>, K<sub>2</sub>, K<sub>SO4</sub></b>	Dissociation Constant		

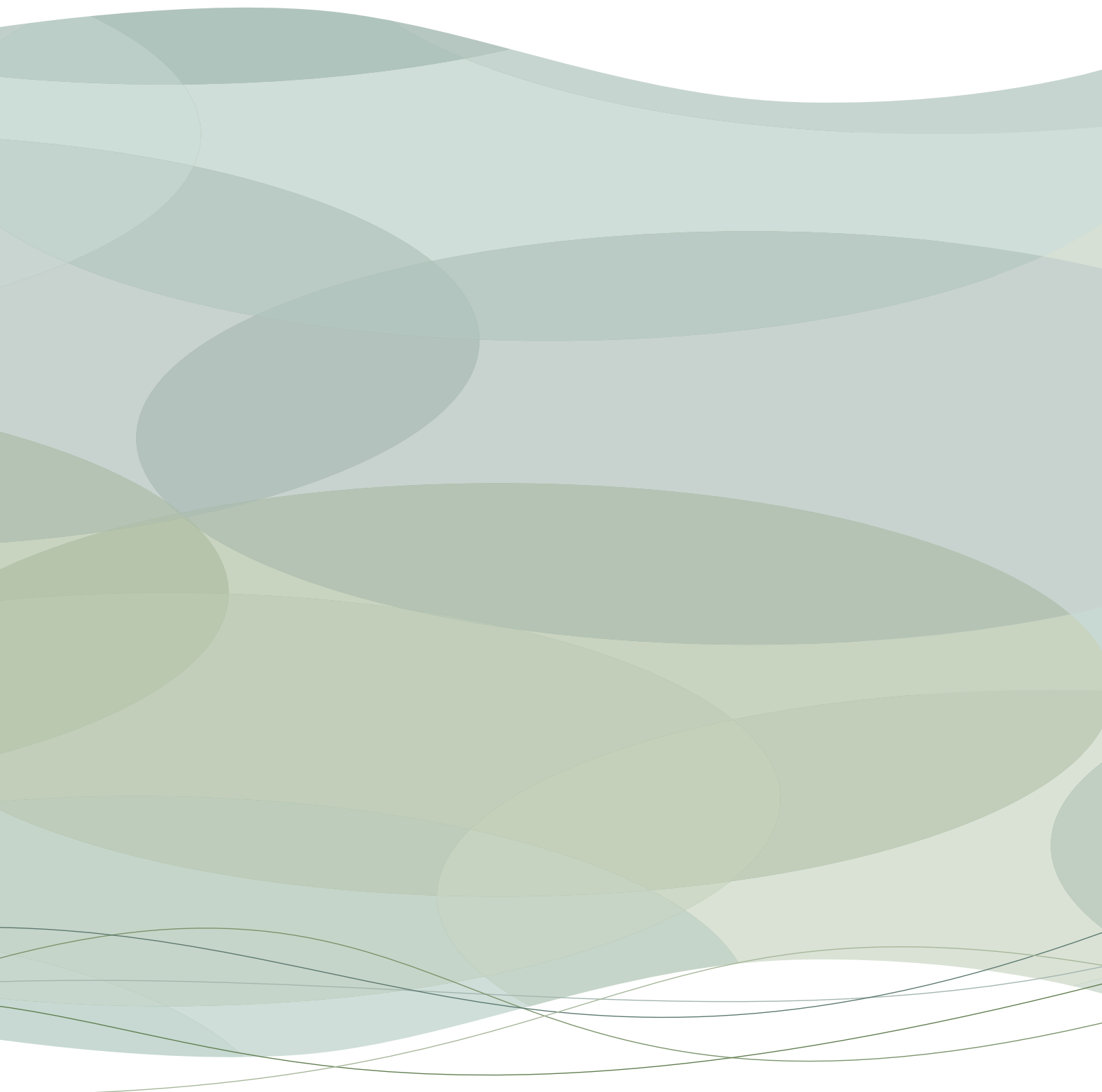












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