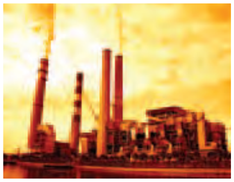
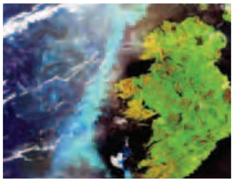
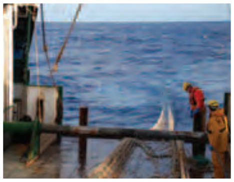
Ocean Acidification: An Emerging Threat to our Marine Environment

May 2010

Sorcha Ní Longphuirt, Dagmar Stengel,
Colin O'Dowd and Evin McGovern







Marine Foresight Series
No.6

SeaChange
Casadh na Taoide

OÉ Gaillimh
NUI Galway

Marine Institute
Foras na Mara

> *"to undertake, to co-ordinate, to promote and to assist in marine research and development and to provide such services related to marine research and development that, in the opinion of the institute, will promote economic development and create employment and protect the marine environment"*
>
> Marine Institute Act 1991

ACKNOWLEDGEMENTS

The authors would like to sincerely thank the following people for their helpful advice and contributions to this report:

External advisory group: Prof. Christoph Heinze (University of Bergen), Dr. Carol Turley (Plymouth Marine Laboratory), Prof. Andrew Watson (University of East Anglia), Dr. Anthony Grehan and Dr. Martin White (NUI Galway), Margot Cronin (Marine Institute);

Project team:
Dr. Rachel Cave, Dr. Caroline Kivimae, Dr. Brian Ward (NUI Galway), Triona McGrath, Dr. Glenn Nolan, Dr. Guy Westbrook (Marine Institute);

And also Geoffrey O'Sullivan, Dr. Michael O'Toole, Eileen Joyce, Aengus Parsons and Dr. Pauhla McGrane (Marine Institute).

Special thanks to Felicity Donnelly for assembling the report and the associated short information leaflet for publication and to Sara Meehan for editorial assistance.

Cover Images:
Mace Head Buoy – © Marine Institute (courtesy of James Ryan)
Coral picture – © NUI Galway (courtesy of Anthony Grehan)
Satellite Image – © courtesy ESA/Envisat | Instrument: MERIS | Acquisition: Jun-2006
Fishing Image – © Marine Institute (courtesy of Fisheries Science Services)

ISSN: 1649-590X

Further copies of this publication may be obtained from:

Marine Institute,
Rinville,
Oranmore,
Galway,
Ireland.

Alternatively you can download a PDF version from www.marine.ie

OCEAN ACIDIFICATION - ESSENTIAL FACTS FOR POLICY DEVELOPMENT

Ocean acidification is caused by increasing anthropogenic CO_2 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_2 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.

EXECUTIVE SUMMARY

ANTHROPOGENIC CARBON DIOXIDE EMISSIONS ARE CHANGING FUNDAMENTAL OCEAN CHEMISTRY.

Atmospheric carbon dioxide (CO_2) concentrations are currently 387 ppmv, 30% higher than the pre-industrial concentration. The oceans have absorbed more than a third of net CO_2 emissions since the industrial revolution, which has resulted in an average pH reduction in ocean surface waters from ~8.2 to ~8.1 pH units since pre-industrial times. Ocean acidification is increasing at a rate one hundred times faster than any previous change for millions of years, with the greatest pH decreases (~0.12 units) occurring at high latitudes. Projections based on the IPCC business-as-usual emissions scenario indicate that atmospheric CO_2 could exceed 800 ppmv by 2100, which would result in a further drop of 0.4 ± 0.1 pH units, a change which has probably not occurred for more than 20 million years. Furthermore, saturation horizons (i.e. the depth below which dissolution of calcium carbonate is favoured over precipitation) are rising. This will limit the habitable depth for calcifying organisms such as cold-water corals.

WHILE OCEAN ACIDIFICATION CAN BE PREDICTED WITH A HIGH DEGREE OF CERTAINTY, THE ECOLOGICAL CONSEQUENCES ARE LESS CERTAIN AND THE POTENTIAL IMPACTS ARE ONLY JUST BEGINNING TO EMERGE.

The extent of impact will depend on the ability of species to adapt to an unprecedented rapid change in ocean chemistry. Marine organisms which form calcium carbonate (aragonite or calcite) structures or shells are most obviously at risk from ocean acidification, through a reduction in calcification rates, and corrosion of biogenic calcium carbonate. Geological records of a past ocean acidification event, which occurred over much longer timescales, coincide with the mass extinction of some calcareous marine organisms. Calcifying organisms at risk include calcifying phytoplankton (coccolithophores), planktonic foraminifera and pteropods, tropical and cold water corals, coralline algae including maërl, bivalves and gastropod molluscs (e.g. mussels, oysters, clams) and echinoderms (e.g. star fish, sea urchins). The base of the oceanic food web depends on calcifying organisms. A range of field observations suggest that ocean acidification is already having a detectable impact on a number of marine calcifiers such as foraminifera and pteropods, that are exhibiting reduced shell weights, and mussels, that have displayed decreased abundance and mean size in areas where seasonal reductions in pH are now occurring.

Ocean acidification may also be expected to have direct and indirect impacts on a range of physiological processes in marine organisms such as photosynthesis, reproductive ability and survival rates of eggs, larvae and juveniles, host-pathogen relationships, impacts on gravity sensory receptors, acidosis (the internal build up of carbonic acid), and the ability of mammals to detect calls and echo-location pulses.

The impacts of ocean acidification will not occur in isolation as organisms may experience a range of impacts simultaneously along with other stressors such as, temperature increases associated with climate change. The response of marine organisms to ocean acidification may vary widely, even between similar species. Current knowledge of the response of organisms, their possible adaptive abilities and survival rates, is limited and is hampered by the difficulty in extrapolating laboratory- and mesocosm-based experiments to natural conditions. Observations at a CO_2 vent site, which provides a ‘natural laboratory’, have shown that major shifts can occur in species dominance and ecosystem functioning across changing pH gradients. These shifts point towards potential ecosystem ‘tipping points’.

OCEAN ACIDIFICATION IS A KEY THREAT TO THE FISHERIES INDUSTRY.

The oceans provide essential services to mankind. Oceans play a key role in regulating climate and biogeochemical cycling, supporting much of the planet's biodiversity and provide food and other resources that underpin the livelihood of millions of people. Ocean acidification will have complex interactions with climate processes which will influence climate change. This includes a reduced ability of the oceans to absorb CO_2 thus exacerbating climate change.

The ocean supports a wide range of economic activities, many of which will be adversely affected by ocean acidification. Understanding ecosystem impacts is key to predicting potentially major socio-economic consequences. Alterations to keystone species (e.g. cold water corals, coccolithophores, macroalgae) could culminate in ecosystem shifts with untold impacts on economically important organisms. Calcifying species at risk include mussels and oysters, which are important for Irish aquaculture. Projections indicate that approximately 70% of cold water coral systems will be exposed to undersaturated waters by 2099.

A whole-ecosystem approach which includes greater research and monitoring of fish stocks, trophic interactions and impacts of acidification and climate change will improve the scientific basis for fisheries management. The adaptive ability of specific species and ecosystems, the fisheries industry, coastal communities and consumers to ocean acidification will dictate the economic costs of ocean acidification.

OCEAN ACIDIFICATION NECESSITATES A RESPONSE FROM POLICY MAKERS AT ALL LEVELS.

Ocean acidification is a global problem which requires an internationally coordinated response. Ocean uptake of CO_2 will continue in response to anthropogenic emissions. There are no practical methods to reverse ocean acidification and natural recovery of the ocean's chemical equilibrium will require tens to hundreds of millennia while the recovery of corals is on a scale of millions of years. While an early commitment to decreased CO_2 emissions is the most immediate action required, future agreements on emission targets should consider the threat of acidification and the consequences for current and future generations.

Ocean acidification needs to be included in climate change policy development at national and international level. A number of methods are currently being considered for the capture of CO_2 and storage of carbon in the oceans or sub-seabed. The risk to the marine environment should be well understood. The environmental status of all marine waters is threatened by ocean acidification. Through several international conventions, such as OSPAR (1992), and EC directives such as the Marine Strategy Framework Directive (2008), Ireland, in cooperation with other European maritime states, has a legal obligation to protect the North-East Atlantic. A coherent network of Marine Protected Areas providing protection to vulnerable species and habitats from other pressures may improve resilience to climate change and ocean acidification.

A COORDINATED COMMITMENT TO MONITORING AND RESEARCH IS REQUIRED.

Ireland has an ideal geographical location for conducting research into ocean acidification and ecosystem impacts in North Atlantic margin and shelf waters. Through targeted research and monitoring of Irish marine ecosystems an opportunity is available to contribute to global efforts to understand ocean acidification and ultimately to protect the Irish marine environment. Long-term monitoring, assessment and research programmes will allow for characterisation of the absorption of CO_2 by the oceans, the subsequent rate at which the chemistry and biology of Ireland's marine ecosystems are reacting and the identification of ecosystems at risk. A multidisciplinary approach is required which considers the overall ecosystem response. Monitoring and research should be linked to international activities where practical and in particular cooperative studies with the UK should be encouraged. Furthermore, future efforts should build on existing capabilities and activities in the Irish marine community, facilitating cost-effective data collection, and should aim to integrate into international efforts to elucidate and mitigate the problems relating to ocean acidification.

TABLE OF CONTENTS

Dog's Bay, Connemara, Co. Galway
This popular beach is formed from tiny foraminifera shell rather than actual sand.
Photo courtesy Dagmar Stengel, NUI Galway

CHAPTER 1. MANKIND'S CO_2 EMISSIONS ARE CHANGING OCEAN CHEMISTRY

1.1 Background

Carbon dioxide emitted to the atmosphere by human activities is absorbed by the oceans making them more acidic (lowering the pH- the measure of acidity). We refer to this process as ocean acidification.

Raven et al., *2005 (Royal Society)*

Anthropogenic emissions of carbon dioxide (CO_2) and other greenhouse gases primarily attributed to fossil fuel combustion, cement production, and land-use change (Burns, 2008; Guinotte and Fabry, 2008) have resulted in an increase in atmospheric CO_2 concentrations from 280 ppmv to 387 ppmv in the last 200 years and a consequent alteration of the earths climate system (IAP, 2009). Similar increases in atmospheric CO_2 have also been measured at Mace Head in Ireland (Figure 1.1). Currently, concentrations far exceed the natural range over the last 650,000 years (Solomon *et al.,* 2007) and are increasing at a rate of ~ 0.5% yr^{-1} (Forster *et al*., 2007). The 20th century increase in CO_2 occurred at a rate more than an order of magnitude faster than any sustained change during the past 22,000 years (Joos and Spahni, 2008).

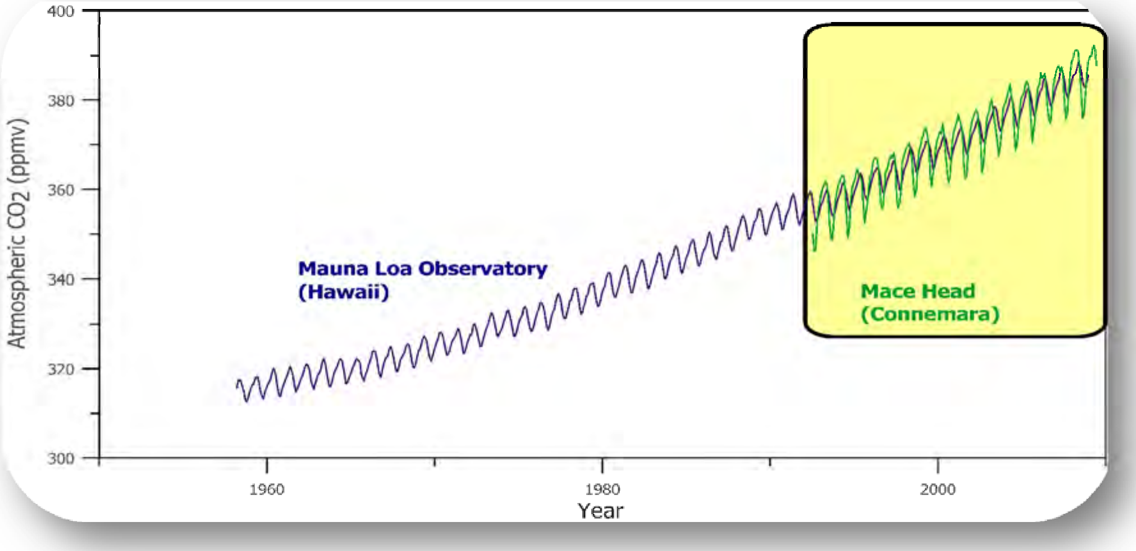


Figure 1.1 : This 50 year time series from Hawaii shows steadily increasing atmospheric CO_2 levels. This is mirrored by the measurements taken since 1992 at NUIG's atmospheric research station at Mace Head, County Galway (inset) Prepared from information courtesy of Dr. Pieter Tans, NOAA/ESRL (Hawaii), and Michel Ramonet, IPSL (France), and Colin O'Dowd, NUI Galway (Mace Head).

Not all CO_2 emitted has stayed in the atmosphere; approximately 50% has been taken up by the oceans and land biosphere combined (Solomon *et al*., 2007), with over a third of net emissions being absorbed by the oceans (42 ± 7% (118 ± 19 billion tonnes - GtC)) between 1750 and 1994 and 37% ± 7% (53 ± 9 GtC) between 1980 and 2005 (Sabine *et al*., 2004, Bindoff *et al.,* 2007)). The global oceans net CO_2 sink is 1.8 $PgCyr^{-1}$ continental margins and estuaries are a small net source at (~0.15 $PgCyr^{-1}$) (Doney *et al*., 2009a).

This terrestrial and oceanic absorption of CO_2 has reduced its accumulation in the atmosphere and so mitigated the negative effects of CO_2 emissions. However, the current absorption rate of CO_2, which is approximately ten times above the historical rate (Feely *et al*., 2006; Schubert *et al*., 2006), has also led to a rapid and persistent change in the carbonate system (i.e. pCO_2, pH, alkalinity and calcium carbonate saturation state) of the world oceans (Zeebe and Wolf-Gladrow 2001; Guinotte and Fabry 2008). This change in the chemistry of marine systems is termed ocean acidification.

The most significant alteration to the marine carbonate system since the beginning of the industrial revolution has been the increased production of carbonic acid which occurs when CO_2 dissolves in sea water. This has resulted in a decrease in the average pH of global ocean surface waters from ~8.2 to ~8.1 units (Raven *et al*., 2005; Orr *et al*., 2005; Figure 1.2). While the pH change may not appear to be substantial, the pH scale is logarithmic which means that a one unit decrease in pH is equal to a ten-fold increase in acidity (see Box 1). Thus the pH decrease already experienced by the oceans corresponds to about a 30% increase in the concentration of H^+ ions (Zeebe and Wolf-Gladrow 2001). A further effect of increased CO_2 absorption is a decrease in the concentration of carbonate ions, the basic building block of the shells and skeletons of many marine organisms. Based on projections of atmospheric CO_2 emissions from Intergovernmental Panel on Climate Change (IPCC), a drop of 0.4 ± 0.1 units by 2100 relative to pre-industrial conditions is highly probable (Caldeira and Wickett, 2003; Meehl *et al*., 2007; Figure 1.2).

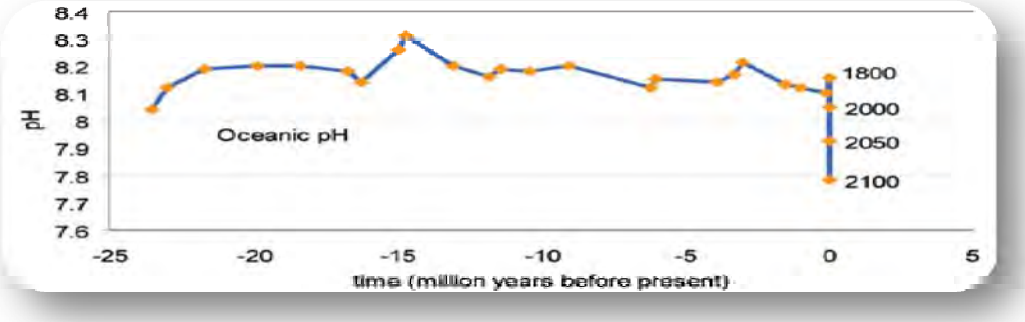


Figure 1.2: Model-derived future predictions (based on IPCC mean scenarios) show that the pH of the oceans could decrease below 8 before 2050, an event which has not occurred in the last 20 million years [From Pearson and Palmer (2000), adapted by Turley* et al*. (2006)]

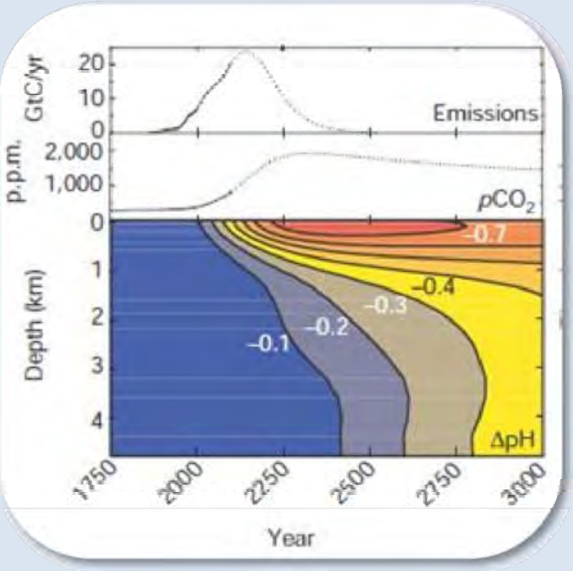
The magnitude of the pH change projected for 2100 has probably not occurred for more than 200 million years (Feely *et al*., 2004). Despite this, the current and future impacts have only recently come to the attention of scientists and policy makers. Research into the consequences of ocean acidification is therefore in its infancy.

Increased acidification rates will have potentially major implications for organisms and ecosystem processes from the inshore and coastal zones to the open ocean (Orr *et al*., 2005; Raven *et al*., 2005; Fabry *et al*., 2008; Guinotte and Fabry, 2008; ICES, 2008). Whilst the most important ramifications are likely to be experienced by calcifiers or organisms that build structures of calcium carbonate ($CaCO_3$), all marine organisms may potentially be affected directly or indirectly, for example by altered seawater chemistry (Box 2), (European Science Foundation, 2009; Gattuso, 2009; IAP, 2009).

Box 1. What is pH and Ocean Acidification?

The pH scale range is from 0 (very acidic) to 14 (very alkaline), with 7 being neutral pH (pure water). The pH of a substance is determined by the concentration of hydrogen ions (H^+) on a logarithmic scale. This is calculated as $pH = -\log_{10} [H^+]$.

The average pH of the surface global ocean has dropped from ~8.2 to ~8.1 pH units as a result of the absorption of anthropogenic CO_2 into the oceans since the start of the industrial revolution. *Ocean Acidification* is the term given to the ongoing decrease in pH. It is important to note that although the pH is dropping, if all the remaining fossil fuels were burnt, the maximum average reduction would be 0.77 (Caldeira & Wickett, 2003). Therefore, while the increase in H^+ implies increasing acidification, it is not projected that the oceans will become acidic, i.e. reach a pH of less than 7. The oceans will in fact become slightly less alkaline.



The figure shows atmospheric CO_2 emissions, historical atmospheric CO_2 levels and predicted CO_2 concentrations from the Intergovernmental Panel on Climate Change's IS92a emission scenario together with changes in ocean pH based on horizontally averaged chemistry (Reproduced from Caldeira and Wickett, 2003).

pH can be measured directly, using a pH probe calibrated with a reference pH (Wootton *et al*., 2008, Section 1.3) or a spectrophotometric technique (Clayton & Byrne (1993) as used in Santana-Casiano *et al*. (2007). There are technical problems in determining pH in high salinity samples using probes. Consequently the preferred approach for high precision monitoring of ocean acidification is to indirectly determine pH from measurements of dissolved inorganic carbon (DIC), total alkalinity (TA), temperature and salinity data. pH can be calculated using methodologies in *inter alia* Dickson *et al*. (2007). Whilst different methods make the comparison of pH measurements difficult, it has been recently advised that carbonate monitoring systems should be standardised and certified reference material used (Section 5.3.1).

1.2 Context of the Report

Ocean acidification has the potential to cause large-scale changes in the structure of ecosystems and may pose a greater threat to ocean ecosystems than the effects of global warming or local effects of fishing.

Wright and Davidson, 2006

Even though the chemical process of CO_2 absorption by the oceans is now relatively well understood much less information is available on how chemical and biological processes respond to increased acidification (Raven *et al*., 2005). Forecasting the impacts of this process is therefore an intricate and considerable task. Geological records have shown that past episodes of ocean acidification, which took place at much slower rates, were associated with mass extinctions of calcareous marine organisms (Zachos, 2005), increasing concern over the impact of more rapid present acidification rates.

There is a growing consensus in the research community that ocean acidification is potentially one of the greatest threats to the world's oceans today (Zeebe *et al*., 2008; Guinotte and Fabry, 2008; Orr *et al*., 2005). As a result organisations and policy makers on both the national and international level have shown increased recognition of this issue and have begun to investigate the possible implications (Raven *et al*., 2005 (Royal Society); MCCIP, 2006, 2008; OSPAR, 2006; Schubert *et al*., 2006 (WBGU); Kleypas *et al*., 2006; ICES 2008; Monaco Declaration 2008; European Science Foundation, 2009; Gattuso, 2009; IAP 2009).

This report aims to provide a concise overview of the present state of scientific knowledge of ocean acidification and its likely impacts on organisms and ocean ecosystems. This is particularly relevant in the context of the possible implications and ramifications of ocean acidification for Irish marine areas. The report is a deliverable from a collaborative project, 'The impacts of increased atmospheric CO_2 on ocean chemistry and ecosystems', between the National University of Ireland Galway (NUI Galway) and the Marine Institute and is SSTI-funded under the Sea Change 'Rapid Ocean Climate Change' initiative.

This report is relevant to policy makers on climate change and environmental protection, and researchers in the areas of ocean, atmosphere and climate science. Furthermore, it is relevant to members of the general public who are interested in improving their understanding of the impact of anthropogenic activities and climate change on the oceans.

1.3 Evidence for pH Change

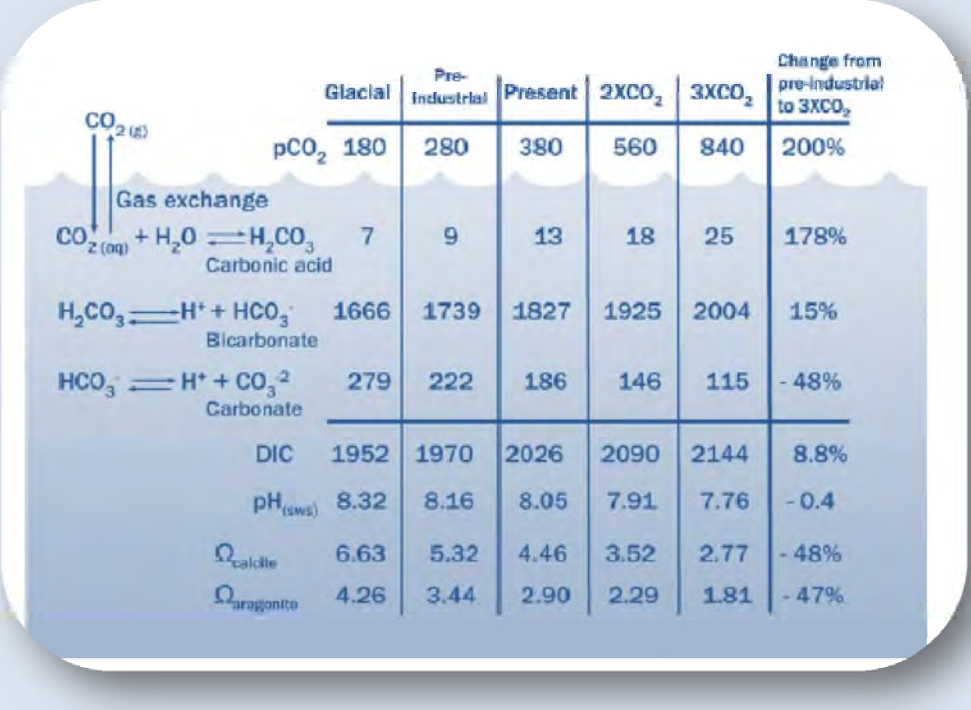
The pH unit change over the past 150 years is probably the greatest seen over the past several million years.

Turley et al.*, 2006*

Anthropogenic perturbations of ocean chemistry and acid-base status have been detectable in upper ocean layers for some decades (Chen and Millero, 1979; Brewer *et al*., 1997; IPCC 2007). Uptake estimations of anthropogenic CO_2 between 1750 and 1994 have enabled researchers to calculate a decrease in surface pH of 0.1 units over the global ocean from the slightly alkaline pre-industrial pH value of ~ 8.2 units (Sabine *et al*., 2004; Raven *et al*., 2005). Localised decreases show that the lowest decrease (0.06 units) has occurred in the tropics and subtropics, while the highest decrease (0.12 units) has taken place at high latitudes. This is consistent with the lower buffering capacity of the high latitudes compared to the low latitudes (IPCC, 2007).

Box 2. The Oceanic Carbon Cycle

As the atmospheric CO_2 concentration increases, the difference in partial pressure between the atmosphere and the seawater results in absorption of anthropogenic CO_2 into the surface layer of the ocean (Henry's Law). As CO_2 dissolves in the surface ocean, it reacts with water to form carbonic acid (H_2CO_3), which dissociates by losing hydrogen ions (H+) to form bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}). Thus CO_2 is stored in the oceans as dissolved inorganic carbon (DIC), which is the sum of the concentrations of these carbon compounds. Currently, <1% of DIC remains in the form of CO_2 (including tiny amounts of H_2CO_3), while the rest is in the form of HCO_3^- (~90 %) or CO_3^{2-} (~9 %). The projected increase in atmospheric CO_2 to about 750 ppm by 2100 is estimated to almost triple surface water CO_2 concentrations relative to preindustrial values (Rost *et al.*, 2008). As a result, DIC will increase and the equilibrium of the carbonate system will shift to higher aqueous CO_2 and HCO_3^- levels, while CO_3^{2-}concentrations and pH will decrease (Rost *et al.*, 2008). The CO_3^{2-} concentration in the ocean surface layer has already dropped by 10% compared to the preindustrial level (Orr *et al.*, 2005). The future CO_2 absorption will result in a 2.5 fold increase in H^+ ions, a resultant 0.3-0.4 pH drop and a 50 % decrease in CO_3^{2-} concentrations by 2100 (Wolf-Gladrow *et al.*, 1999; Caldeira & Wickett 2003; Orr *et al.*, 2005).



	Glacial	Pre-Industrial	Present	$2XCO_2$	$3XCO_2$	Change from pre-industrial to $3XCO_2$
pCO_2	180	280	380	560	840	200%
$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_3$ Carbonic acid	7	9	13	18	25	178%
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ Bicarbonate	1666	1739	1827	1925	2004	15%
$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ Carbonate	279	222	186	146	115	- 48%
DIC	1952	1970	2026	2090	2144	8.8%
$pH_{(sws)}$	8.32	8.16	8.05	7.91	7.76	- 0.4
$\Omega_{calcite}$	6.63	5.32	4.46	3.52	2.77	- 48%
$\Omega_{aragonite}$	4.26	3.44	2.90	2.29	1.81	- 47%

Figure reproduced with permission from Fabry et al., 2008. Units: $CO_{2(g)}$ ppmv; DIC species mmol kg^{-1}; pH as seawater scale and Ω is aragonite and calcite saturation state of average surface seawater. See Fabry **et al.*****, (2008) for assumptions used.***

Box 2 continued. The Oceanic Carbon Cycle

The ability of the ocean to absorb atmospheric CO_2 over century and longer timescales will depend on the amount of calcium carbonate ($CaCO_3$) dissolution in the water column or sediments (Doney *et al*., 2009). Calcium carbonate, from the shells and skeletons of marine organisms, is either dissolved in the water column or is deposited in shallow or deep-sea sediments (Berelson *et al.*, 2007). The formation and dissolution rates of calcium carbonate will depend on the saturation state which is in turn dependant on a number of environmental factors (Doney *et al*., 2009). The reduction in CO_3^{2-} concentration, and hence reduction in the calcium carbonate saturation state, has significant impacts for marine calcifiers.

The amount of carbon absorbed by the oceans over the past two centuries (118 ± 19 billion tonnes-GtC) as a result of human activity has been measured through global oceans observation programmes such as the World Ocean Circulation Experiment and the Joint Global Ocean Flux Study in the 1990s. The exchange fluxes of CO_2 across the air-water surface boundary, and hence the amount of anthropogenic CO_2 stored in the oceans, is dependent on local wind patterns, horizontal ocean currents, vertical exchange and biological processes (OSPAR, 2006). As a result, the absorption of CO_2 by the oceans is spatially heterogeneous. The highest uptake rates of CO_2 are found in the North Atlantic. This ocean basin stores 23% of the global oceanic anthropogenic CO_2 even though it covers only 15% of the global ocean area (Sabine *et al*., 2004). Coastal marine areas can behave either as a sink or a source of CO_2 to the atmosphere. For example if estuaries and salt marshes are taken into account, the coastal ocean behaves as a source for atmospheric CO_2 and the uptake of atmospheric CO_2 from the global ocean decreases by 12% (Borges, 2005). At high and subtropical and tropical latitudes, the coastal ocean is a source of CO_2 but at temperate latitudes, it is a moderate sink. Upscaling from coastal oceans is constrained by the poor amount of data sets available and accuracy of estimations of the surface area of inner estuaries (Borges, 2005). Anthropogenic activities such as fossil fuel combustion and agriculture also produce atmospheric inputs of dissociation products of strong acids (HNO_3 and H_2SO_4) and bases (NH_3) to the coastal and open ocean. These inputs are particularly important close to major source regions in coastal regions, primarily in the northern hemisphere, and cause decreases in surface seawater alkalinity, pH, and DIC (Doney *et al*., 2007).

Recently published time-series data have confirmed that, while many factors (biological, physical) can alter pH over different temporal scales, localised inter-annual decrease in pH levels are being recorded which can be linked to increasing atmospheric CO_2. An 8-year high resolution time-series in the temperate region of the Eastern Pacific has revealed a 0.045 pH unit yr^{-1} decline from direct measurements of pH levels (Wootton *et al*., 2008). A time-series of seawater CO_2 data collected in the subtropical gyre of the North Atlantic near Bermuda shows a decline in seawater pH of 0.0017 ± 0.0001 pH units yr^{-1} since 1983, relating primarily to the uptake of anthropogenic CO_2 (Bates and Peters, 2007). Direct measurements of pH from the European Station for Time Series in the Ocean at the Canary Islands (ESTOC) located in the Atlantic subtropical gyre has showed an inter-annual reduction averaging 0.0017 ± 0.0004 pH units yr^{-1} between 1995 and 2004 (Santana-Casiano *et al*., 2007). A 25-year time-series (1983-2008) of winter observations in Icelandic waters reveals that the local rates of pH surface water decrease are 0.0014 yr^{-1} for the northern Irminger Sea and 0.0024 yr^{-1} for the Iceland Sea (Olafsson *et al.,* 2008).

A recent study of a 20-year data set (1988-2008) from Station ALOHA in the central North Pacific Ocean near Hawaii has shown a long term decreasing trend of 0.0019 ± 0.0002 pH units yr^{-1} (Dore *et al*., 2009) while a strong seasonal pH oscillation driven by temperature, mixing and net photosynthetic CO_2 assimilation was also evident.

While CO_2 emissions are globally the most important cause of ocean acidification, fossil fuel combustion and agriculture result in atmospheric inputs of dissociation products of strong acids (HNO_3 and H_2SO_4) and bases (NH_3) to the coastal and open ocean (Doney *et al*., 2007). Furthermore, coastal ecosystems can receive inputs of acidic waters from river water and as a result of terrigenous materials and interactions with bottom sediments (Salisbury *et al*., 2008). Although these inputs contribute only a small fraction of the acidification caused by anthropogenic CO_2, they are concentrated in coastal waters where the ecosystem response will have more important ecological and socio-economic responses.

1.4 Future acidification projections

Projected changes in ocean carbonate chemistry should serve as a guideline for policy protocols that identify CO_2 *emission targets to reduce the effects of human-made ocean acidification.*

Zeebe et al.*, 2008*

In order to understand past changes in ocean carbon cycling and study future scenarios, numerical ocean circulation carbon cycle models that predict the uptake of anthropogenic CO_2 in the oceans are used (Caldeira and Wickett, 2003, 2005; Heinze, 2004; Orr *et al*., 2005). For a ‘business-as-usual’ emission scenario IS92a (see Box 3) CO_2 emissions to the atmosphere are projected to grow at a rate of 2% yr^{-1} until 2100 (Hansen *et al*., 2007).

By the year 2100, the CO_2 concentration are projected to rise by about a factor of two, relative to the present value to *ca* 750 ppmv, and could increase by a factor of three towards the middle of the next century (Houghton *et al*., 2001). This will cause surface seawater pH to further drop by 0.3 and 0.6 pH units, respectively, in addition to the 0.1 unit decrease that has occurred since pre-industrial times (Caldeira and Wickett, 2003, 2005; Riebesell *et al*., 2007). A recent coupled carbon cycle-climate model (Steinacher *et al*., 2009) suggests that the largest pH changes will take place in Arctic surface waters.

Recent field observations on the continental shelf of western North America reveal that ocean acidification is occurring in some areas at a rate faster than that predicted by global ocean models. Feely *et al*. (2008) observed seasonal upwelling of waters with low pH and under-saturated with respect to aragonite onto large portions of the continental shelf. While this upwelling is a natural phenomenon the areal extent of the affected area had not been projected to occur until 2050.

Box 3. Projected Climate Change Scenarios

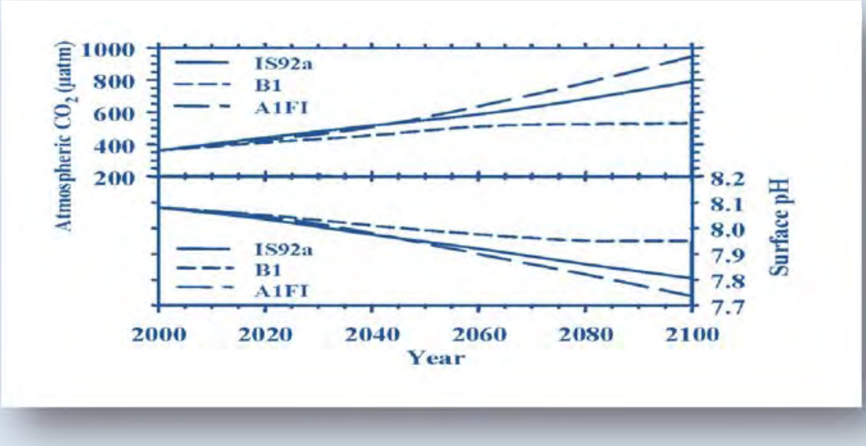
IS92 Scenarios (1992)**:** In 1992 the IPCC released emission scenarios (supplementary report to the IPCC Assessment) to be used for driving global circulation models to develop climate change scenarios. Six alternative IPCC scenarios (IS92a to f) which embodied a wide array of assumptions affecting how future greenhouse gas emissions might evolve in the absence of climate policies beyond those already adopted. IS92a has been widely adopted as a standard 'business-as-usual' scenario for use in impact assessments.

SRES: Special Report on Emission Scenarios (2000).

SRES scenarios cover a finite, albeit a very wide, range of future emissions. A set of scenarios was developed to represent the range of driving forces and emissions in the scenario literature so as to reflect current understanding and knowledge about underlying uncertainties. The set of scenarios consists of four scenario families (A1, A2, B1, and B2), each of which consists of a number of scenarios:

- The A1 storyline is a case of rapid and successful economic development, in which regional average income per capita converge - current distinctions between "poor" and "rich" countries eventually dissolve.
- The A2 scenario family represents a differentiated world. Compared to the A1 storyline it is characterized by lower trade flows, relatively slow capital stock turnover, and slower technological change.
- The central elements of the B1 future are influenced by a high level of environmental and social consciousness, combined with a globally coherent approach to a more sustainable development.

A study of global emissions for 2000-2004 reported an emissions growth rate greater than the most fossil-fuel intensive of the IPCC emissions scenarios (Raupach *et al.*, 2007).



The above figure, courtesy of Victoria Fabry, shows projected increases in atmospheric CO_2 over the next 100 years (top) will be accompanied by reductions in pH (bottom). Even with the most conservative scenarios (B1) a large drop in pH will occur. [SRES scenarios are: IS92a "business-as-usual" CO_2 emissions scenario, and the most and least conservative scenarios, B1 and A1F1, respectively (Reproduced from Fabry *et al.*, 2008)]

1.5 Is the ability of the oceans to absorb CO_2 under threat?

The oceans hold around 38,000 gigatonnes of carbon (GtC). They presently store about 50 times more than the atmosphere and twenty times more than the terrestrial biosphere and soils.

Schubert et al., *2006*

In the past atmospheric CO_2 levels have increased, albeit slowly, such as at the end of the last ice age when the concentration rose by 80 ppmv over a period of 6,000 years (Schubert *et al*., 2006). During this time the slow uptake of CO_2 by the global oceans, was equalled by a slow physical mixing down to the deep sea. As sediments came in contact with the more acidic waters there was dissolution of carbonate resulting in an increase in pH, this allowed the ocean to self-regulate the pH level (Raven *et al.,* 2005). In recent times this self-regulatory process has not had the time to counteract the acidification process and the other alterations to the carbonate system. This is due to the high uptake rates of CO_2 and the slow mixing of surface waters to intermediate (1000m) and deep (4000m) waters.

Canadell *et al*. (2007) estimated the contribution to the increase in atmospheric CO_2 growth rates since 2000, due to the decline in the efficiency of CO_2 sinks on land and oceans, was 18 ± 15%. The efficiency of the global ocean as a carbon sink appears to be reducing. Observational data have shown that from 1750 to 1994 the oceans absorbed 42 ± 7% of net CO_2 emissions, while from 1980-2005 this value was only 37 ± 7% (Bindhoff *et al*., 2007). Although the largest vertically integrated concentrations of CO_2 are found in the North Atlantic (23% of the global oceanic anthropogenic CO_2, Figure 1.3) the sink strength in this ocean is highly variable (Doney *et al*., 2009a). In the early years of the 21st century the North Atlantic absorbed 50% less than in the mid-1990s. Recent data shows that this CO_2 sink is slowly recovering although more long-term observations are needed to better understand this variation and its causes (Friedlingstein *et al*., 2006).

Stratospheric ozone depletion, and the resulting increased ventilation (strong winds) of carbon rich deep waters, have been put forward as processes which has reduced the uptake of CO_2 by the Southern Ocean (Lenton *et al*., 2009). It is proposed that the mixing increases the carbon concentration of the upper ocean, and subsequently decreases the uptake rates through a reduction in the gradient between the atmosphere and the ocean. While uptake is reduced, the increase in surface carbon ventilation leads to an acceleration of ocean acidification.

Reduced absorption can be the result of feedback and climate change induced processes (Doney *et al*., 2009a). As CO_2 is absorbed and the carbonate concentration in the surface layers is reduced there is a lowering of the capacity of the oceans to take up additional CO_2. Climate change in itself will further reduce this uptake capacity through increased temperatures (which lowers the solubility of CO_2 in water) and increased stratification of the water column (which will reduce the mixing and transport of CO_2-rich surface waters to greater depths) (Greenblatt and Sarmiento, 2004; Schubert *et al*., 2006). A further process influencing the uptake capacity of the oceans is the ‘biological pump’. Carbon is transferred to the deep sea from surface layers through the sinking of organic material such as phytoplankton, grazers, predators and bacteria (Eppley and Peterson, 1979). As this material sinks, a large amount is broken down and recycled, while that which reaches the bottom is sequestered into the sediments.

This ‘biological pump’ effectively removes CO_2 from the atmosphere for hundreds to millions of years. Elevated levels of CO_2 may decrease the calcification rates of globally abundant calcifying phytoplankton (coccolithophores) or shift their distributions which could impact the $CaCO_3$ budget and ocean carbon cycle as a whole (Armstrong *et al*., 2002; Iglesias-Rodriguez *et al*., 2002). Latest model predictions show that the continued CO_2 emissions will gradually weaken the sink strength of the oceans, resulting in a temporary, but large, increase of CO_2 in the atmosphere (Friedlingstein *et al*., 2006). However, even if the future oceans take up slightly smaller fractions of CO_2 than presently, ocean acidification processes are likely to continue, increase in amplitude, and be with us for centuries.

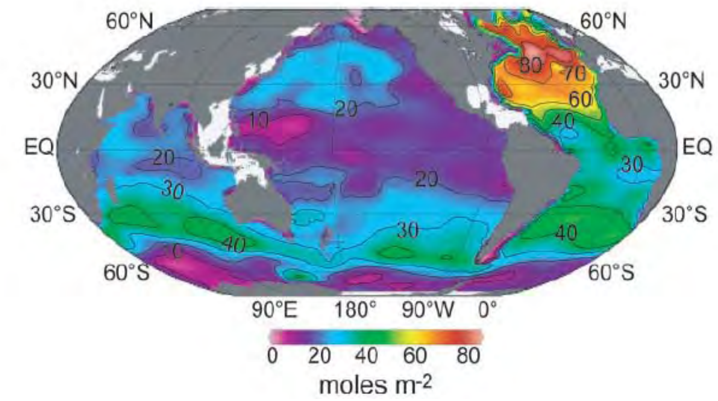


Figure 1.3: Global map of the column inventory (summed from surface to sea floor) of anthropogenic carbon in the ocean from Sabine* et al. *(2004).

1.6 Saturation horizons

The formation and dissolution of calcium carbonate skeletal structures by marine organisms will vary depending on the calcium and carbonate ion concentrations (denoted $[Ca^{2+}]$ and $[CO_3^{2-}]$ respectively) or saturation state of their surrounding water. The saturation state (Ω) can be defined as (Doney *et al*., 2009b): $\Omega = [Ca^{2+}][CO_3^{2-}]/K'_{sp}$.

The apparent solubility product K'_{sp} is dependent on temperature, salinity, pressure and the particular mineral phase; for example, aragonite is approximately 50% more soluble than calcite (Mucci, 1983). As $[Ca^{2+}]$ is closely proportional to salinity, Ω is largely determined by variations in $[CO_3^{2-}]$, which will decrease with the increasing absorption of CO_2 by the oceans.

When Ω is less than 1, the water is under-saturated with respect to calcium carbonate and dissolution is favoured; when the Ω is above 1, precipitation can occur. The solubility of calcium carbonate increases with increasing pressure and decreasing temperature. As a result, cold high-latitude regions and deep waters have lower saturation states, and calcium carbonate dissolution occurs at a faster rate than in tropical zones (Feely *et al.,* 2004). This also means that calcium carbonate shells and skeletons of marine organisms will dissolve more quickly as they sink to deeper waters.

A saturation horizon is the water depth above which supersaturated waters occur ($\Omega>1$) and calcium carbonate can form, and below which waters are under-saturated and hence net dissolution is thermodynamically favoured. Organisms that produce calcium carbonate shells are found above the saturation horizon. Increasing CO_2 absorption by the oceans is decreasing the saturation state of calcium carbonate and raising the saturation horizons of the oceans closer to the surface (Raven *et al*., 2005). As the saturation horizons drift upwards, the supersaturated upper layer of the sea will become thinner and calcium carbonate formation will become more and more vertically confined. This will have considerable consequences for calcifying marine organisms. Calcifiers that produce more soluble aragonite (corals and pteropods) have a higher vulnerability than those that construct more stable calcite shells (coccolithophores, foraminifera).

Changes in the saturation state and shoaling of horizons will not be uniform as anthropogenic CO_2 does not enter the oceans at the same rate in all geographic areas and because some areas have naturally lower saturation states than others. Evidence of aragonite under-saturation in the thermocline regions of the North Pacific and Indian Oceans has been observed (Feely *et al*., 2002; Sabine *et al*., 2002). Recent studies have shown a seasonal upwelling of seawater with a Ω_{arag} <1.0 onto the western continental shelf of North America (Feely *et al*., 2008), and an increase in the areal extent of shallow under-saturated regions in the eastern tropical Atlantic (Chung *et al*., 2003, 2004).

Although the aragonite saturation horizon for the North Atlantic is currently very deep (~2000m, Feely *et al*., 2004), in the eastern South and North Atlantic, migration upward of approximately 80 to 150 m between 50°S and 15°N (Feely *et al.*, 2004) has been observed. Predictions for the North Atlantic for 2100 show that while surface waters will probably remain saturated with respect to aragonite, the aragonite saturation horizon could shoal dramatically; for example, between 50°N and 70°N it may shoal from 2,600 m to 115 m using the IPCC 'business-as-usual IS92a scenario' (CO_2 at 788 ppmv) or to 612m using the IPCC S650 'stabilisation' scenario (CO_2 at 563 ppmv) (Orr *et al*., 2005).

A more recent study (Steinacher *et al.,* 2009) has concluded that within a few decades high latitude waters could become under-saturated with respect to aragonite, and waters above about 50°N are projected to be completely under-saturated in 2100 for the SRES A2 scenario (CO_2 at 840 ppmv). The ramifications of this will be important particularly for cold water corals. Under-saturation events are already being observed; for example in the deep waters off Iceland the invasion of anthropogenic CO_2 is resulting in exposure of the seafloor to under-saturation conditions with respect to aragonite at a rate of 1 km^2 per day (Olafsson *et al*., 2008).

1.7 Impacts of ocean acidification

1.7.1 Ocean life

Marine life is adapted to a range of ambient CO_2 and pH conditions, from the high concentrations found in vent systems, to the fluctuating levels experienced in the intertidal zone. The adaptive responses of the organisms exposed to ambient levels will partially define the extent to which they will react to the progressively lower pH levels in the future.

Biological activity in the oceans takes place primarily in the surface layer through which the sunlight penetrates i.e. the photic zone. This layer is also the area which experiences the highest alterations in carbon chemistry and ocean acidification. Surface dwelling organisms can therefore be directly exposed to rapid alterations in carbonate chemistry. In shelf seas, because they are well mixed in winter, benthic organisms are also exposed to pH variations and will experience the increased levels of atmospheric CO_2 very quickly (ICES, 2008). In the open ocean, the natural pH range, and the likely subsequent change, is a function of depth, with the greatest range in the surface layers.

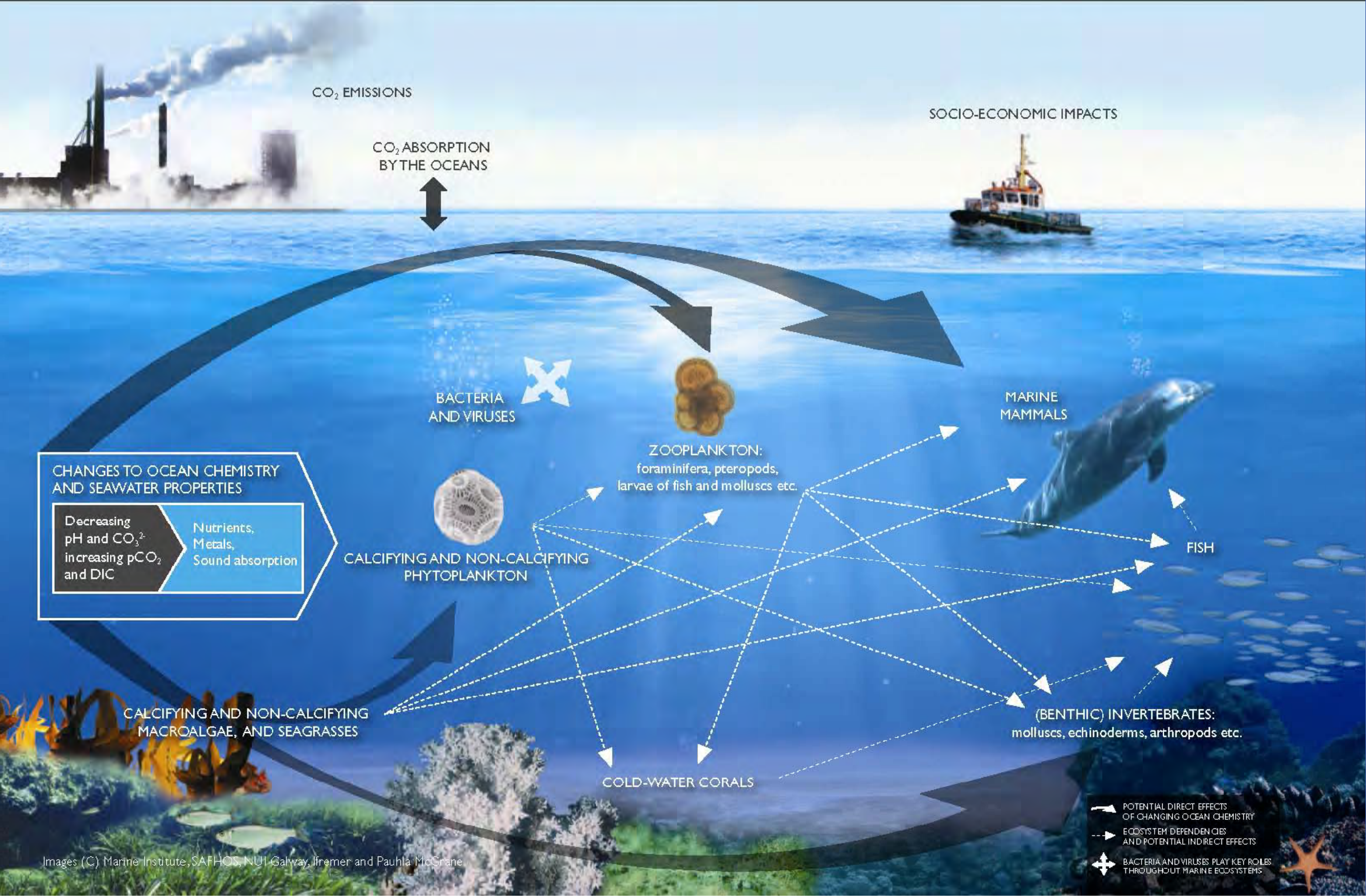
One of the most important and serious implications of changing acidity relates to the building of calcium carbonate shells and plates by marine organisms such as molluscs, corals, echinoderms, foraminifera and calcareous algae (for reviews see Raven *et al*., 2005; Kleypas *et al*., 2006). Increased uptake of CO_2 and concomitant changes in ocean carbon chemistry could lead to a reduction in the rate of calcification and also the corrosion of biogenic calcium carbonate. Most research to date on the effects of ocean acidification has focused on these calcifying organisms, however comparatively little attention has been devoted to the impact of acidification on non-calcifiers, and ecosystem components and processes such as nutrient speciation and availability, trophic interactions, reproduction, metabolism, diseases, etc. which may impact on all organisms but most critically primary producers (Vézina and Hough-Guldberg, 2008).

Rapid modifications due to ocean acidification could have direct effects on a range of physiological processes of marine life at all stages of their life cycle. Indirect effects may influence the interactions between communities at different trophic levels and the availability of nutrients for primary producers. Impacts experienced by any single species, and specifically keystone species (structurally important macroalgae, reef building oysters, sea urchins etc.) may have ramifications throughout all levels of the ecosystem so that a multidisciplinary ecosystem approach to future research in this area is required. Elucidating the impacts on the full range of marine organisms, and in particular on higher trophic levels that rely on calcifiers for shelter and nutrition, will be complex. Nevertheless in the coming decades it will be an extremely important focus area for marine research.

1.7.2 Ocean systems

Ocean acidification will not occur in isolation from the oceanic systems as considerable interaction will occur between the range of localised chemical and biological cycles and larger scale processes. The reduction in calcifying organisms, the shifting of primary producer community dominance away from calcifying phytoplankton in certain ecosystems during specific seasonal periods, and a possible increase in carbon consumption are all likely future events. These would have implications for a number of biological and biogeochemical processes, including perturbations to the cycling of carbon and nitrogen, the aforementioned ‘biological pump’, global food chains and oxygen levels and ‘dead zones’ in the ocean.

OCEAN ACIDIFICATION MAY HAVE DIRECT AND INDIRECT IMPACTS ON MARINE LIFE



CO_2 EMISSIONS

CO_2 ABSORPTION BY THE OCEANS

SOCIO-ECONOMIC IMPACTS

CHANGES TO OCEAN CHEMISTRY AND SEAWATER PROPERTIES

Decreasing pH and CO_3^{2-} increasing pCO_2 and DIC

Nutrients, Metals, Sound absorption

BACTERIA AND VIRUSES

CALCIFYING AND NON-CALCIFYING PHYTOPLANKTON

ZOOPLANKTON: foraminifera, pteropods, larvae of fish and molluscs etc.

MARINE MAMMALS

FISH

CALCIFYING AND NON-CALCIFYING MACROALGAE, AND SEAGRASSES

COLD-WATER CORALS

(BENTHIC) INVERTEBRATES: molluscs, echinoderms, arthropods etc.

POTENTIAL DIRECT EFFECTS OF CHANGING OCEAN CHEMISTRY

ECOSYSTEM DEPENDENCIES AND POTENTIAL INDIRECT EFFECTS

BACTERIA AND VIRUSES PLAY KEY ROLES THROUGHOUT MARINE ECOSYSTEMS

Images (C) Marine Institute, SAFHOS, NUI Galway, Ifremer and Pauhla McGrane

CHAPTER 2. CONSEQUENCES OF OCEAN ACIDIFICATION

Changes in ocean chemistry precipitated by acidification are likely to exert profound and highly adverse impacts on ocean species and ecosystems.

Burns, 2008

Ocean acidification can be expected to impact a wide range of biological and chemical processes and even small variations in the response of different species (for example, reduced recruitment success) could be amplified over successive generations resulting in major changes through ecosystems (Doney *et al*., 2009b). In this sense, the individual impacts on nutrients, metals, dissolved organic matter, organisms and processes needs to be considered in the context of their possible implications for: the interaction and competition between organisms, food web dynamics, shifts in the spatial and temporal abundances of organisms, habitat structure, and the basic cycling of carbon and nutrients through the ecosystem (Figure 2.1).

Organisms that migrate vertically in the water column and those living in intertidal areas or near hydrothermal vents experience oscillating variations in CO_2 levels and in some cases hypoxia which require specific adaptations for tolerance (Childress and Seibel, 1998; Fabry *et al*., 2008). Although these variations can at times be greater than those expected from ocean acidification it is unknown whether the ability of organisms to adapt to short term variations will ensure their tolerance to chronic ocean acidification such as is expected over the next century (Fabry *et al*., 2008).

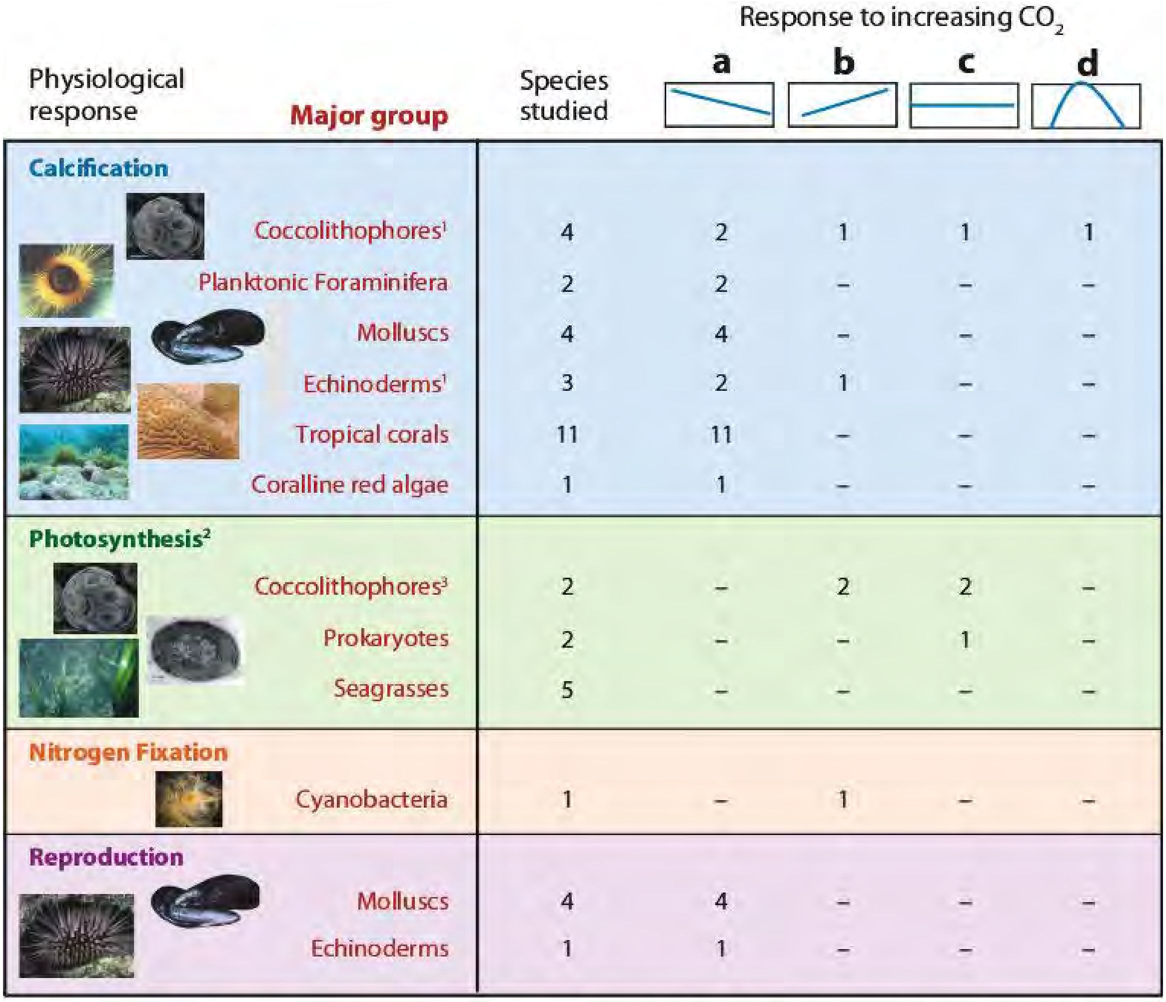
2.1 Calcification

Biogenic calcification first appeared during the Cambrian period (543-490 million years ago). It is thought to have evolved as a detoxification mechanism in response to a corresponding increase in Ca^{2+}, which can be toxic to cellular processes (Brennan *et al*., 2004). The process of calcification in modern day organisms can serve multiple functions such as protection from predation or microbial infections, a cementing and structural component for benthic species, or a ballast method for planktonic organisms.

Ocean acidification will result in a decline in the availability of the chemical constituents needed for calcification making it more difficult and/or require more energy for the formation of biogenic calcium carbonate. Investigations to date show a dramatic but mixed response of calcifying organisms to increased pCO_2 and acidification (Fabry *et al*., 2008). Reduced calcification rates could compromise the fitness and competitive advantage of organisms, resulting in a possible shift towards non-calcifiers in calcium carbonate dominated systems. However, the degree of sensitivity varies between species and organisms revealing the complicated nature of response mechanisms (Doney *et al*., 2009b; Ries *et al*. 2009; Table 2.1).

Opposite Page:
Figure 2.1: Simple ecosystem schematic highlighting potential direct effects of changing ocean chemistry and indirect effects arising from ecosystem dependencies

Table 2.1: ***Experimental studies have shown that species from different groups of marine biota (left) respond in very diverse ways to increased CO_2. The response curves on the right indicate that there can be (a) linear negative, (b) linear positive, (c) level, and (d) nonlinear parabolic responses to increasing levels of seawater pCO_2 for each of the groups (from Doney*** et al. ***2009b). [Note that in some cases strains of the same species exhibited different behaviour in different experiments (cf. Fabry*** et al.***, 2008; Guinotte and Fabry, 2008)]. (Courtesy S. Doney)***



Physiological response	Major group	Species studied	Response to increasing CO_2 a	 b	 c	 d
Calcification						
	Coccolithophores[1]	4	2	1	1	1
	Planktonic Foraminifera	2	2	–	–	–
	Molluscs	4	4	–	–	–
	Echinoderms[1]	3	2	1	–	–
	Tropical corals	11	11	–	–	–
	Coralline red algae	1	1	–	–	–
Photosynthesis[2]						
	Coccolithophores[3]	2	–	2	2	–
	Prokaryotes	2	–	–	1	–
	Seagrasses	5	–	–	–	–
Nitrogen Fixation						
	Cyanobacteria	1	–	1	–	–
Reproduction						
	Molluscs	4	4	–	–	–
	Echinoderms	1	1	–	–	–

1) Increased calcification had substantial physiological cost; 2) Strong interactive effects with nutrient and trace metal availability, light, and temperature; 3) Under nutrient replete conditions.

2.1.1 Response of pelagic calcifiers to ocean acidification

Plankton (drifting organisms found in the water column) such as coccolithophores, foraminifera (calcite secreting) and pteropods (aragonite secreting) account for approximately three quarters of the global marine calcium carbonate production (Schubert *et al*., 2006). As a result they are also responsible for almost all of the export of calcium carbonate to the deep sea, although their respective contributions can vary over regional and temporal scales (Fabry *et al*., 2008). The response of planktonic calcifying organisms to ocean acidification will depend on a large number of factors such as the type of calcium carbonate secreted (calcite, aragonite or amorphous), the impacts of other environmental factors (e.g. temperature, nutrients), the life stage of the organisms and their calcifying mechanism (Kleypas *et al*., 2006; Rost *et al*., 2008).

The phytoplanktonic **coccolithophores** are one of the most abundant marine primary producers found in the oceans. However to date, the response of only 4 of the approximately 250-500 coccolithophores species have been studied (Young *et al*., 2005; Doney *et al*., 2009b). While most studies have reported reduced calcification (25-66%) at elevated pCO_2 levels (Riebesell *et al*., 2000; Zondervan *et al*., 2001, 2002; Sciandra *et al*., 2003; Delille *et al*., 2005; Engel *et al*., 2005), others have shown a doubling in calcification rates (Iglesias-Rodríguez *et al*., 2008), or no significant change (Langer *et al*., 2006). Increases in pCO_2 levels have also been demonstrated to directly affect the cell physiology through an alteration of the net growth rate and elemental ratios of uptake and production (Engel *et al*., 2005). Initial studies have further suggested that increased pCO_2 coupled with under-saturating light intensities (Zondervan *et al*., 2002), nitrogen limitation (Sciandra *et al*., 2003) or trace metal (zinc, iron) limitation can reduce calcification rates or organic carbon production (Schulz *et al*., 2004).

The small, amoeba-like, eukaryotic **foraminifera** are abundant in the oceans. Laboratory experiments have shown that foraminifera shell mass decreases as carbonate ion concentrations decrease (Spero *et al*., 1993; Bijma *et al*., 1999, 2002). A reduction in the shell weights of foraminifera over the last two decades has already been measured in the Southern Ocean (Moy *et al*., 2009). As with coccolithophores, environmental conditions such as temperature and food supply will strongly affect calcification (Fabry *et al*., 2008).

Shelled **pteropods** are planktonic snails and an important component of polar and subpolar ecosystems (Bathmann *et al*., 1991; Pane *et al*., 2004). Data for *Clio pyramidata* (species of pteropod) indicates that when the saturation state reaches levels projected for the Southern Ocean surface waters by 2100 ($\Omega_{arag}< 1.0$) net dissolution will occur (Orr *et al*., 2005; Fabry *et al*., 2008; Figure 2.2). A recent study has shown that decreases in shell weights are already occurring in the Southern Ocean (Roberts *et al*., 2008).

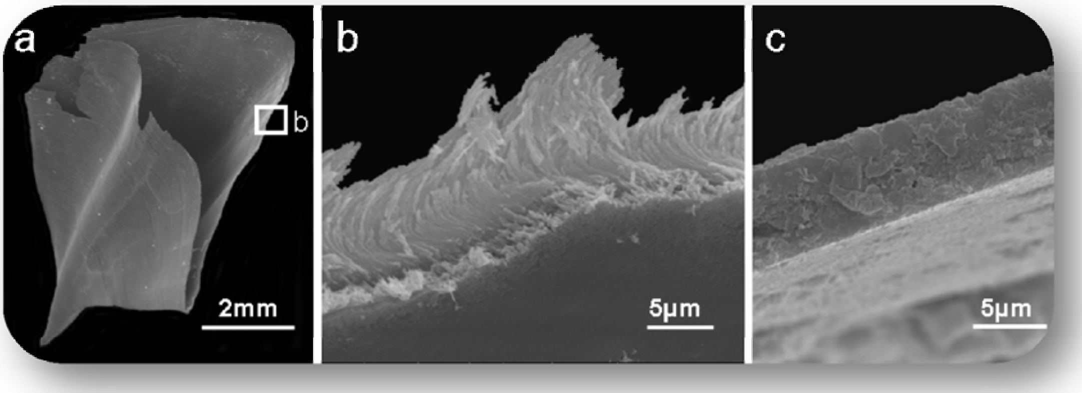


Figure 2.2: When a pteropod* (Clio pyramidata) *was placed in a closed container for 48 hours (a), the respiration of the animal forced the aragonite saturation state to Ω = 1, and resulted in partial dissolution of the shell. SEM photographs, taken at the end of the experiment of a magnified portion of the shell reveals dissolution of aragonitic rods in the leading edge of the shell (b); this can be compared to the magnified leading edge of the shell of a control animal incubated in seawater that remained supersaturated with aragonite for the duration of the experiment (c). (from Fabry* et al.*, 2008)

Examination of Atlantic Ocean sediments from the last glacial maximum suggests that adaptation to changing pCO_2 concentrations is possible. The shells of the coccolithophore *Coccolithus leptoporus* exhibited no malformations during this period when surface water pCO_2 was approximately 200 µatm. This suggests that this species subsequently adjusted to the elevated pCO_2 levels found today (Doney *et al*., 2009b). Interestingly, a recent study of a high resolution sediment core showed a clear increase in the average coccolithophore mass from 1960-2000 that follows the rise in atmospheric CO_2 (Iglesias-Rodríguez *et al*., 2008). This implies that at the current time there are gaps in our knowledge of how species will evolve and adapt to changing carbonate chemistry, and further investigation is required.

2.1.2 Response of benthic calcifiers to ocean acidification

The major benthic calcifying organisms include corals, calcifying macroalgae, benthic foraminifera, molluscs and echinodermata. A recent review showed that for a suite of benthic species studied to date, calcification rates can decrease by 3% to 60% for a doubling in pCO_2 (Kleypas *et al*., 2006).

2.1.2.1 Corals

The hard skeletons produced by coral species and calcifying algae is thought to elevate the organism above the substrate into higher light and better flow conditions, increase competitiveness for space, provide protection from predation and in the case of tropical corals, provides protection from periodic natural events such as tsunamis and cyclones. Ocean acidification and decreased calcification rates may therefore have potentially dramatic affects on the long-term survival of these reef systems (Gattuso *et al*., 1998; Doney *et al*., 2009b).

As early as 2050 the average atmospheric CO_2 could reach 560 ppmv, and at this level **tropical coral** calcification rates would be reduced by *ca* 30% due to insufficient aragonite saturation (Guinotte and Fabry, 2008; Monaco Declaration, 2009). Furthermore, rates of calcification would also be exceeded by reef erosion at this CO_2 concentration, and in conjunction with the impacts of increasing temperature and nutrient changes is expected to severely alter reef systems (Burns, 2008; Kleypas *et al*., 2006; Orr *et al*., 2005).

A study of 69 reefs of the Great Barrier Reef has shown that calcification has already declined by 14.2% since 1990 (De'Ath *et al*., 2009). While the specific cause of this decline is unverified, increasing temperature coupled with a declining saturation state of aragonite has been proposed (De'Ath *et al*., 2009). In a recent study two species of corals exposed to highly acidified water (pH ~ 7.4) completely lost their skeletons, remained healthy throughout the study (Figure 2.3), and re-grew their skeletons after being returned to seawater of normal pH (Fine and Tchernov, 2007).

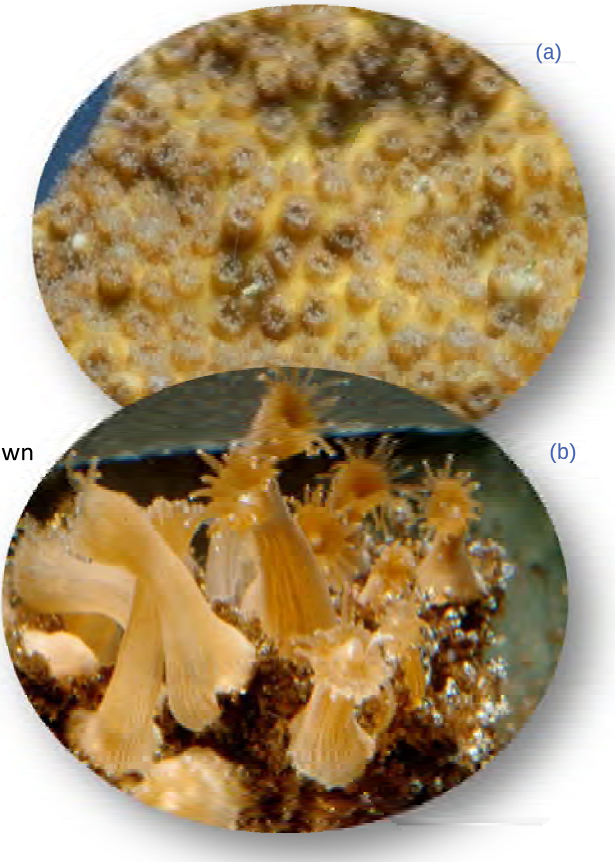


Figure 2.3(a): After exposure to acidified seawater (pH = 7.4) for 12 months the scleractinian coral (*Oculina patagonica*) exhibited complete skeleton dissolution (b) and the biomass of the polyps were three times as high as those of a control colony exposed to a pH of 8.2 for the same period (a). The skeleton free corals survived the 12 month exposure period and calcified and reformed colonies when returned to ambient pH conditions. Reprinted with permission from AAAS (from Fine & Tchernov, 2007.

Courtesy of M. Fine, photo credit Avinoam Breitstein).

Although further study is required these preliminary findings are supported by records of the sudden reappearance of scleractinian corals *ca* 14 million years after the Permian extinction event, suggesting that some corals species could exist as 'naked corals' and may be able to adapt until ocean chemistry becomes favourable for skeletal formation (Stanley and Fautin, 2001).

Cold water corals build highly complex carbonate (aragonite) structures that provide habitats for many organisms and support fisheries (Kleypas *et al*., 2006; Doney *et al*., 2009b). A recent study has shown that on exposure to lower pH the coral *Lophelia pertusa* exhibits reduced calcification (Maier *et al*., 2009; Box 4).

The maximum depth of these species appears to coincide with that of the aragonite saturation horizon which reaches an average depth of > 2000m in the North Atlantic (Feely *et al*., 2004). Increased ocean acidification and a decrease in the depth of aragonite saturation horizon can be anticipated to reduce the depth distribution of the North Atlantic corals. The deepest communities will experience under-saturated conditions, and therefore be affected first (Feely *et al*., 2004, Doney *et al*., 2009b). Projections suggest that 70% of deep water corals will be under-saturated with respect to aragonite by 2099 (Guinotte *et al*., 2006).

Box 4. The cold-water coral *Lophelia pertusa* exhibits reduced calcification when exposed to lower pH (Maier *et al*., 2009).

The cold-water coral *Lophelia pertusa* builds reef-like structures in the deep oceans (30-1000 m) and their distribution is believed to be largely controlled by temperature (4-12 °C). These slow-growing bioherms are likely to be one of the first affected by ocean acidification.

Deep bottom trawling methods are known to destroy large areas of cold-water coral bioherms (Hall-Spencer *et al*., 2002, but more recently climate change induced problems such as temperature change and acidification has been recognised as a threat. During a cruise in Skagerrak in the North Sea, polyps were exposed to ambient and lowered (by 0.15 and 0.3 units) pH levels. Growth rate was measured using calcium-45 labelling. The pH reduction led to a strong decrease in calcification, 30 to 56%, respectively. The growth reduction was strongest for faster growing young polyps (59%) than for older polyps (40%).

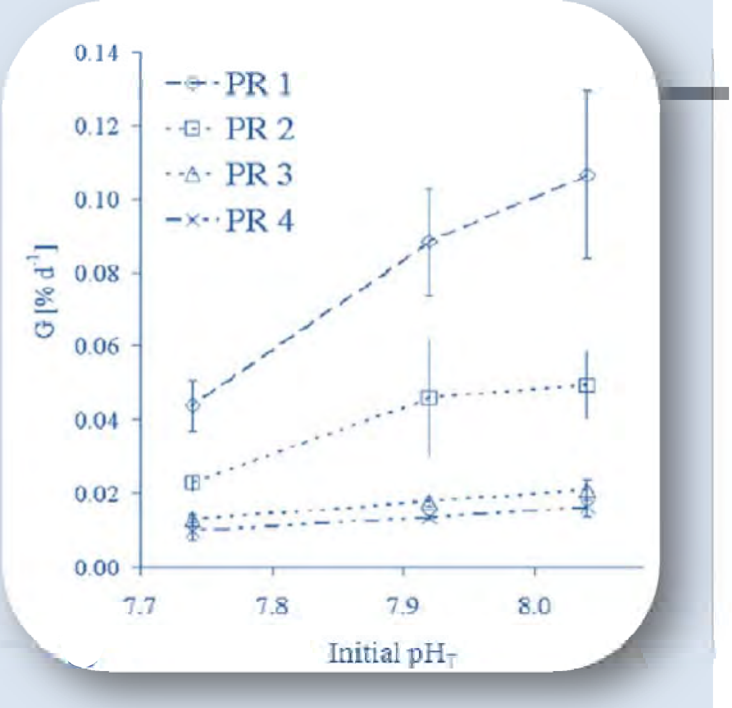


Figure courtesy of C. Maier

Nevertheless *L. pertusa* revealed a positive net calcification at an aragonite saturation state of below 1. This may indicate some adaption to an environment which is already low in aragonite saturation.

2.1.2.2. Benthic calcifying algae

The calcifying green algal genus ***Halimeda*** and **coralline red algae** (e.g. maërl) are globally important but often overlooked calcifiers (Milliman and Drolex, 1996; Foster 2001; Rees *et al*., 2007). *Halimeda* can be important habitats for adult fish and may serve as nursery grounds for juvenile fish and invertebrates (Beck *et al*., 2003).

Red coralline algae are also an important food source for several species of sea urchins, fish and molluscs (Guinotte and Fabry, 2008). At CO_2 concentrations twice those of current day levels, reductions in growth (40%), recruitment (78%), total area cover (92%), and increases in non-calcifying algae have been observed (Buddemeiser 2007; Kuffner *et al*., 2008, Figure 2.4).

Figure 2.4: A seven-week experiment revealed that the recruitment rate and growth of crustose coralline algae can be severely inhibited due to elevated levels of pCO_2 (765 µatm) (right cylinder); while the percentage of non-calcifying algae can increase. An adjacent control cylinder (left, 400 ± 47 µatm pCO_2, ~ contemporary CO_2 levels) exhibited normal recruitment at the end of the experiment (with permission from Kuffner **et al.*****, 2008).***

2.1.2.3 Benthic invertebrates

Calcification rates in **mussel** (*Mytilus edulis*) and **oyster** (*Crassostrea gigas*) species have been shown to decrease by 25% and 10% respectively in response to exposure to 740 ppmv CO_2 concentrations as predicted for 2100 by the IS92a emissions scenario (Gazeau *et al*., 2007). However, one oyster species (*Saccostrea glomerata*) selectively bred to resist disease, has shown more resistance to acidification impacts (Parker *et al*., 2008), which suggests that under the right circumstances some organisms may be able to adapt to some degree.

Echinoderms (sea urchins, star fish and brittle stars) can be important keystone predators which have a large impact on the functioning and structure of coastal ecosystems. The calcite structures of these organisms contain larger amounts of magnesium which dissolves far more readily than aragonite under increased pCO_2 conditions. Reduced shell growth has been observed in two sea urchin species when grown at 560 ppmv over a 6-month period (Shirayama and Thornton, 2005).

While adult gastropods and bivalves secrete aragonite or calcite many **larval species**, (e.g. clam, *Mercenaria mercenaria*, oyster, *C. gigas*) produce more soluble amphorous calcium carbonate as a transient precursor to adult shells and are more vulnerable to acidification during their different life-cycle stages (Weiss *et al*., 2002, Figure 2.5). Reduced fertilization success, development rates, larval size, larval malformation or lack of mineralization have been observed in species of sea urchins, oysters and clams with increasing CO_2 (Green *et al*., 2004; Kurihara and Shirayama, 2004; Kurihara *et al*., 2007). A recent study (Miller *et al*., 2009) demonstrated that under a range of pCO_2 treatments (280-800 µatm) the veliger larvae of two oyster species (*C. virginica, C. ariakensis*) showed differing results in terms of shell area and calcium content, although both species did show net calcification and growth. These results suggest that biological responses can be species-specific and more complex than reported previously.

Calcium carbonate skeletal elements are also present in other benthic invertebrates such as crustaceans, cnidarians, sponges, bryozoans, annelids, brachiopods and tunicates. However to date no data are available on the impact of increased acidification on these organisms (Fabry *et al*., 2008).

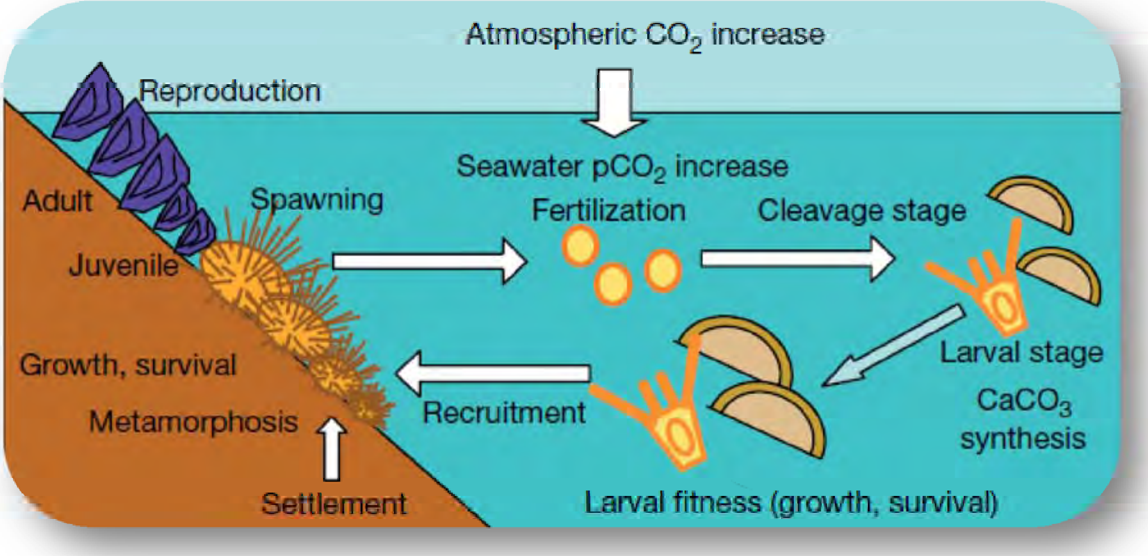


Figure 2..5: Ocean acidification can affect marine organisms in different ways during their entire life cycle. For benthic calcifiers this cycle can include stages which include reproduction, fertilization, planktonic larva, settlement, metamorphosis, juvenile and benthic adult stages (Kurihara, 2008). In some cases it has been shown that the early stages of the cycle could be the most vulnerable to ocean acidification.

2.1.3 Gravity sensory receptors

Many zooplankton, benthic invertebrates and fish species possess statoliths, statocysts, or statocontia which are gravity sensory receptors thought to be mainly amorphous Ca-Mg-phosphate, gypsum or aragonite (Lowenstam and Weiner, 1989). Statocysts in planktonic gymnosome snails are also actively involved in the motor neural programme that underlies search movements for prey during hunting (Levi *et al*., 2004). The effect, if any, of ocean acidification on such gravity receptors has not as yet been investigated but will depend on the ability of the organisms to regulate the acid-base balance in the tissues surrounding these structures.

2.2 Photosynthesis and primary productivity

Marine **phytoplankton** (diatoms, coccolithophores, dinoflagellates, cyanobacteria, etc.) are responsible for approximately 50% of the global biological uptake of CO_2 and at the base of most marine food webs (Field *et al*., 1998). As CO_2 represents only 1% of the reservoir of dissolved inorganic carbon in the ocean the enzyme involved in photosynthesis, rubisco, operates at low efficiency (Raven and Johnston, 1991). Studies have shown a small increase (10% or less) in the rate of photosynthesis and CO_2 uptake with a doubling in seawater CO_2 concentrations (Raven *et al*., 2005). A mesocosm study showed a 27% increased uptake of CO_2 in a natural phytoplankton community with atmospheric concentrations of 700 ppmv (Riebesell *et al*., 2007). Furthermore, the concentration of excreted transparent exopolymeric particles (TEP), which facilitates the aggregation and sinking of organic material, increased four-fold (Arrigo *et al*., 2007). Thus increased CO_2 may lead indirectly to increased sinking of organic carbon from the surface sea layers and a subsequent enhancement of CO_2 absorption by the ocean (Riebesell *et al*., 2007).

However, various groups of phytoplankton studied have been shown to exhibit different responses to increased pCO_2 and pH due to differences in the type of carbon assimilated (CO_2 versus HCO_3^-) and differences in the photosynthetic saturation rates. Furthermore, the impact of increased CO_2 availability for photosynthesis will also depend on other environmental parameters such as nutrient availability and temperature. In areas where nutrients, such as nitrate, are limiting, primary production will not necessarily be increased due to the higher CO_2 in seawater. Global increases in surface seawater temperature are expected to lead to increased stratification and therefore decreased exchange with nutrient-rich deeper waters. This has been related to an overall observed decrease in biomass and productivity on a global basis (Behrenfeld *et al*., 2006) but different effects can be expected in eutrophic and coastal regions.

Relatively little information is available on the influence of ocean acidification and high CO_2 levels on **macroalgal** species (Raven *et al*., 2005). The recent work of Hall-Spencer *et al*. (2008) does however show that at a naturally occurring CO_2 vent site a suite of algal genera proved to be resilient to naturally high pCO_2 (for example the genera *Caulerpa, Cladophora, Asparagopsis, Dictyota* and *Sargassum*), some of which include invasive alien species.

Seagrasses form biologically rich and productive marine ecosystems which also represent critical nursery grounds for fish, invertebrates and molluscs. As they use CO_2 rather than bicarbonate (HCO_3^-) for photosynthesis, any increase in CO_2 levels will be beneficial to these species. Indeed, they respond with higher biomass, productivity and proliferation when exposed to increased CO_2 levels (Zimmerman *et al*., 1997; Palacios and Zimmerman, 2007; Guinotte and Fabry, 2008). While this should support organisms that live in these ecosystems, negative impacts of increased temperature on vegetative growth also need to be considered (Ehlers *et al*., 2008).

Reduced pH may have direct effects on nutrient uptake by photosynthetic organisms through changing chelating compounds needed for nutrient uptake or changes in the cell surface structure affecting binding sites. Thus ocean acidification could counteract beneficial effects of increased primary productivity, although predictions are currently difficult.

2.3 Metal and nutrient speciation

Weak acid chemical species that undergo acid-base reactions in seawater will be subjected to **speciation shifts** with decreasing pH (Zeebe and Wolf-Gladrow, 2001). Among the essential nutrients which are required for algal growth, the weak ions ammonia, phosphate, and silicate will be significantly altered (de Baar and Gerringa, 2009), the major element boron will be affected, as will trace elements such as iron, zinc, vanadium, arsenic, and chromium (Doney *et al*., 2009b). Dissolved organic matter that undergoes hydrolysis reactions in seawater (e.g. organic acids, amino acids, nucleic acids, proteins, humic materials) will also be strongly influenced by alterations to pH. The chemical speciation of the trace metal aluminium shows majors shifts with increasing ocean acidification, which could affect the role of this element in the building of diatom frustules, which are important primary producers (de Baar and Gerringa, 2009). Overall, the alterations may have impacts on the primary production of marine algae and plants in ways which are as yet to be elucidated.

Increased pCO_2 may result in a higher bioavailability of iron which could fuel increased primary production (Breitbarth *et al*., 2009). However, similar increases in the solubility and bioavailability of other metals may have toxic impacts on flora and fauna and/or result in increased bioaccumulation. Understanding these changes will be important for the bottom up control of food webs and the parameterisation of models which describe the response of phytoplankton and other organisms to pH change (Huesemann *et al*., 2002).

2.4 Impacts on the physiology and reproduction of marine organisms

2.4.1 Microorganisms

Non-photosynthetic **bacteria and archaea** are important for biogeochemical processes, the decomposition of organic material and nutrient regeneration and as a food source for lower trophic levels (Azam *et al*., 1983). The work of Coffin *et al*. (2004) suggests that bacterial production rates are reduced with elevated pCO_2, however additional studies are required. Indirect alterations could also occur through changes to the plankton community structure and the speciation of nutrients. **Viruses** can impact the health and physiology of organisms from phytoplankton to higher trophic levels and often result in the lysis of cells and alterations to the trophic transfer efficiency of nutrients and energy. At present it is unknown how changes to the carbonate system would impact the efficiency of viruses or host-pathogen relationships (ICES, 2008).

2.4.2 Multicellular organisms

Marine fish appear to be highly tolerant of CO_2 (Kikkawa *et al*., 2004, 2006; Fabry *et al*., 2008), although elevated pCO_2 levels may require fish to use increased amounts of energy on physiological adaptations, in particular internal ion and acid-base regulation via direct proton excretion which helps restore internal fluid to near normal levels and cardio-respiratory control (Ishimatsu *et al*., 2004, 2008). A recent study has shown that when exposed to elevated pCO_2 levels (0.6 kPa pCO2) the locomotory performance of the Atlantic Cod (*Gadus morhua*) was not affected, however elevated enzyme activity (Na^+/K^+-ATPase) was recorded, suggesting an adjustment to the ion regulatory capacity to cope with the CO_2-induced acid-base loads (Melzner *et al*., 2009).

While acidification may be tolerable to adults, perhaps the most important impact on fish will relate to early development stages including reproduction, eggs, larvae and juveniles (McKim 1977; Kikkawa *et al*., 2004; Ishimatsu *et al*., 2004). The impacts on survival rates of juveniles could alter overall population size and structure (Guinotte and Fabry, 2008; Ishimatsu *et al*., 2008). For example larval clownfish reared in reduced pH (7.8 and 7.6 pH units) showed an alteration in their attraction to olfactory stimuli which would potentially impair their sensory ability to locate reef habitats and suitable settlement sites; this type of reaction could reduce the sustainability of marine species (Munday *et al*., 2009).

Some organisms may be threatened by a build up of carbonic acid in body fluid called **acidosis**; this can lead to lowered immune responses, metabolic decline and difficulties in the areas of reproduction and respiration (Fabry *et al*., 2008). Species living near hydrothermal vents or other areas of high CO_2 such as stagnant tide pools have evolved greater capacities for buffering, ion exchange, and CO_2 transport to counteract this process (Siebel and Walsh, 2003). A number of fauna are also capable of compensating for high CO_2 levels through bicarbonate accumulation (Cecchini *et al*., 2001; Michaelidis *et al*., 2007; Spicer *et al*., 2007); however if compensation of the acid-base imbalance is not achieved the metabolism of some species may be depressed and could decrease the chance of larval recruitment and potentially disrupt community compositions (O'Donnell *et al*., 2009).

2.4.3 Noise levels and pH

Ocean acidification can result in significant decreases in ocean sound absorption for frequencies lower than ca 10 kHz due to pH dependent chemical changes in boric acid species (Hester *et al*., 2008). The reduction in pH in the last 200 years has resulted in a frequency dependent decrease in sound absorption in parts of the North Atlantic of over 15%. This decrease could be as much as 40% by 2100. As a result of these changes the auditory range critical for environmental, military and economic interests are set to increase significantly. The ability of m**arine mammals** to detect calls and echolocation pulses can be affected and concerns range from interruptions of activities such as resting, feeding or social interaction to short and long term displacement from noisy areas (Richardson *et al*., 1998).

2.5 Ecosystem structure (population and ecosystem responses)

Given that many taxa experience species-specific effects, each change is likely to affect community dynamics in complicated ways.

Doney et al.*, 2009b*

2.5.1 Pelagic communities

Decreases in calcification of marine plankton may affect their competitive advantage and may influence their latitudinal distribution, vertical depth ranges and abundance and consequently the composition and abundance of food sources for higher trophic levels (Riebesell, 2004). For example, the undersaturation of aragonite could reduce the spatial range of organisms such as pteropods to lower depths and lower latitudes (Orr *et al*., 2005). While carnivorous zooplankton and fish that feed on pteropods such as cod, pollock, haddock, mackerel (Le Brasseur, 1966; Lalli and Gilmer, 1989) may be able to switch prey types, this could result in greater predation pressure on other organisms and juvenile fish. Also, species which feed exclusively on pteropods, such as gymnosomes, would have to switch their geographic distribution concurrently to their prey (Fabry *et al*., 2008). A lack of baseline information on the current distribution and abundance of these organisms will however make it difficult to detect population shifts due to acidification (Doney *et al*., 2009b).

Calcite under-saturation is projected to occur approximately 50-100 years following that of aragonite (Orr *et al*., 2005) with important ramifications for coccolithophores and foraminifera. Coccolithophores produce a third of the total marine calcium carbonate, and can form vast blooms which play a significant role in the global carbon cycle and the transport of calcium carbonate to the deep sea (Riebesell *et al*., 2000). As such, a reduction in their abundance could alter phytoplankton biodiversity and result in a shift to diatom-dominated phytoplankton communities, which could restructure pelagic ecosystems at all trophic levels. In the North Atlantic it has been shown that changes in the phytoplankton can be passed on up through the food web from algal-feeding zooplankton to predatory zooplankton (Richardson and Schoeman, 2004).

2.5.2 Benthic communities

Calcifying organisms may adapt to changing seawater chemistry, shift their geographical positioning to latitudes where carbonate ions are more abundant, or be adversely affected (Doney *et al*., 2009b). In each of these scenarios there may be significant impacts on the associated flora and fauna (Burns, 2008). The potential loss of important habitats such as cold-water coral reefs or maërl beds would result in localised consequences for biodiversity and fisheries and possibly tourism revenue. Reductions in calcification rates may also reduce the ability of organisms to compete with non-calcifying organisms and could lead to an increase in the area of macroalgae species and seagrass meadows (Kuffner *et al*., 2008).

Sediment habitats dominate a large fraction of ocean area and play a key role in the functioning of ecosystems through benthic-pelagic coupling mechanisms relating to the regeneration of organic material and nutrient and carbon fluxes (Raven *et al*., 2005). As CO_2 increases, the average carbonate saturation state of shallow sediment pore-waters could move towards the surface resulting in the dissolution of carbonate from the sediment (Andersson *et al*., 2003; Kleypas *et al*., 2006). Communities which inhabit benthic sediments have adapted to the current saturation gradients, with different species being found at different depth horizons (Barnes and Hughes, 1988). Therefore, while benthic systems may be subject to large gradients of pH, the species which inhabit them are not necessarily adapted to these gradients (OSPAR, 2006). The change in saturation state could result in the selection of more tolerant species and thereby a change in the structure and functioning of sediment communities.

2.6 Ecosystem impacts and climate feedbacks

> *Ocean biology is not in steady-state and fundamental biological and biogeochemical processes are likely to respond to climate change, resulting in either positive or negative feedbacks that are difficult to predict.*
>
> *Arrigo, 2007*

The oceans play a significant role in the regulation of global temperature, and through their absorption of CO_2, the carbon cycle. There is a high degree of certainty that increasing atmospheric CO_2 concentrations will have large impacts on the ability of the oceans to absorb anthropogenic outputs (see section 1.5).

While the net impact will depend on a number of conflicting processes which will increase or decrease the rate of ocean absorption, latest model predictions suggest that overall the oceans capacity for absorbing CO_2 will more than likely decline over the next two decades (Friedlinstein *et al*., 2006; Doney *et al*., 2009b).

Laboratory studies have shown that higher pCO_2 resulted in a higher fixation of nitrogen by the important cyanobacteria *Trichodesmium.* If observed in the field, this would provide additional new nitrogen in low nutrient areas, or zones that will be affected by future stratification processes and reduced nutrient inputs from below (Barcelos e Ramos *et al*., 2007). The actual increase in nitrogen fixation needs to be considered in relation to the availability of phosphate and iron for primary production.

A recent model simulation has shown that due to higher respiration and other physical processes at higher pCO_2 a 50% increase in sub-oxic waters (dissolved oxygen < 5%) in the oceanic regions by 2100 could occur (Oschlies *et al*., 2008). These sub-oxic regions or ‘dead zones’ are hostile to most life forms and are also areas where fixed nitrogen is converted into biologically inaccessible N_2 gas. An increase in these zones would curtail the distribution of marine organisms and reduce primary production through a decrease in nitrogen availability.

Coccolithophore blooms can be extensive (100s-1000s km^2) and, as a result of their calcium carbonate shells, can lighten the colour of surface waters. This results in the reflection of light energy back into the atmosphere. A reduction in coccolithophore blooms will increase the amount of solar radiation absorbed by the ocean thereby reducing the global albedo up to 0.13% and slightly accelerate global warming (Tyrell *et al*., 1999).

2.7 Ecological tipping points and synergistic impacts

Ocean acidification is occurring at the same time as a number of anthropogenically-induced stressors relating to climate change, eutrophication, invasive species and fishing pressure (Doney *et al*., 2009b). The interaction of these stressors is poorly understood. As a result the ecological effects of ocean acidification could be magnified, especially because the pace of the changes is unprecedented except for the most abrupt catastrophic events (Schippers *et al*., 2004; Hutchins *et al*., 2007). During long term exposure experiments, elevated pCO_2 (700ppm) coupled with increased temperature (+3°C) has been shown to cause a decrease in the calcification of Mediterranean coralline algae by 50%, while elevated temperature or pCO_2 alone did not induce a reduction in calcification (Martin and Gattuso, 2009). In this case, the synergistic influence of these two parameters far outweighed their individual effects.

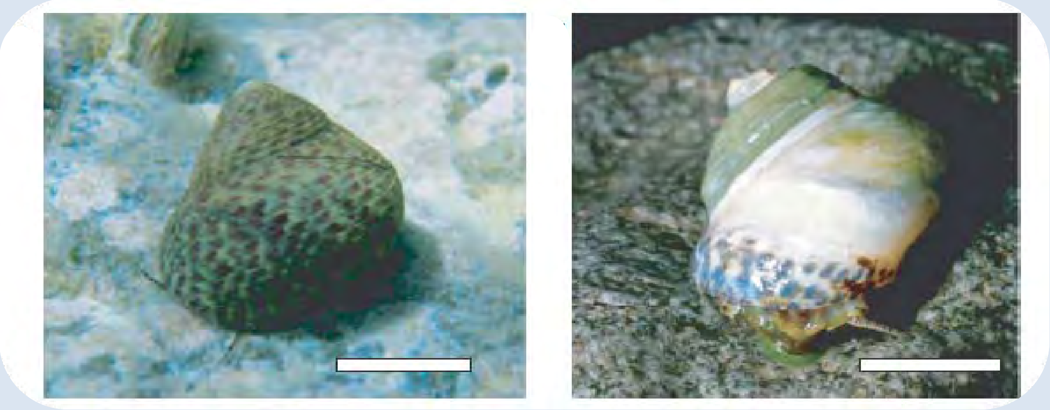
Marine organisms and ecosystems can be controlled by critical boundaries whereby a small change in a forcing factor such as temperature or acidification may trigger an abrupt and potentially irreversible shift in ecosystem functioning across several trophic levels (Beaugrand *et al*., 2008). Ecosystems can thus shift into entirely new configurations after a sudden disturbance pushes these stressed communities past an ecological ‘tipping point’ (Cooley and Doney, 2009b). The combined impact of ocean acidification and other parameters and the definition of critical tipping points in ecosystems is an important future area of research.

Box 5. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. (Hall-Spencer *et al.*, 2008)

Marine CO_2 vents are abundant in the Mediterranean and can be used as natural experiments to increase our understanding of the influence of ocean acidification. Along a gradient for normal pH (8.1-8.2) to lower pH (mean 7.8-7.9, minimum 7.4, 7.5), typical rocky shore communities with abundant calcareous organisms shifted to communities lacking scleractinian corals with significant reductions in sea urchins and coralline algal abundance. Rocky shore stations with a mean pH of 7.8-7.9 showed a 30 % mean reduction in species number (notably cacifiers) compared to stations with normal pH. Organisms with aragonite skeletons (*Halimeda* algae and coral species) were common outside the vents but were absent at mean $\Omega_{arag} \leq 2.5$, providing *in situ* support of predictions of global coral reef dissolution at these concentrations. Coralline algal cover fell from > 60 % outside the vent area to 0 % within it. Non-calcareous algal cover (for example, *Caulerpa*, *Cladophora*, *Asparagopsis*, *Dictyota* and *Sargassum*) increased significantly from near 0 % to > 60 %, proving their resilience to naturally high amounts of pCO_2; furthermore, some of these species are invasive alien species that have begun to alter shallow marine ecosystems worldwide.

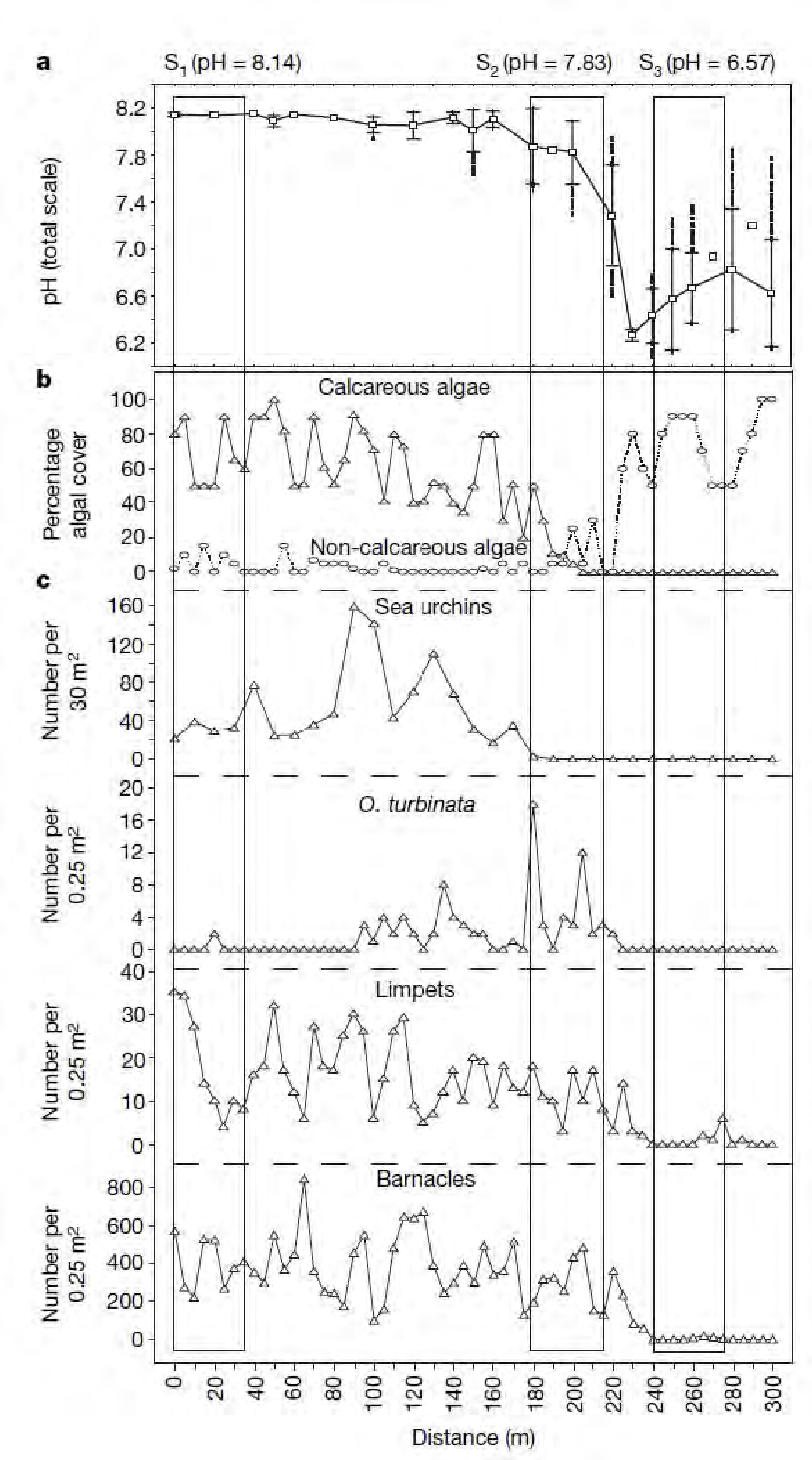
Sea urchins (*Paracentrotis lividus*, *Aracia lixula*) which have high magnesium calcite skeletons, were the most common large invertebrates on sublittoral rock outside the vents but their abundance was significantly reduced where pH reached maxima of 7.4-7.5. Loss of sea urchins can drive deteriorations in ecosystem complexity and stability. Juveniles of gastropod species were absent in areas with pH minima ≤ 7.4, where all adult gastropod shells were weakened by the acidified sea water; an effect which increases their risk of predation. This study shows that decreases in pH can lead to substantial changes in community structure. It is also a first step towards the identification of 'tipping points' at which principal groups of marine organisms are affected by lowered pH.

Explanation of the figure on following page: Variation in pH, cover of algae and abundance of species at CO_2 vents south of Castello d'Aragonese. A: The mean pH ± s.d. (cross bars) is shown. Ranges are denoted by the dotted line; n=6 at 0 m, n=11 at 50 m, 100 m, 250m and 300 m, n= 9 at 220 m, 260 m, 280m and n=12 at 150 m and 200 m. b: The percentage cover of calcareous (triangles) and noncalcareous algae (circles) is shown. C: The abundances of sea urchins, *O. turbinata*, limpets and barnacles.



Inset: *O. turbinata* with the periostracum intact at pH 8.2 and with old parts of the periostracum removed at mean pH 7.3.

Box 5 continued. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification (Hall-Spencer *et al.*, 2008)



Mussel longlines in Clew Bay
Photo courtesy of Alan Drumm,
Marine Institute

CHAPTER 3. OCEAN ACIDIFICATION: AN EMERGING CAUSE FOR CONCERN

Changes in the global biogeochemical cycles operate on different time scales. Uptake of CO_2 and transport to the ocean interior is a rather rapid process (of the order of weeks to centuries). The effect of increased sedimentary carbonate dissolution (compensating ocean acidification) operates on intermediate timescales of the order of thousands of years. Ultimate recovery of the oceans from ocean acidification, however, is achieved only through weathering on timescales of millions of years.

European Science Foundation, Policy Briefing 37, 2009

3.1 Past responses of the ocean to changing atmospheric CO_2

Geological records of past variations may provide 'analogues' by which to infer possible impacts of ocean acidification. Recent evidence suggests that ocean acidification was a primary reason for past mass extinction and reef gaps, which took time periods in the order of millions of years to recover (Stanley, 2006; Veron, 2008). Zachos (2005) calculated that if the entire fossil fuel reservoir were combusted, the impacts on deep-sea pH and biota would probably be similar to those in the Paleocene-Eocene Maximum (PETM), 56 million years ago, which may be the best analogue for current and future anthropogenic acidification. The PETM was marked by the mass extinction of deep sea calcareous marine organisms although the evidence of surface water undersaturation is not clear (Bown and Pearson, 2009; Kump *et al.*, 2009).

An archive of air bubbles trapped in Antarctic ice has shown that there was a variation in atmospheric CO_2 from 190 to 300 ppmv over the past 42 000 years (IPCC 2001). At constant temperature and alkalinity this would have represented a pH variation of 0.16 units, with highest pH values when atmospheric CO_2 values were lowest, at glacial maxima. As this carbon release was much slower than current emissions, the dissolution of calcareous sediments would have had sufficient time to neutralize anthropogenic CO_2. Ocean acidification-induced impacts on surface ocean pH and biota will probably be more severe than during periods in the geological past, such as the PETM, as dissolution processes will not have time to counteract pH changes (Zachos, 2005). It is difficult to draw comparisons between geological and current events as there are no perfect analogues for today and the current rate of CO_2 release from reservoirs may well be unprecedented (Kump *et al.*, 2009).

3.2 Socio-economic impacts

Expanding job losses and indirect economic costs will follow harvest decreases as ocean acidification broadly damages marine habitats and alters marine resource availability.

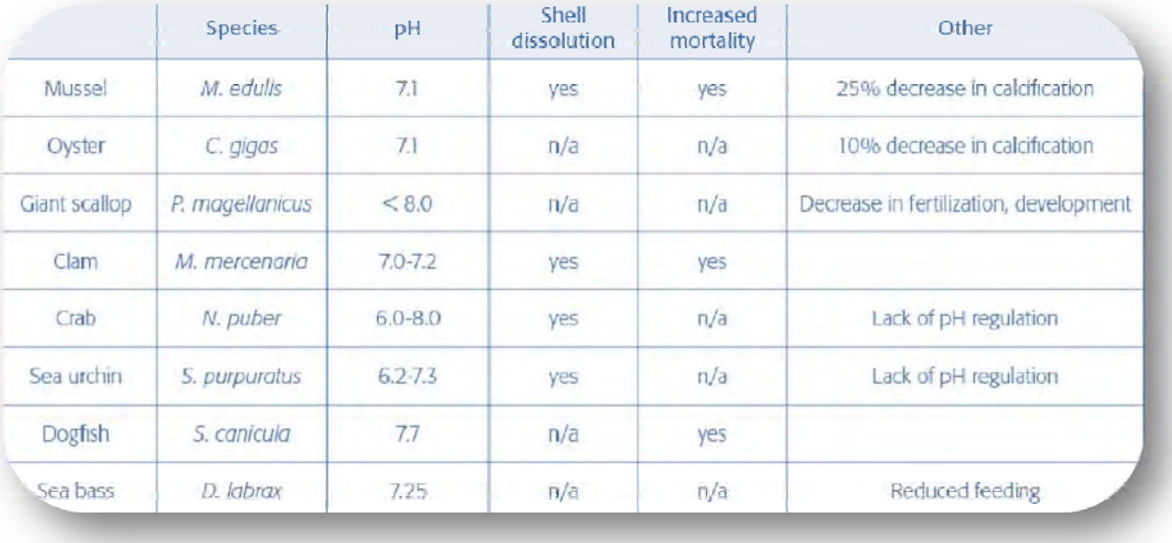
Cooley and Doney, 2009b

Coastal marine systems from intertidal areas to the shelf break are among the most ecologically and socio-economically important on the planet (Harley *et al*., 2006). They provide numerous ecosystem services that benefit human-kind including biodiversity, tourism, sites for the release of wastes and pollution, and fisheries which contribute to global employment and economic activity (Raven *et al*., 2005).

Projecting the socio-economic consequences of ocean acidification on ecosystems is difficult as the biological responses and adaptive ability of many species are as yet unknown (Table 3.1). At the moment it is unclear if species will degrade slowly over time, adapt to gradual change, or exhibit collapse at as yet undefined CO_2 thresholds. The loss of a single species could culminate in entire ecosystem shifts which would compound economic effects over time (Cooley and Doney, 2009b).

Alternatively, gradual adaptation by commercial fisheries and aquaculture could allow a shift to more abundant, adapted or acidification-resistant species. The socio-economic impacts of ocean acidification will consequently depend on the adaptation ability of marine ecosystems and the human resource management of fragile systems.

Table 3.1: A number of economically important shell- and finfish have been studied in an attempt to understand their response to ocean acidification. Many of the species studied exhibit a negative response leading to questions about the possible economic consequences [“n/a”- not available, response is unknown. (Cooley & Doney, 2009b).



	Species	pH	Shell dissolution	Increased mortality	Other
Mussel	*M. edulis*	7.1	yes	yes	25% decrease in calcification
Oyster	*C. gigas*	7.1	n/a	n/a	10% decrease in calcification
Giant scallop	*P. magellanicus*	< 8.0	n/a	n/a	Decrease in fertilization, development
Clam	*M. mercenaria*	7.0-7.2	yes	yes	
Crab	*N. puber*	6.0-8.0	yes	n/a	Lack of pH regulation
Sea urchin	*S. purpuratus*	6.2-7.3	yes	n/a	Lack of pH regulation
Dogfish	*S. canicula*	7.7	n/a	yes	
Sea bass	*D. labrax*	7.25	n/a	n/a	Reduced feeding

Permission has been granted to reprint Table 2 (on page 16) from "Anticipating Ocean Acidification's Economic Consequences on Commercial Fisheries" by Sarah R. Cooley and Scott C. Doney from Current: The Journal of Marine Education, Vol. 25, No. 1, 2009, published by The National Marine Educators Associations (NMEA). For more information about the NMEA, please visit their website at www.marine-ed.org.

Ocean acidification is likely to impact key species which underpin and provide habitats for commercial species. In the context of the Irish marine area, organisms for which acidification may have direct or indirect economic ramifications include: zooplankton and phytoplankton which are a food source for pelagic and benthic commercial species, harvested shellfish and those which support fish species, deep-water corals, macroalgal beds (wrack, kelp, maërl), and fish species.

The economic effects of ocean acidification will impact those directly involved in the fisheries industry, coastal communities, middlemen, retailers, and consumers. The way in which these groups respond to ocean acidification will partly dictate the total economic and social costs. Comprehensive research is therefore urgently required to understand the impacts of ocean acidification on commercially valuable species and their ecosystems. This will enable a reduction in the uncertainty of modelling the economics of climate policy (Miles and Bradbury, 2009).

3.2.1 Aquaculture

> *Any threat to marine ecosystems, such as ocean acidification, will reverberate through our economy and food supply.*
>
> *Feely* et al.*, 2006*

The total landed value of world marine fisheries production is presently $104 billion/year and approximately 18% of this comes from marine aquaculture (Kite-Powell, 2009). The first economic impacts of ocean acidification is likely to be declining revenues from calcium carbonate forming species, their predators and associated organisms (Cooley and Doney, 2009b) although impacts on finfish production should also be considered. The total value of Irish aquaculture production in 2007 was € 105.6 million; this was split between shellfish production at € 47.2 million and finfish at € 58.4 million. The impacts of ocean acidification on this industry therefore need to be considered in order to mitigate and adapt to projected impacts.

3.2.1.1 Shellfish

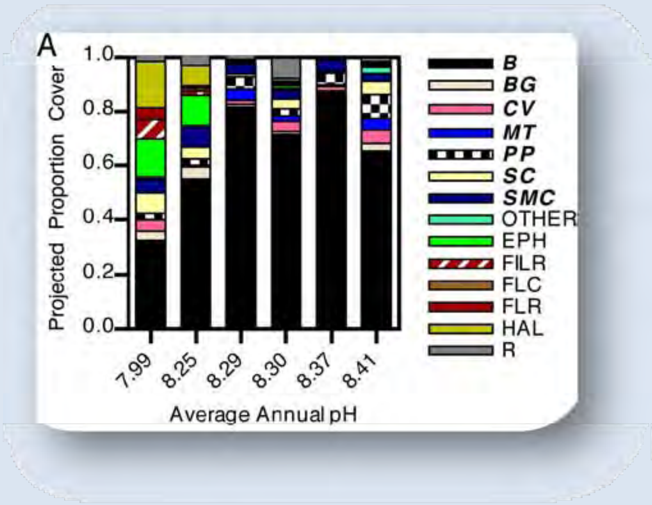
While the impacts of ocean acidification are not yet known for every commercially valuable organism, it is anticipated that the numbers or quality of many calcareous species will decrease leading to declines in economic revenues (Cooley and Doney, 2009b). In the USA ocean acidification driven declines in commercial shellfish and crustaceans harvests are projected to reduce primary commercial revenues by $860 million to $14 billion (Cooley and Doney, 2009b). The greatest impacts will be experienced by coastal economies with little economic resilience.

In 2006, the highest volume and value of shellfish production in Ireland was bottom mussels followed by the pacific oyster (Figure 3.1). These economically significant bivalves are also ecologically important ecosystem engineers, providing habitat and other services to a rich diversity of organisms (Gutiérrez *et al*., 2003; Fabry *et al*., 2008). Experimentally observed decreasing calcification rates of these two species (calculated on a doubling of CO_2 to 740 ppmv) translated into comparable population losses, would result in a 25% decrease in mussel harvests and a 10% decrease in oyster harvests before the end of the century (Cooley and Doney, 2009a; Gazeau *et al*., 2007). Based on the 2007 figures for the Irish mussel and oysters harvest values (€ 45.7 million, Status of Irish Aquaculture 2007, Browne *et al.* 2008) this could result in a total decrease of € 8.9 million in direct revenue.

An 8-year study of a north-temperate coastal site has shown that the abundance and mean size of the dominant calcareous species, the California mussel (*Mytilus californianus*) decreased with declining pH, while an increase in acorn barnacles and algae was evident (Wootton *et al*., 2008, Box 6). This study reveals that pH reductions are already leading to systematic shift in community structure in some areas.

Box 6. Ecological impacts of declining ocean pH in a coastal area. (Wootton *et al*., 2008)

At a north-temperate Pacific coastal site a high resolution dataset spanning 8 years revealed a reduction in pH with increasing CO_2 levels. Variations were also observed over multiple time-scales in response to biological processes and physical conditions. Strong links were revealed between species dynamics and pH variations, with calcareous species generally performing more poorly than noncalcareous species in years with low pH. Calcareous species showed increased probability of replacement by other species as pH decreased. Model results based on observations exhibited a systematic change in community structure as a function of mean annual pH. The abundance and mean size of the dominant species, the California mussel (*Mytilus californianus*) declined as did that of other calcareous species. While in contrast, the abundance of acorn barnacles and algae increased with declining pH. The results indicate that pH decline has important ecological and possible economical importance in near shore benthic ecosystems. They also highlight the urgent need for more 'spatially distributed and temporally intensive' studies of ocean pH dynamics.



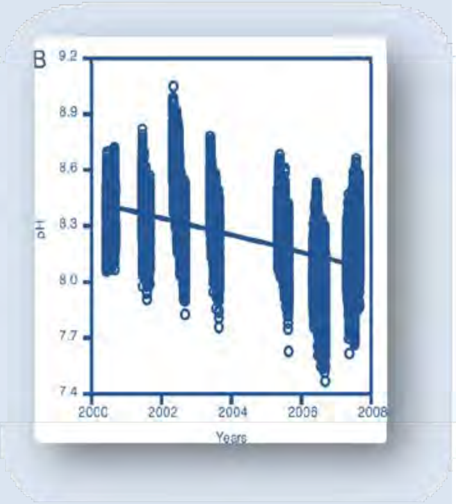


Figure A: Relationship between long-term predictions of sessile species composition derived from Markov chain models, in relation to average annual pH with calcareous taxa indicated by bold italics. (B-big Mytilus californianus, BG-Balanus glandula, CV-Corallina vancouveriensis, HAL-Halosaccion glandiforme, MT-Mytilus trossulus, PP-Pollicipes polymerus, SC-Semibalanus cariosus, SMC-small Mytilus californianus, FILR-filamentous Rhodophytes, FLR-foliose Rhodophytes, FLC-fleshy crustose algae, R-rock and diatoms, EA-ephemeral algae (Porphyra and Ulva spp.), and OTH-other rare sessile species. Taxa with calcareous skeletons or shells indicated in italics. OTHER category includes both calcareous and non-calcareous species. Copyright (2008) National Academy of Science, USA.

Figure B: Patterns of ocean pH through time at Tatoosh Island (N_24,519). (B) pH readings as a function of date and time taken between 2000 and 2007. The decline is significant (P <0.05).

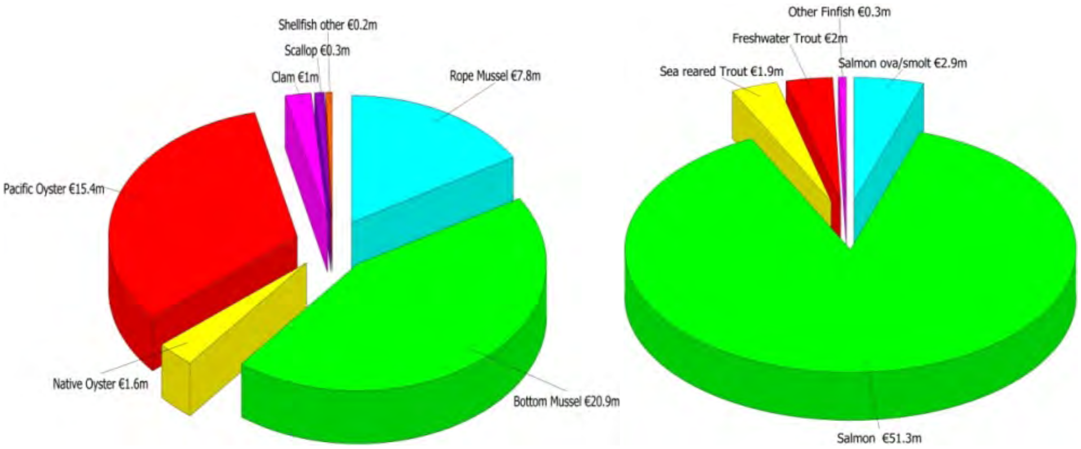


Figure 3.1: A large proportion of shellfish aquaculture production in Irish waters in 2007 (expressed as value) was due to bottom and rope mussel production, followed by oysters (data from Browne et al., 2008). These two economically important shellfish have exhibited decreased calcification rates as a result of the doubling of CO_2 levels above current concentrations (Gazeau et al., 2007).

Aside from reductions in calcification rates, bivalves exhibit extremely high mortality rates (>98%) in their transition from larvae to benthic juveniles (Green *et al*., 2004) and any further increase in juvenile mortality as a result of ocean acidification would further affect the bivalve population and harvest (Section 2.1.2.2). A recent study suggests that responses to ocean acidification are species-specific; therefore research on the responses of locally important species is required (Miller *et al*., 2009).

The abundance, frequency and species composition of phytoplankton species which support aquaculture may also be affected by ocean acidification. The presence of harmful microalgae which produce natural toxins is an ongoing concern for aquaculture as blooms of these microalgae frequently result in prolonged closures of Irish production areas (Browne *et al*., 2008). While the likely impacts of ocean acidification on the physiology of these species are unknown, a reduction in coccolithophore abundance could result in an increase in other phytoplankton such as dinoflagellates, a group which includes some of the most harmful algae (Moore *et al*., 2008). Coupled with warmer temperatures and other environmental changes, an alteration in the range of some species may also occur. A further consideration is the impact of ocean acidification on viruses and parasites and their relationship with host bivalve species.

3.2.1.2 Finfish

Salmon and trout are currently the most economically important finfish produced in Ireland (Figure 3.1). Most farmed finfish experience a range of salinities and pH conditions in the wild. It is therefore unlikely that local pH changes will have a direct effect. However, in combination with a number of factors, such as thermal stress and low oxygen, it could cause problems.

Farmed finfish are currently subjected to pressures as a result of parasites (e.g. Sea lice *Lepeophtheirus salmonis*) and disease (ex. infectious pancreatic necrosis) (Browne *et al.,* 2008). It is currently unknown if there will be any negative impacts of ocean acidification on parasites and disease or the immune response of finfish and host-pathogen relationships. Protection of vulnerable organisms (both shellfish and finfish) in aquaculture facilities has been suggested. Measures may include the control of pH at a local scale in coastal tanks or ponds that are filled with coastal seawater or a switch to complete onshore controlled tanks (Cooley and Doney, 2009b; Kite-Powell, 2009). In practical terms this may lead to difficulties and increase in the overheads of aquaculture operations.

3.2.2 Fisheries

The seafood industry has a strong stake in understanding and confronting ocean acidification.
Warren, 2009

Fisheries are an important part of the Irish economy. Irish waters are critically important in the life-cycle of many species. For example the largest and most valuable migratory pelagic stocks in the Northeast Atlantic (mackerel, horse mackerel and blue whiting) all spawn off the west coast of Ireland. Large stocks of hake, anglerfish and megrim also spawn along the continental slope west and south of Ireland. There are important herring, cod, haddock, whiting, plaice and sole spawning areas in the Irish Sea and the Celtic Sea. The shelf area and coastal waters are important nursery areas for young fish. Shellfish stocks such as prawn, crab, lobster, shrimp, scallop, whelk and cockles are also abundant regionally or locally (Marine Institute, 2009).

The total number of fishermen in Ireland in 2004 was 4,754 (Safefood, 2006). The approximate value of Ireland's 2009 Total Allowable Catch (TAC) was €196 million, although other than Nephrops the majority of shellfish and crustacean species are not regulated by TAC (Marine Institute, 2009). The breakdown of the most valuable fisheries is shown in Figure 3.2. Direct toxic effects of ocean acidification on adult fish are not expected as acute sensitivity is beyond the predicted concentrations. The reproductive success of commercially important fish may however be affected and reductions in fertilization success and the survival of juvenile fish are possible (Section 2.3.2). In a worst case scenario, multiple recruitment failures could cause population collapse even if conditions remain acceptable for adults (Cooley and Doney, 2009b).

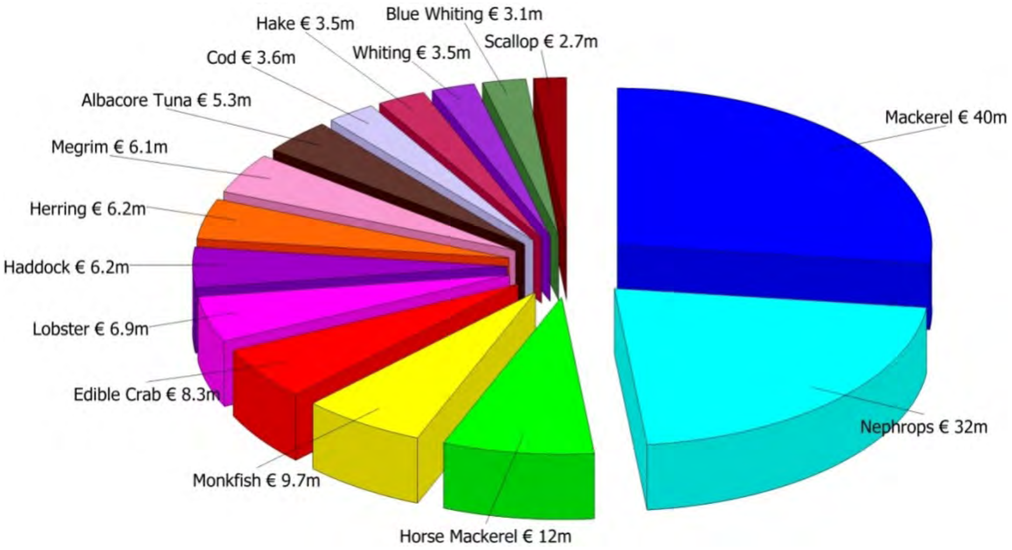


Figure 3.2: Breakdown by value of the 15 most economically valuable species landed by Irish vessels in 2008

Indirect effects on fish stocks and fisheries may occur due to: changes in primary producers including plankton prey base abundance and composition, the impact of multiple stressors (e.g. overfishing, thermal change, pollution), the vulnerability of ecosystems which sustain fisheries to changes in the carbonate system (i.e. cold-water corals, maërl beds) and competition with species with a tolerance for low pH levels (Guinotte and Fabry, 2008; Warren, 2009).

In the North Pacific, for example, pteropods can account for > 60% by weight of the diet of juvenile pink Salmon (Armstrong *et al*., 2005). As a result of increasing ocean acidification the depth range of pteropods are likely to contract with a potential shift to lower latitudes and could result in adverse affects on the dependent fisheries. Similar relationships between harvested fish species and coccolithophores or foraminifera in Irish marine waters could be important.

Along the western edge of Ireland's continental shelf the coccolithophore *Emiliana huxleyi* produces large seasonal blooms in early May (McGrane, 2007; Figure 3.3). However detection of acidification-driven shifts in population distributions and resultant impacts on ecosystem functioning and trophic interactions with commercial fish species will be difficult due to the lack of baseline studies on their current status (Doney *et al*., 2009b).

***Figure 3.3: Coccolithophore blooms* (Emiliania huxleyi) *are a common occurrence in the spring off the West Coast of Ireland. ESA/Envisat |Instrument: MERIS | Acquisition: June 2006. Inset Photo:* E. huxleyi,**
Photo credit Pauhla McGrane

Elevated temperatures may impact on fish stocks through increased mortality of eggs and larva, later spawning migrations, and alterations to ecosystems (Keller and Klein-MacPhee, 2000; Loukos *et al*., 2003; Sims *et al*., 2004). Sea surface temperature time-series in Irish waters between 1850 and 2007 have exhibited a warming trend averaging 0.3°C, which compares well with the global warming trend attributed to greenhouse gases (Cannaby and Hüsrevoğlu, 2009). Ocean acidification added to this warming, which is predicted to increase annually, could lead to combined or synergistic pressures on marine fish species distribution and abundance.

Economically important crustaceans such as lobsters, crabs and shrimp exert high biological control over calcification and as a result the impacts of ocean acidification are expected to be less than on other calcifying organisms (Cooley and Doney, 2009a). However, the responses will also depend on factors such as individual history or genetic variability and the local environmental changes (Hall-Spencer *et al*., 2008; Cooley and Doney, 2009a).

While the surface ocean, to a depth of 1000m, directly provides almost all the global seafood catch, it also indirectly fuels aquaculture production through that industry's dependence on feeds made from marine fish (Warren, 2009). Fisheries support many associated businesses involved in seafood processing, transportation, preparation and sales while recreational fishing and tourism adds further economic benefits (Cooley and Doney, 2009a). The global revenue from fisheries in 2004 was around US $148.1 billion, with marine capture fisheries representing 60% of this figure (FAO, 2007).

While the future impacts on fisheries revenue are currently unknown due to the uncertainty in predicting losses, constraints are expected in the long-term (Warren, 2009). Greater knowledge of fish stocks, and experimentation and modelling of direct and indirect effects, would improve confidence intervals in our projections of the impacts of ocean acidification on fisheries. The threat from ocean acidification also calls for a fisheries management plan that aims at achieving strong and robust fish stocks with high genetic diversity to ensure the maximum potential for adaptation to changing environmental conditions (Fosså *et al*., 2008).

3.2.3 Cold water coral ecosystems

Along the continental shelf off Ireland cold water coral mound systems are well developed (Figure 3.4); and recently an extensive major new coral reef province (200 km^2) has been discovered at the southern end of the Porcupine Bank (west coast of Ireland). These deep-water reefs are hotspots for carbon cycling (van Oevelen *et al*., 2009) and biodiversity; Roberts and Gage (2003) documented over 1300 species living on *Lophelia pertusa* reefs in the NE Atlantic.

They can also play an important role as a refuge, feeding and nursery ground for deep-sea organisms, including commercial fish (Turley *et al*., 2007; Guinotte and Fabry, 2008; D'Onghia *et al*., 2009). Large aggregations of redfish (*Sebastes* spp.), ling (*Molva molva*), and tusk (*Brosme brosme*) have been documented in the *Lophelia pertusa* reefs of the North Atlantic (Husebo *et al*., 2002). Documenting the impact of ocean acidification on this valuable resource and the associated organisms will be difficult as the functional relationships and ecology of these systems is not well known (Turley *et al*., 2007). Understanding coral-fish associations and functioning of these ecosystems is impeded by their relative inaccessibility and the low number of research groups working on this subject. However, the NUI Galway led EU 7th Framework Programme Integrated Project 'CoralFISH' studying the interactions between corals, fish and fisheries, is expected to improve our understanding of these critical processes when completed in 2012 (cf. http://eu-fp7-coralfish.net).

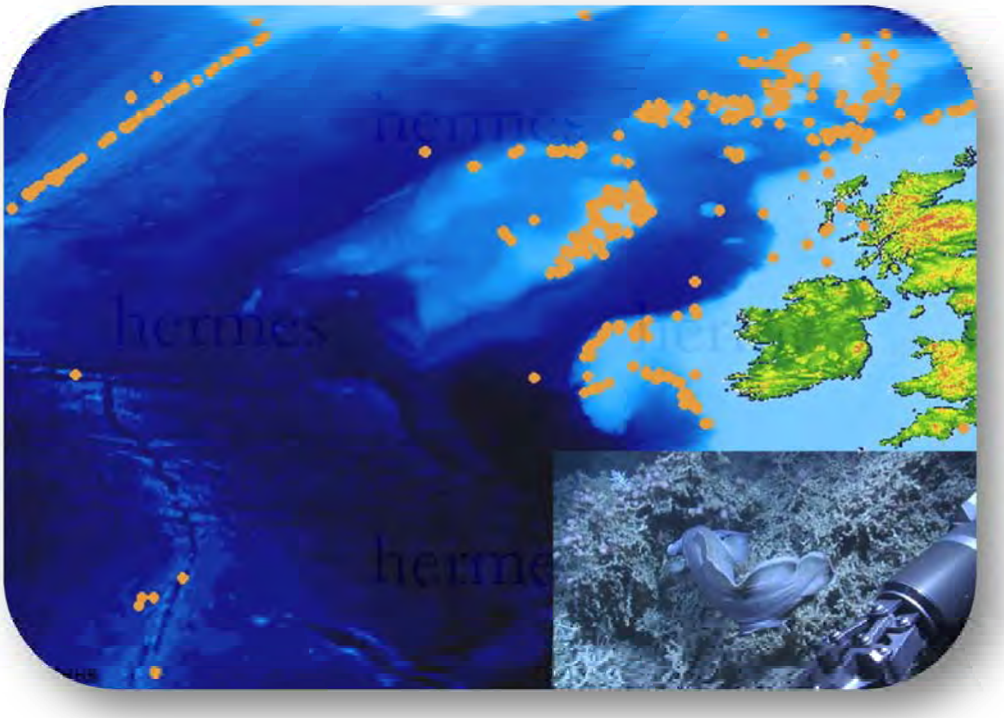


Figure 3.4: Coldwater corals are found in deep waters along the continental slopes off Ireland. They feed by filtering particles from the water column and so do not need light to survive. The most common species found is* Lophelia pertusa*. Modelling studies suggest that as much as 70% of deep water corals will be undersaturated with respect of aragonite by 2100.

[i) Copyright NUI Galway (courtesy of Anthony Grehan) (for the coral image) and ii) Courtesy HERMES (for the map)]

3.2.4 Coastal and estuarine ecosystems

Coastal and estuarine systems are subject to a number of anthropogenic inputs including hydrological and land-use changes which alter freshwater inputs, acidification and eutrophication. The west coast of Ireland contains a number of coastal ecosystems which can be defined by their macro-algal component ranging from intertidal beds of *Ascophyllum nodosum* (knotted wrack), to shallow subtidal kelp or calcareous red algal maërl beds (Hession *et al*., 1998; De Grave *et al*., 2000). These species are both ecologically and economically important. Moreover they have an important, if albeit as yet unquantified, role in the carbon cycle of Irish shelf waters.

The canopy-forming *Ascophyllum nodosum* (Figure 3.5) is the most prevalent intertidal seaweed on the sheltered rocky shores. It is also an important structural species that has a major influence on community composition and richness (Bertness *et al*., 1999; Wells and Wilkinson, 2001). Economically, it is also the most widely harvested species in Ireland (Hession *et al*., 1998). Similarly, kelpbeds are the most extensive community inhabiting sublittoral rocky coasts and are found in varying degrees of abundance over 56% of the western coastline (Hession *et al*., 1998). The beds provide food and shelter for a host of marine life and also support biodiversity and are currently unexploited. The impact of ocean acidification on macroalgal communities has as yet to be explored, and the relationships with grazers and the possible increased photosynthesis due to higher availability of carbon should be considered under different climate change and ocean chemistry scenarios.

Figure 3.5:* Laminara hyperborea *(above) and* Ascophyllum nodosum *(below) are important structural species in Irish Coastal waters. They also have economic importance as they are harvested for use in the pharmaceutical and food industries.

(Photo credit Dagmar Stengel)

In Ireland coralline red algae are present in the form of maërl (e.g. *Lithothamnion corallioides*, *Phymatolithon calcareum*, Figure 3.6) recorded along the Irish west coast from counties Cork, Galway to Donegal (total resource: approximately 57 x 106 m^3, De Grave *et al*., 2000). Since the 17th century maërl has been collected in Ireland for its use as a fertiliser on limestone poor soils. These photosynthetic organisms form highly biodiverse and heterogeneous habitats composed of a surface layer of unattached calcareous (calcium and magnesium) red algae (Hall-Spencer and Moore, 2000; Kamenos *et al*., 2004). They are considered one of the most diverse marine ecosystems found in Europe and their conservation is of international interest (Hall-Spencer *et al*., 2003; Wilson *et al*., 2004). The possible implications of ocean acidification for these ecosystems has yet to be deciphered, however a recent study suggests that calcification and recruitment rates will decline if atmospheric CO_2 levels rise to double that of today's concentrations (Kuffner *et al*. 2008; Section 2.1.2.1)

Figure 3.6: Species of maerl and coralline algae are found along the west coast of Ireland. Clockwise from top left:* Lithophyllum dentatum*,* Phymatolithon calcareum*,* Lithophyllum sp.*, calcified crustose algae and erect algal species:* Corallina officinalis*, crustose red algae.

(Photo credit Dagmar Stengel)

3.2.5 Corrosion of metal and marine structures

Decreases in ocean pH have the potential to increase current rates of metal corrosion, with economic consequences for industries responsible for shipping and marine structures. However at predicted rates of acidification this will be unlikely to cause a serious increase in corrosion rates (Raven *et al*., 2005). A more plausible implication is the degradation of the inorganic coating (largely consisting of calcium carbonate) which reduces corrosion rates of metal in seawater (Lacque, 1975).

Mussels © Image Marine Institute

CHAPTER 4. IMPLICATIONS AND ACTIONS

The nature of future changes is difficult to predict with any precision. This is not only because of the great complexity of the Earth System, but also because future anthropogenic impacts depend on future carbon dioxide emissions and therefore the degree to which the international community is able to agree on emission cuts.

Tyrrell, 2007

4.1 The need for an immediate response

Stabilization of the atmospheric CO_2 concentration at 450 ppmv by 2100 (Category I, IPCC 2007) would lead to an average global pH decrease in the ocean surface layer of 0.17 units as compared to the pre-industrial level and would result in damage to a number of oceanic systems (Caldeira and Wickett, 2005; Cao and Caldeira, 2008). If CO_2 emissions are not regulated pH could be reduced by 0.5 units. Once this acidification has occurred and as long as CO_2 levels are not lowered, the pH change will not rise again in the foreseeable future (Schubert *et al*., 2006; Raven *et al*.,2005); furthermore, biological recovery may require even longer timescales. The potentially profound alterations that may occur right through the marine environment require an immediate reaction by both policy makers, international and national bodies and the research community.

Ireland is strategically positioned at the edge of the European continental shelf, adjacent to an ocean area where some of the most important water masses driving the global ocean conveyor interact or are generated. This presents Ireland with a unique opportunity for marine research in these critically important waters. Our marine waters host rich and diverse ecosystems, from deep cold-water coral systems to shallow maërl beds, and due to their high productivity coastal waters are particularly important in terms of economics, food resources and leisure activities. Recognition of current and impending problems and reaction to ocean acidification is necessary not only to ensure the health of our marine environment but we also have a responsibility to protect our maritime regions, resources and ecosystems for future generations. Ireland should therefore actively strive to participate in international dialogue on ocean acidification in particular with respect to issues concerning North Atlantic waters.

4.2 Policy drivers

4.2.1 Ocean acidification in the context of global climate change response

Ocean acidification has been a topic of increasing discussion and concern for both international organisations and governments. This international interest reiterates the importance and concern being placed on this topic and the requirement for more research to elucidate the ecological and socio-economic consequences. Furthermore, it shows the increasing need for recognition by policy makers that ocean acidification is not a peripheral issue.

The **Royal Society** (The National Academy of Science of the UK) published a report on the possible impacts of ocean acidification (Raven *et al.* 2005) and this report brought the issue into the wider scientific and marine/climate policy domain. A follow-on policy statement by the Society recommended a major international research effort to study this process and its implications.

The **Intergovernmental Panel on Climate Change** (IPCC) gives an objective source of scientific, technical and socio-economic information for policy makers. Ocean acidification was, for the first time, predicted as having future negative impacts on the marine environment within the panels recently published 4th assessment report (AR4, IPCC, 2007).

The **United Nations Framework Convention on Climate Change** (UNFCCC) and the **Kyoto Protocol** did not consider ocean acidification a priority when commitments to CO_2 reductions were adopted in 1997. A number of priorities of the UNFCCC do however require a consideration of this process, particularly in consideration of the 'stabilization of greenhouse gas concentrations to levels that would prevent dangerous anthropogenic interference with the climate system' (Article 2 of UNFCCC).

The **InterAcademy Panel on International Issues (IAP)** has also released a recent statement calling for acknowledgement that ocean acidification is a direct result of increasing CO_2 levels and calling for dramatic reductions in emissions by at least 50% by 2050. The **United States** have also reacted to international concern. In the US the Federal Ocean Acidification Research and Monitoring Act of 2009: H.R. 4174 was in the House of Representative and the Senate in March 2009. This Act requires that federal agencies work together to establish a research and monitoring plan for ocean acidification.

A number of recent reports documented the threat from ocean acidification and the policy response and research requirements. These included:

- the second International Symposium on "The Ocean in a High-CO_2 world" (2008) and the **Monaco Declaration on Ocean Acidification;**
- the **European Science Foundation** Science Policy Briefing (37) on the 'Impacts of Ocean Acidification' (2009);
- the international scientific **Climate Congress** which took place in Copenhagen in March 2009 on '**Climate Change: Global Risks, Challenges and Decisions**' which included a dedicated session on ocean acidification;
- Ocean Acidification Workshop in Hawaii (convened by The Nature Conservancy) and the '**Honolulu Declaration on Ocean Acidification and Reef Management**' (2008);
- Ocean Acidification: Australian Impacts on the Global Context (Howard and Tilbrook, 2008);
- the **International Council of the Exploration of the Sea** (ICES) an intergovernmental scientific forum that supports research, monitoring and management for the North Atlantic. (ICES, 2008)
- "Scientific Synthesis of the Impacts of Biodiversity" Secretariat of the **Convention on Biological Diversity** (2009).

4.2.2 Legal obligations to protect the North East Atlantic

Policymakers need to realize that ocean acidification is not a peripheral issue. It is the other CO_2 problem that must be grappled with alongside climate change. Reining in this double threat, caused by our dependence on fossil fuels, is the challenge of the century.

Monaco Declaration, 2008

Ireland has a number of European legal obligations and is a signatory to various global and regional conventions with relevance for the protection of the North East Atlantic marine area.
The European Union's **Marine Strategy Framework Directive** (MSFD Dir. 2008/56/EC) was adopted in June 2008. The MSFD requires member states to take the necessary measures to achieve or maintain Good Environmental Status (GES) of the marine environment by 2020 and the protection of the resource base upon which marine-related economic and social activities depend. It also promotes the integration of environmental considerations into all relevant policy areas and as such each Member State is required to develop strategies for their marine waters. The Directive has specified the

requirements necessary for the monitoring and ongoing assessment of marine waters and ecosystem components.

Within this context explicit reference has been made to the measurement of ‘pH, pCO_2 profiles or equivalent information used to measure marine acidification’. This, combined with the other measurements mentioned in the Directive, will allow for an analysis of the predominant pressures and impacts, including anthropogenic activity, on the environmental status of the marine waters and will allow for measures to be developed to protect the marine environment. Ocean acidification will compromise member states’ ability to maintain GES as defined by many of the qualitative GES descriptors given in Annex VIII of the directive (Table 4.1).

The **OSPAR Convention** is the current legal instrument guiding international cooperation on the protection of the marine environment of the North-East Atlantic and is likely to provide the regional mechanism for implementing key elements of the MSFD. The OSPAR Biodiversity and Ecosystem Committee (BDC) has shown considerable interest in investigating the potential impact of ocean acidification on marine biodiversity. A report (OSPAR 2006) and a recent OSPAR Decision 2007/1 recognised ocean acidification as a potentially critical issue for the future health of the ocean. The 2010 Quality Status Report for the North East Atlantic, due to be published in September 2010, will highlight ocean acidification as a key emerging issue. OSPAR is considering incorporating ocean acidification into its monitoring and assessment activities.

The **London Convention** (1972/1996) was created to protect the marine environment from anthropogenic activities. A recent amendment (CO_2 Sequestration, Amendments to Annex 1 to the London Protocol 1996) listed ocean acidification, and its consequences, as one the main reasons for allowing the storage of CO_2 in sub-seabed geological formations.

4.3 National Strategies

Ocean acidification is a powerful reason, in addition to climate change, for reducing global CO_2 emissions.

Raven et al.*, 2005 (Royal Society)*

The Irish Government has recently published a new **National Climate Change Strategy** (NCCS) 2007-2012. This strategy provides a framework for action to reduce Ireland’s greenhouse gas emissions and will also help to ensure that Ireland reaches its emission reduction target under the Kyoto Protocol. The NCCS recognised ocean acidification as a consequence of climate change.

Sea Change – A Marine Knowledge Research and Innovation Strategy for Ireland 2007-2013 aims to provide a framework for a programme of selective and managed investment that will help to maximise the potential of the marine sector and resources. Within this framework in the marine environment research programme the research development and innovation (RTDI) requirements includes the establishment of a suite of appropriate climate change indicators and assessment tools within which ocean acidification is included as a related issue of emerging significance.

Table 4.1: Qualitative Descriptors for determining Good Environmental Status (GES) for the Marine Strategy Framework Directive (MSFD Directive 2008/56/EC) and possible consequences of Ocean Acidification (OA)

GES Qualitative Descriptors Annex 1 MSFD (Dir. 2008/56/EC)	Potential long-term consequences of OA for GES
(1) Biological diversity is maintained. The quality and occurrence of habitats and the distribution and abundance of species are in line with prevailing physiographic, geographic and climatic conditions	OA is an alteration to habitat characteristics which may alter the distribution and abundance of species and consequently the biodiversity
(2) Non-indigenous species introduced by human activities are at levels that do not adversely alter the ecosystems	There is a possibility that OA may favour some alien species increasing the probability of their becoming established in new areas
(3) Populations of all commercially exploited fish and shellfish are within safe biological limits, exhibiting a population age and size distribution that is indicative of a healthy stock	There may be direct impact of CO_2 and pH on some shellfish and fish species. Impacts on habitats (e.g. coral nurseries) and prey/foodwebs may further impact fish and shellfish stocks and place additional pressure especially on overfished stocks
(4) All elements of the marine food webs, to the extent that they are known, occur at normal abundance and diversity and levels capable of ensuring the long-term abundance of the species and the retention of their full reproductive capacity	OA may lead to changes in species distribution and abundance, for example in certain primary producers, and thus may impact on food web structures
(5) Human-induced eutrophication is minimised, especially adverse effects thereof, such as losses in biodiversity, ecosystem degradation, harmful algae blooms and oxygen deficiency in bottom waters	OA may alter ecological response to nutrient enrichment. Nutrient enrichment may affect OA especially in coastal and near shore waters
(6) Sea-floor integrity is at a level that ensures that the structure and functions of the ecosystems are safeguarded and benthic ecosystems, in particular, are not adversely affected	Areas of the seafloor will experience reduced aragonite/calcite saturation and may become undersaturated with shoaling of the saturation horizons. This may impact on benthic ecosystems such as deep sea corals
(7) Permanent alteration of hydrographical conditions does not adversely affect marine ecosystems	No clear consequence
(8) Concentrations of contaminants are at levels not giving rise to pollution effects (9) Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards	Speciation of contaminants may be affected, potentially influencing their uptake and/or toxicology. Organisms may be less well able to withstand exposure to contaminants with additional stress of OA
(10) Properties and quantities of marine litter do not cause harm to the coastal and marine environment	No clear consequence
(11) Introduction of energy, including underwater noise, is at levels that do not adversely affect the marine environment	OA will increase underwater noise transmission

4.3.1 CO_2 emission reductions

> *Climate-change negotiations focused on stabilizing greenhouse gases must consider not only the total radiation balance; they must also consider atmospheric CO_2 as a pollutant, an acid gas whose release to the atmosphere must be curtailed in order to limit ocean acidification.*
>
> *Monaco Declaration, 2008*

The most important requirement for ensuring ocean acidification and its subsequent effects do not reach critical levels is to reduce CO_2 emissions to the atmosphere. While climate change negotiations focus on terrestrial concerns and the thermal impacts of a number of greenhouse gases, including CO_2 but also methane, hydroflurocarbons (HCFs), nitrous oxide N_20 etc, emission targets must also consider levels of atmospheric CO_2 alone as a pollutant which increases the acidic level of the oceans (Monaco Declaration, 2008; Warren, 2009). If we consider a stabilisation of CO_2 concentrations at 450 ppmv, 10% of the surface ocean would experience a pH decrease of more than 0.2 units which is in violation of the criteria set forth by the U.S. Environmental Protection Agency (*EPA*) that '*for open ocean waters … the pH should not be changed more than 0.2 units from the naturally occurring variation*', and the 'guard rail' set by the German Advisory Council on Global Change (Schubert *et al*., 2006). Emissions reductions therefore need to be calculated in consideration of the CO_2 levels which impact on ocean system functioning, economic impacts on fisheries and aquaculture and socioeconomic impacts of reduced ocean 'health' (Cao and Caldeira, 2008; Warren, 2009).

Emission reductions require commitment on an international scale. The EU has committed to an overall reduction by at least 20% on the 1990 levels by 2020. A more immediate target is the reduction of emissions by 13% of 1990 levels for the period of 2008-2012 which would ensure compliance with the Kyoto Protocol.

A number of actions to ensure compliance with the targets set out for Ireland have been outlined in the NCCS. These include:

- Approximately 79% of reductions will result from emission cuts across a range of sectors, transport, residential, industrial, waste and agriculture. According to the Strategy these cuts should be incorporated into the development of all sectoral policies.

- Reductions credited to the Government in return for investments in emission-reduction projects in developing economies will account for 21% of reductions.

4.4 Mitigation and adaptation

The difference between a given emission pathway and the emissions allowable under an atmospheric CO_2 stabilization pathway could be thought of as a carbon gap that would need to be made up by increased carbon storage in biological, geological, or oceanic reservoirs.

Caldeira and Wickett, 2005

Efforts to mitigate the effects of ocean acidification can include 'adaptation, which accepts lower pH levels in the oceans and adjusts economic activity and resource management to take this into account; and remediation, which seeks to restore ocean pH levels to something approximating preindustrial levels to avoid the negative effects altogether' (Kite-Powell, 2009). At present it is impossible to consider remediation as a viable practical option.

There is a need to identify mitigation and adaptation actions required. The recent Monaco Declaration (2008) has urged policy makers to launch four pertinent initiatives:

1. Improve understanding of the impacts of ocean acidification by promoting research in the field.

2. Build links between economists and scientists to evaluate the socioeconomic extent of impacts and costs for action versus inaction.

3. Help improve communication between policymakers and scientists so new policies are based on current findings and scientific studies can be widened to include the most policy-relevant questions.

4. Prevent severe damages from ocean acidification by developing ambitious, urgent plans to cut emissions drastically.

Aside from the key requirement for CO_2 emission reduction, a number of future recommendations to ensure the integration of ocean acidification into mitigation and adaptation actions include:

- Adopt management goals, specifically in the areas of monitoring, research and public awareness. These should include collaborations nationally and also at an international level.
- Consider the negative influences on long-term ecosystem functioning and stability and associated services such as fisheries, aquaculture and recreation. While the economic value of these activities can be quantified the possible impact of ocean acidification on these important resources needs to be elucidated through research and monitoring. Ultimately, management strategies should include ecosystem based fisheries management which consider ocean acidification, monitoring critical fisheries, reducing fishing pressure and environmental stresses (Cooley and Doney, 2009a; Miles and Bradbury, 2009).
- Develop a coherent network of Marine Protected Areas. Protection of vulnerable species and habitats from other pressures may improve their resilience to climate change and ocean acidification.
- Include of ocean acidification in the €15m multi-annual climate change awareness campaign outlined by the government in the Climate Change Strategy 2007-2012. This will ensure local recognition of the impacts and enable consumers to make better informed choices.
- Further reinforce the need for a reduction in CO_2 emissions.

4.4.1 Carbon Storage in the oceans

Research and development of methods for the removal of CO_2 from the atmosphere and its storage in the marine environment can vary in timescales of CO_2 sequestration and holding limits. However, in the light of the consequences of climate change, international mitigating initiatives have been proposed to reduce net emissions in future decades. These initiatives will be defined by international policies and while, for some methods direct actions may not be proposed for Irish or even Atlantic waters, considering the global nature of the problem, their implications are a global concern. Current knowledge of the sequestration ability and potential risks of these initiatives, particularly in relation to acidification, differ significantly.

- Iron fertilization of the oceans to stimulate the production of phytoplankton. This method would relate specifically to areas of iron limitation such as the Southern Ocean and would therefore not be specifically applicable to Irish waters. While currently topical, iron fertilization includes a number of challenges as questions have been raised about its efficiency in sequestering CO_2 over long time scales and the impacts of large-scale iron additions on the marine ecosystem. A recent (non-binding) resolution by the London Convention states that ‘Given the present state of knowledge, ocean fertilization activities other than legitimate scientific research should not be allowed’ and scientific research proposals should be assessed on a case-by-case basis.

- Injection and subsequent dissolution of CO_2 in the deep oceans. CO_2 injected in this way could remain isolated from the atmosphere for several centuries (IPCC, 2005). However, over long time periods the equilibrium between the atmospheric and seawater CO_2 concentrations would be re-established. This therefore only offers a short-term resolution as future generations would be subjected to irreversible and undesirable effects (see below).

- Storage of CO_2 as a liquid or hydrate on the sea floor. This would be possible at water depths below 3000m due to its greater density at this depth. Again this technology would, as a result of the lack of a physical barrier, result in a slow dissolution of CO_2 into the overlying water column. Chemical changes and subsequent biological influences of this type of storage are likely to be significant (Cladeira and Wickett, 2005). This is especially true when considering the stable environment to which organisms at such depths are exposed and their subsequent inability to adapt to rapid changes. Risks also arise from out-gassing into the atmosphere. If a large plume should rise to the sea surface, the possible ecological results could be considerable. The recent OSPAR Decision 2007/1 currently prohibits the storage of carbon dioxide streams in the water column or on the sea-bed.

- Carbon Capture and Storage (CCS). This involves the injection of CO_2 into geological formations such as deep saline formations, and oil and gas reservoirs, below the seafloor (See Box 7).

- The sequestration of CO_2, while reducing atmospheric concentrations, does not alleviate the current dependence on fossil fuels. Thus carbon sink activities can be regarded as an option which allows increased time to develop renewable energies.

Box 7: Carbon Capture and Storage (CCS)

This technique involves the separation of CO_2 from a point source, its transportation and storage in isolation from the atmosphere (IPCC, 2005, 2007). CCS techniques have the potential to sequester and retain carbon on geological time scales and have been used for some time in the oil and gas industry to flush out residual petroleum resources from reservoirs. Sustainable Energy Ireland recently published a report assessing the potential for CCS in Ireland (2008). Major point source emissions in Ireland were identified and power stations emerged as the priority candidates for capture. The depleting Kinsale Head gas field was presented as a possible location. The study estimated that Ireland has a total storage capacity of 93,115 Mt.

Although the potential of this technique is recognised, significant research into the possible environmental impacts during capture, transport and storage is required, especially in the long term (IPCC, 2007). Transportation risks include the rupture or leaking of pipelines, which could lead to the accumulation of dangerous levels of CO_2 in the air. While accident numbers for comparable CO_2 pipelines are very low, there are risks of localised accumulation (IPCC, 2005). There remain a number of barriers including legal, safety and public perception concerns. Concerns about storage sites include the risk of seismic activity which could cause a rapid release of CO_2 and the impact of old and poorly sealed well bores on the storage integrity of depleted oil and gas fields. A key concern for sub-seabed CCS is the possible impact on marine ecosystems due to leakage and in particular due to pH changes.

In 2007 both the London and OSPAR Conventions were amended to address the international legality of CO_2 injection into sub-seabed settings. A CCS Directive was adopted in March 2009 by the EU to provide a legislative framework for the full source to sink CO_2 chain. The need for a clear and rigorous regulatory framework on CCS has been recognised. In the longer term, the Government of the nation in which the injection/storage site is situated may take over stewardship of each site, with stringent independent monitoring of the sites carried out by internationally recognised bodies required.

4.5 Necessary Actions

There appears to be no practical way to remove additional CO2 from the oceans after it has been absorbed, nor any realistic way to reverse its widespread chemical and probable biological effects.

Raven et al.*, 2005 (Royal Society)*

There is a pressing requirement for improved knowledge of the future impacts of ocean acidification. As stated in the Marine Strategy Framework Directive, a precautionary principle should be applied to the marine environment and preventative action should be taken. In order to adapt, it is important to increase our understanding of the current condition of Irish marine waters and the possible impacts (direct and indirect) on areas such as fisheries and aquaculture and marine goods and services. Information is required to predict impacts with greater certainty to facilitate development of mitigation strategies and adaptation to the impending effects of ocean acidification.

4.5.1 Information needs

In order to assess the current state of the marine environment and determine the future monitoring and research requirements a number of significant questions need to be answered:

1. What is the current pH variability (temporal and spatial) in Irish waters?

2. What is the seasonal and annual atmospheric-water CO_2 flux?

3. Which organisms are most at risk from decreasing pH and what is their role in ecosystem stability and function?

4. How will impacts on individual organisms undermine the utilisation of marine resources?

5. Which ecosystems are vulnerable to acidification?

6. In the Irish context, what processes and ecosystem interactions need to be studied?

7. What are the potential long-term impacts for society?

The monitoring, assessment and research needs to address these are discussed in Chapter 5.

Mace Head Atmospheric Research Station,
Photo courtesy of Colin O' Dowd, NUI Galway

CHAPTER 5. RESEARCH AND INFORMATION NEEDS

A major internationally coordinated research effort should be launched. The scale of this needs to be commensurate with that on the effects of climate change arising from enhanced greenhouse emissions.

Raven et al.*, 2005 (Royal Society)*

5.1 Background

Awareness of ocean acidification as an emerging threat to ocean ecosystems has only permeated the wider scientific community during the last few years. This is reflected in the recent international research effort in this area. During the four years to September 2008 there have been 168 scientific papers on ocean acidification, while during the preceding 55 years (1949-2004) there were 158 (Gattuso, 2008). Given the breadth of the subject area and the range of potential impacts, this is still surprisingly low, although clearly growing exponentially.

Ocean acidification has now been widely acknowledged and recognised by a number of countries as an important research priority and has often been referred to as 'the other CO_2 problem'. The recent report by the 2nd international symposium on 'The Ocean in a high-CO_2 world' highlighted the importance of improved collaboration, increased funding and greater public awareness in the area of ocean acidification (Orr *et al*., 2009).

Ireland's marine location and extensive marine resources in our shelf seas, Atlantic waters and habitats of the west coast mean we are uniquely positioned to contribute to international scientific efforts to monitor and understand the impacts of ocean acidification. Monitoring and research of key biological, chemical and physical factors in these regions will allow us to determine the current status of Irish Marine waters, the rate of change in the carbonate cycle and the influence of this change on natural communities and ecosystems.

There are localised variations in the level of CO_2 uptake by marine systems. Furthermore, there is a complexity in the impacts of these variations on ecosystems. In this context it is important to identify the variability in ocean acidification and its effects on local ecosystems. Species, functional groups and ecosystems that are most at risk need to be identified and monitored. Research into their adaptive abilities with reference to future pCO_2 and pH predictions needs to be investigated.

Existing activities, capacities and infrastructure should be maximised to ensure economic efficiencies and a consolidation of national research efforts. Research efforts will provide a knowledge base for policy makers and, as such, research projects need to be formulated so as to take the information needs of policy makers, as critical end users, into account (Orr *et al*., 2009).

5.1.1 National research and cooperation

Ireland should develop a national monitoring network supporting research activities in this field. Synergies between current and future national research and monitoring efforts and international efforts should be encouraged. Cooperation and collaborations with international partners will enhance research capabilities, ensure consistent protocols, avoid replication and foster the widest possible dissemination of research outcomes. Further, it will ensure data management and access at a global scale. By building a research capability this will allow Ireland to fully participate in the international research effort in this area and to avail of international funding. In particular there are clear advantages in collaborating with the UK in monitoring and research activities and exchange of information given the shared waters and expertise that exists in many Institutions within the UK such as Plymouth Marine Laboratory, University of East Anglia, and the National Oceanography Centre, Southampton.

The Marine Institute’s SSTI funded Sea Change programme includes a Rapid Climate Change programme. Under this, a two year collaborative project between NUI Galway and the Marine Institute ‘Impacts of increased atmospheric CO_2 on ocean chemistry and ecosystems’ is developing capabilities for measuring pCO_2, and air-sea CO_2 fluxes, inorganic carbon chemistry and pH and is initiating baseline measurements of these parameters in coastal and offshore waters. This report, summarising the issues and state of knowledge and communicating ongoing monitoring and research needs into ocean acidification, is a deliverable of this project.

Box 8. Impacts of Increased Atmospheric CO_2 on Ocean Chemistry and Ecosystems

A NUI, Galway & Marine Institute collaborative SSTI-funded Project (2008 – 2010) under the Sea Change Programme.

The objectives of the project include:

- initiation of research into ocean carbon processes in Irish Shelf Sea waters including the investigation into air-sea CO_2 fluxes;
- establishment of high-quality chemical measurement capabilities to describe dissolved inorganic carbon chemistry (DIC) in seawater;
- deployment of automated systems on moorings and on the *RV Celtic Explorer* to measure CO_2 in seawater;
- consideration of the potential indicators of ecological impacts of Ocean Acidification; and,
- formulation of recommendations for future Irish research and long-term monitoring.

Specific activities within the project include:

- development of capabilities for making specialised high precision measurements of the carbonate system and subsequent determination of accurate pH;
- a meteorological and ocean chemistry buoy was deployed in July 2008 at Mace Head. This provides continuous sea surface measurements for various parameters to parallel atmospheric measurements made at the NUIG Mace Head atmospheric research centre;
- measurements of air-sea CO_2 fluxes are made at Mace Head and on research surveys using specialist equipment installed on the RV Celtic Explorer; and,
- seasonal baseline surveys of the carbonate system. Sampling is undertaken on transects across the shelf and in deeper waters of the Rockall Trough and in the Porcupine Seabight on board the *RV Celtic Explorer*. These studies are tied into broader multidisciplinary surveys to facilitate cost-effective collection of integrated datasets. DIC, dissolved oxygen and nutrient data are collected alongside other oceanographic data.

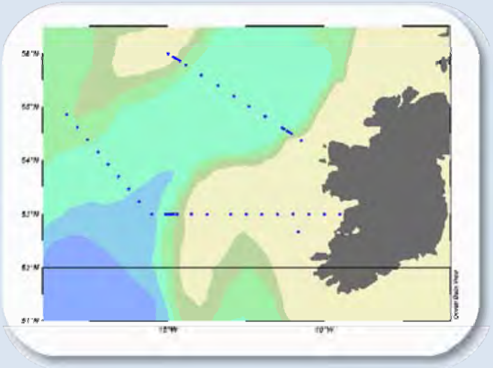


Photo: Mace Head Buoy, Photo courtesy of James Ryan, Sustainable Energy Authority Ireland (SEAI). Map: Stations sampled for carbon system parameters during an oceanographic survey on board the *RV Celtic Voyager* (Feb. 2009)

5.1.2 Current international research efforts

International Research efforts with respect to carbon cycling include among others (Annex 1), in the US the Ocean Carbon and biochemistry program (OCB) and in Europe the CARBOOCEANS project. The surface ocean lower atmosphere study (SOLAS) network, of which the Irish research community is a member, is an international research initiative into understanding the interaction between key biogeochemical-physical interactions and feedbacks between the ocean and atmosphere. The UK Natural Environmental Research Councils (NERC) centre is currently responsible for Carbon-ops, which is involved in automated atmospheric CO_2 measurements and CASIX is a centre for the observation of air-sea interactions (Annex 1). NERC, Defra and DECC (Department of Energy and Climate Change) are co-funding a 5 year £11m UK Ocean Acidification research programme while Germany has also launched a 3 year research programme (Annex 1).

2008 saw the start of the first major EU initiative in this field; the FP7 European Project on Ocean Acidification (EPOCA). This involves collaboration between 27 partners in 9 countries although there is no Irish partner. Broadly, the project aims to document changing ocean acidification across space and time primarily using paleo-reconstruction techniques to investigate the impact of ocean acidification on marine organisms and ecosystems; to integrate the chemical, biological and biogeochemical impacts of ocean acidification into biogeochemical, sediment and coupled ocean-climate models; to assess uncertainties, risks and thresholds (‘tipping points’) related to ocean acidification at various scales. The latter includes assessing pathways of CO_2 emissions required to avoid the identified thresholds.

5.2 Monitoring and assessment needs

Developing good observing and monitoring systems will be fundamental for understanding how ocean acidification and other global changes interact.

Orr et al.*, 2009*

Long-term monitoring efforts of key parameters (carbonate parameters, pH, related physico-chemical parameters, key species and ecosystems) are vital and require a commitment to long-term funding. The requirements in this area will require new or redirected resources in a sustained dedicated effort. However, investment in specific expertise and capacity would underpin cost effective monitoring by facilitating addition of ocean acidification data collection to existing monitoring activities, thus adding value to these activities. The resultant outcomes should allow us to:

- contribute to national statutory monitoring commitments such as those under the MSFD;
- assess the current status of Irish marine waters and monitor changes which are pertinent to local climate and biogeochemical conditions;
- increase the spatial coverage of data sets globally. This will allow for a more precise validation of models and long-term times series data sets will allow for the evaluation of trends in ocean acidification (ICES, 2008; Orr *et al*., 2009);
- identify if mitigation undertaken is effective;
- assess the impacts on marine life, ecosystems and biodiversity;
- provide a basis to assess impacts to marine ecosystems goods and services;
- develop the ability to report on the socio-economic impacts on communities relying on goods and services derived from affected ecosystems.

Such monitoring programmes should:

- be multi-disciplinary and strategic in nature and where possible be coupled with complementary activities. A starting point would be to build on the capabilities gained in the NUI Galway-Marine Institute project on ocean acidification and to continue to collect data on acidification parameters during seasonal marine climate change surveys. These surveys equally require a commitment to long-term monitoring and a multidisciplinary approach to data collection which will ensure the efficient use of resources;
- co-ordinate and make best use of currently available infrastructure and resources to deliver cost effective monitoring. For example, the Inshore Coastal Observatories (SmartBay), the Irish National Weather Buoy Network (www.marine.ie/databuoy), National Research Vessels (Figure 5.1);
- build on areas where Ireland has research strengths and has recently made advances that can be coupled to existing observational programmes, research ships or ships of opportunity and existing moored buoys;
- develop and strengthen critical capacity and expertise to underpin these activities; and
- link to international activities and especially UK and French initiatives in ocean regions contiguous to Irish waters to ensure data exchange, high data quality and to complement, rather than replicate, studies. Monitoring programmes should follow a cause and effect framework to elucidate the long-term influence of changing carbonate parameters and other parameters (temperature, invasive species, CO_2-uptake characteristics of primary producers, etc.) on Irish coastal and shelf systems. This requires appropriate indicators for biological and ecological impacts of ocean acidification in the North East Atlantic to be agreed, for example, through OSPAR.

Figure 5.1:** The* **R. V. Celtic Explorer** ***(left) is a 65.5 m multipurpose research vessel that can accommodate 16-18 scientists. The **R.V. Celtic Explorer** ***is based in Galway on the Irish west coast. The*** **R. V. Celtic Voyager** ***(right) is also used for oceanographic research cruises in Irish waters.***

5.2.1 Monitoring of CO_2 fluxes and the carbonate system

> *International cooperation in the development of a 'coordinated global network of ocean observations' will enable the use of existing infrastructure and programs and also identify additional sites for monitoring*
>
> *Orr* et al.*, 2009.*

Figure 5.2: The Mace Head Atmospheric Research Station is situated on the west coast of reland. Research is conducted here on atmospheric composition (greenhouse gases, CFCs, HCFCs, reactive gases, atmospheric aerosols and aerosol-cloud interactions) and essential climate variables. Within the project 'Impacts of Increased Atmospheric CO_2 on Ocean Chemistry and Ecosystems' eddy co-variation measurements of air-sea CO_2 fluxes is performed on a 22 m flux tower (top left). The Mace Head meteorological and ocean chemistry buoy (bottom right), located 3 km off-shore from Mace Head. pCO_2 measurements are performed with a Pro Oceanus instrument.

There is the potential for technological advances in instrumentation and sensors for *in situ* autonomous measurement of carbonate system parameters. Technological developments will allow the building and maintenance of expertise/capacities for complicated measurements.

The requirements to describe the carbonate system in Irish marine waters should account for the following:

- Determination of the CO_2 exchange fluxes and budgets for Irish coastal shelf waters. Both seasonal and spatial data are required. This should focus on coastal, shelf and oceanic waters as areas subject to varying degrees of biological activity.
- Identification of high-sensitivity coastal and continental shelf regions along with key water masses. New monitoring and process study sites could then be established to detect the current status and changes in the carbonate system.
- Transect sampling of carbonate parameters along land-ocean continuum (river-estuarine-coastal-shelf). This would enable the determination of seasonal and annual trends in the influence of river inputs and biological activity on variations observed. This would allow determination calcium carbonate saturation depths over vertical and horizontal spatial scales along the continuum.
- Assessment of the status and change within variable coastal waters through coastal sentinel stations. These are required for the generation of datasets of high temporal resolution through the use of *in situ* measurements and frequent sample collection. Mace Head offers a unique location for coupling atmospheric and coastal seawater monitoring given the limited influence of continental air masses, limited freshwater inputs and the excellent facilities already in place (Figure 5.2).
- Continuation and expansion of a network of autonomous sensors. These should include existing buoys, the Mace Head inshore buoy and the proOceanus pCO_2 sensor on the RV Celtic Explorer (Section 5.5). Total alkalinity, pH, and DIC still require collection of discrete samples for shipboard or laboratory analysis.
- Carbonate monitoring systems and protocols should be standardised according to the methodology of Dickson *et al.* (2007). pH should be calculated from measurements of DIC and TA. Quality assured measurements of dissolved inorganic carbon and total alkalinity should be underpinned by use of existing certified reference material (CRMs) (Orr *et al*., 2009).
- Concurrent measurement of other parameters such as ocean temperature, salinity, dissolved oxygen, fluorescence, currents, wind data, nutrient concentrations, trace metal speciation, phytoplankton biomass and abundances are essential. This will ensure integrated data sets for each study area.

5.2.2 Monitoring the impacts on marine life and natural ecosystems

A number of biological parameters have recently been identified which could allow for the detection of changes to natural systems over time (Orr *et al*., 2009). These include: shell weight and thickness of calcifying organisms, calcification rates, abundance and size of calcifying and non-calcifying organisms, average particulate inorganic carbon concentrations in open ocean waters, biochemical signatures of physiological stress and ecosystem species composition.

Programmes that already monitor organisms or ecosystems could be expanded to monitor carbonate chemistry and other appropriate biological parameters (e.g. calcification rates) to allow us to link changes in ecosystem functioning to changes relating to ocean acidification and the carbon cycle. Such programmes would help us to predict how future chemical changes due to ocean acidification will result in ecosystem changes. In line with international initiatives, for example those of OSPAR, key biological indicators of ocean acidification should be identified for the Irish Marine Region and monitored at time-series sites (seasonally and annually). These could include:

- **Planktonic primary producers** such as coccolithophores, diatoms, flagellates.
- **Deep water coral systems** such as those along the margins of the Rockall Trough.
- Regions of **coccolithophore** blooms and abundance.
- **Bivalve species** of high socioeconomic importance in shallow coastal sites such as mussels and oysters.
- Coastal **maërl** (calcareous red algae) systems on the west coast of Ireland.
- **Keystone faunal species** in shallow benthic systems (polychaetes, echinoderms etc).
- **Keystone macroalgae** including fucoids and kelps species of ecological and economic importance.

5.3 Research needs and focus areas in Irish coastal and shelf waters

Research into ocean acidification is in its infancy although rapidly expanding. As an issue of global importance Irish researchers should be supported and encouraged to contribute to the growing body of knowledge and tie in with international work in this field. A number of recent publications and reports have highlighted the key research needs in the area of ocean acidification (Raven *et al*., 2005 (Royal Society); Kleypas *et al*., 2006; Schubert *et al*., 2006; ICES, 2008; Doney *et al*., 2009b; Orr *et al*., 2009). The next section (including Box 9 and 10) aims to synthesise the recommendations made in these documents. The EPOCA project is developing a *Guide to Best Practices in Ocean Acidification Research and Data Reporting* which will be of help to researchers in this field.

Tracking acidification and its impacts requires large-scale and sustained programmes of *in situ* measurements (Orr *et al*., 2009). Fundamental research is an essential part in this process as it allows us to define and parameterise key environmental and ecological processes. This, in turn, will allow more refined and accurate model predictions of future impacts on marine ecosystems.

Box 9: Research needs linking ocean acidification and biogeochemical cycles and feedbacks

- **Carbon Cycle:** What is the role of the Irish marine system in the global carbon cycle, and are Irish Shelf waters to the west of Ireland a source or sink of CO_2? The carbonate system in key Irish Marine water masses needs to be defined on seasonal, annual and decadal time scales. How will ocean acidification influence the efficiency of the biological carbon pump?

- **Ocean Circulation:** How will changes in ocean circulation, and increased stratification interact with acidification (amplify or dampen?)

- **Nutrient Speciation:** How will decreasing pH affect the speciation of nutrients such as P and Si? Speciation of trace metals (Fe, Zn, Co, Mn, Cu, Cd) may also be affected. Indirectly the oxidation/reduction chemistry of crucial elements may be affected (Fe, Co and Mn).

- **Nitrogen:** Will nitrogen fixation, denitrification and nitrification be induced by changes in phytoplankton species composition and oxygen levels? How will this, in turn, influence primary production and localised foodwebs?

- **Dimethyl sulfide (DMS)**: Increased primary production in surface layers due to increased pCO_2 could result in an increased production of DMS; this, in turn, would increase cloud formation and so become a negative feedback to climate change. Could this occur in Irish marine waters and what would be the impacts on Irish weather systems?

5.3.1 Impacts on species and ecosystems

To-date most experiments on the effects of ocean acidification have been short-term (hours to weeks). Some species can acclimatise over long time periods while others can survive short-term exposure to low pH but suffer from long-term exposure. Hence there **is a need for long-term exposure experiments that realistically simulate natural conditions**.

Experimental **research approaches can include small-scale laboratory experiments, benthic and pelagic mesocosm studies, observations of ocean systems and open-ocean CO_2 enrichment type perturbation experiments** (Orr *et al*., 2009). Laboratory experiments can isolate various factors and specific processes which can increase our understanding of results from larger scale mesocosm and field studies. Mesocosms can produce useful results about species composition changes. Furthermore, as different responses can be observed in the laboratory and the field (ICES 2008), experiments that manipulate pCO_2 *in situ* while leaving other parameters undisturbed need to be undertaken.

Keystone species, functional groups and ecosystems that are most sensitive to ocean acidification should be targeted and their role and broader influence should be defined. Sensitivity indicators such as mortality, stress, changes in performance and susceptibility to disease should be examined to try and understand the mechanistic basis for sensitivity. Also tracking of abundance and depth distribution of natural populations of key calcifying and non-calcifying organisms will enable the detection of possible shifts and discrimination between natural variability and anthropogenically forced changes. Furthermore, **critical biological thresholds or tipping points, and the adaptive ability of species/functional groups to deal with ocean acidification should be examined**. Plasticity, acclimatisation and evolutionary adaptation should be investigated. The plasticity in responses to changes in pH and carbonate parameters, genetic diversity and the relationship of genetics to sensitivity should be examined at the population level.

While a whole-organism approach with multiple endpoints, both physiological and behavioural, should be applied in order to understand cause and effect, it is important to integrate molecular and biochemical mechanism studies (Pörtner, 2008). In this context **knowledge of the mechanistic links between CO_2-dependent functions from molecule to ecosystem level is required**. This requires investigations into the metabolic costs to maintain intracellular pH, lower protein synthesis and decreased growth rates, proper functioning of trans-membrane intracellular pH, the production and functioning of mucus, and cell-cell signalling.

Determination of the affects on community structure and composition and how species-specific responses will affect community composition at all levels, from bacteria to vertebrates, is required. Therefore, **ecosystem-wide multidisciplinary studies** will allow consideration of how changes will influence such things as habitats, prey loss, and biodiversity (Cooley and Doney, 2009a).
The interactive effects of **ocean acidification and other factors such as temperature, sediment processes, anthropogenic nutrient loadings, metal toxicity, invasive species, overfishing, increased stratification, decreased oxygen in warmer waters, changes in salinity due to heating and precipitation effects, and changes in ocean circulation and wind need to be considered** when determining the impact of ocean acidification. In particular, thermal tolerance windows of species and how this relates to ocean acidification induced changes should be studied. Elevated CO_2 may enhance sensitivity of organisms to thermal extremes due to a reduction in tissue functional capacity (Pörtner, 2008).

As the exact response of seawater to increasing CO_2 depends on the chemical constituents and natural environmental conditions of each area, there will be geographical differences in the response to increased atmospheric CO_2 levels. There is therefore a need for localised studies of the possible effects of acidification. The **identification and study of ecosystems and species in Irish Marine waters that have global importance (e.g. deep sea corals, seaweed beds, and oyster and mussel beds) is required**.

Box 10. Research Needs - Species and Ecosystems at Risk

- **Economically important molluscs (mussels, oysters, etc.):** How will increasing pCO_2 impact the precipitation of $CaCO_3$ by benthic calcifiers? Considerations should also include reproduction, fertilisation, larval and other life stage development and mortality, recruitment and susceptibility to disease.
- **Deep sea coral reefs:** How will the corals that define these ecosystems be affected by ocean acidification and how will this affect the communities and species that depend on them (nutrition, nursery etc)? For example the Rockall Trough on the western edge of Ireland's continental shelf, hosts a vast array of cold water corals at different depths along its flank (Masson *et al.*, 2002, Akmetzhanov *et al.*, 2003) which interact with a range of deep water masses. This could provide an ideal system for studying the impact of ocean acidification.
- **Calcifying plankton (coccolithophores, foraminifera, pteropods):** What is the importance of calcifying plankton in Irish coastal and shelf ecosystems (benthic and pelagic)? What will be the effect of decreased saturation states and decreased pH on shell formation and dissolution, and physiological processes? Will seasonal and long-term abundances change? What effect will this have on associated species (diatoms, other bloom forming phytoplankton) and up through the food web? What is the feedback influence of coccolithophore bloom formation on the pH state of seawater, albedo of the earth's surface and biological pump of carbon?
- **Non-calcifying phytoplankton:** Will specific phytoplankton species gain from increased pCO_2 levels due to CO_2 being energetically less expensive? Will potential changes in nutrient and trace metal speciation change production and biomass and/or induce species shifts? Will the stoichiometry (elemental composition) of microalgal species be influenced? How will the projected changes alter ecosystem processes and biogeochemical cycles?
- **Key fisheries species:** How will increased pH alter eggs and larval stages of important fish species? In order to understand the possible impacts of ocean acidification increased knowledge of processes relating to key fisheries species is required (migration, spatial population structure, community and ecosystem structuring processes, including competition and predation). Geographical information on fish stocks, the thermal tolerance of species and projected spatial and temporal changes in temperature, fish stock distribution and pH change should be combined to determine the possible synergetic influence of temperature and ocean acidification on fish stocks (ecologically and economically important).
- **Macroalgae:** What will be the effect on intertidal and subtidal macroalgal species? In particular the habitat forming species such as *Ascophyllum nodosum*, kelp forests and maërl beds, and also invasive species such as *Sargassum muticum*? Will there be alterations in productivity, grazing, seaweed quality and ecosystem structure?
- **Harmful Algal Blooms (HABs):** What is the potential impact of higher pCO_2 oceans on HABs?
- **Echinoderms:** Enchinoderms are key stone species in many ecosystems. What will the effect of ocean acidification be on these species, their growth rate and larval stages?
- **Invasive species:** How will reduced pH levels combined with other climate changes alter the colonisation of coastal areas by invasive species?
- **Noise and marine mammals:** How will reduced low frequency absorption and increased noise levels due to increased acidification influence marine mammals in Irish waters.

5.3.2 Tipping points

Are there biological/ecological tipping points or thresholds beyond which dramatic irreversible influences on species and ecosystems will occur? Critical biological thresholds need to be identified for species and ecosystems. Also we need to consider how tipping points in other factors such as sea surface temperature (SST), currents and physical pumps might alter the projections of how ocean acidification will progress.

5.3.3 Modelling studies

Modelling will allow us to predict future pH and carbonate change and identify geographical areas most at risk and threats due to changing saturation horizons. This in turn will allow focus to be placed on these areas and the ecosystems, and communities therein. Coupled physical, biochemical and trophic level models would allow us to assess the possible influences on ecosystem-wide processes, aquaculture and fisheries. In this context a multi-disciplinary approach is necessary. Modelling studies will allow us to identify what areas or processes need to be studied and will thus have a feedback to research efforts. Furthermore, modelling may also support predictive studies on climate feedback loops associated with oceanic carbon processes.

5.3.4 Mitigation

Carbon sequestration: The direct storage of CO_2 in geological reservoirs, ocean fertilisation and direct injection of carbon into the deep ocean are being considered to mitigate rising atmospheric CO_2. Baseline and continuing monitoring and research of the possible implications for the marine areas is required. The possible risk to local ecosystems needs to be determined.

5.3.5 Technological opportunities

The *Sea Change* Foresight exercise identified market opportunities for Ireland in advanced technologies for autonomous monitoring of oceanic and atmospheric conditions and there is ongoing investment building research capacity in the area of sensor technologies (www.marine.ie/home/services/operational/SmartBay/). Currently, of the carbonate parameters only pCO_2 can be measured *in situ* and other parameters such as DIC, TA and pH remain the preserve of a few specialised research laboratories. While the technological challenges of developing novel sensors with sufficient precision and accuracy should not be underestimated, there is a potential market opportunity for any company that can deliver robust and reliable technology.

5.3.6 Socio-economic implications

As the research findings in this area emerge there will undoubtedly be further impacts and adaptations that need to be considered from a socioeconomic perspective. Further research on direct impacts on economically important species is needed. As the results from fundamental experimental research and monitoring efforts emerge implications for fisheries, aquaculture and tourism (due to biodiversity loss and habitat modification/loss) need to be explored. In particular ocean acidification effects on fisheries, and the ecosystem functions that support it, require significant further research to facilitate the prediction of impacts with a reasonable degree of certainty.

Box 11. 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_2 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 CO2 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).

BIBLIOGRAPHY

Andersson A.J., Mackenzie F.T., Ver L.M. (2003) Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO_2. Geology 31 (6): 513-516

Armstrong J.L., Boldt J.L., Cross A.D., Moss J.H., Davis N.D., Myers KW, Walker R.V., Beauchamp D.A., Haldorson L.J. (2005) Distribution, size, and interannual, seasonal and diel food habits of northern Gulf of Alaska juvenile pink salmon, *Oncorhynchus gorbuscha*. Deep Sea Research II 52: 247-265

Armstrong R.A.C., Lee C., Hedges J.I., Hobjom S., Wakeham S.G. (2002) A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep-Sea Research II 49: 219-239

Arrigo K.R. (2007) Marine Manipulations. Nature 450: 491-492

Azam F., Fenchel T., Field J.G., Gray J.S., Meyer-Reil L.A., Thingstad F. (1983) The ecological role of water-column microbes in the sea. Marine Ecology Progress Series 10: 257-263

Barcelos e Ramos J., Biswas H., Schulz K.G., LaRoche J., Riebesell U. (2007) Effect of rising atmospheric carbon dioxide on the marine nitrogen fixer *Trichodesmium*. Global Biogeochemical Cycles, 21, GB2028, doi:10.1029/2006GB002898

Barnes R.S.K., Hughes R.N. (1988) An introduction to Marine Ecology. Blackwell Scientific Publications. 351 pp

Bates N.R., Peters A.J. (2007) The contribution of atmospheric acid deposition to Ocean Acidification in the subtropical North Atlantic Ocean. Marine Chemistry 107: 247-558

Bathmann U.V., Noji T.T., von Bodungen B. (1991) Sedimentation of pteropods in the Norwegian Sea in autumn. Deep Sea Research 38: 1341-1360

Beaugrand G., Edwards M., Brander K., Luczak C., Ibanez F. (2008) Causes and projection of abrupt climate-driven ecosystem shifts in the North Atlantic. Ecology Letters 11: 1157-1168

Beck M.W., Heck K.L., Able K.W., Childers D.L., Eggleston D.B., Gillanders B.M., Halpern B.S., Hays C.G., Hoshino K., Minello T.J., Orth R.J., Sheridan P.F., Weinstein M.P. (2003) The role of nearshore ecosystems as fish and shellfish nurseries. Issues in Ecology 11: 1-12

Behrenfeld M.J., O'Malley R.T., Siegel D.A., McClain C.R., Sarmiento J.L., Feldman G.C., Milligan A.J., Falkowski P.G., Letelier R.M., Boss E.S. (2006) Climate driven trends in contemporary ocean productivity. Nature 444: 752-755

Berelson W.M., Balch W.M., Najjar R., Feely R.A., Sabine C., Lee K. (2007) Relating estimates of $CaCO_3$ production, export, and dissolution in the water column to measurements of $CaCO_3$ rain into sediment traps and dissolution on the sea floor: a revised global carbonate budget. Global Biogeochemical Cycles 21, GB1024, doi:10.1029/2006GB002803

Bertness M.D., Leonard G.H., Levine J.M., Schmidt P.R., Ingraham A.O. (1999) Testing the relative contribution of positive and negative interactions in rocky intertidal communities. Ecology 80: 2711-2726

Bijma J., Spero H.J., Lea D.W. (1999) Reassessing foraminiferal stable isotope geochemistry: impact of the oceanic carbonate systems (experimental results). In Use of Proxies in Paleoceanography: Examples from the South Atlantic, Eds. G. Fisher, and G. Wefer. Springer-Verlag, New York, pp. 489-512

Bijma J., Honisch B., Zeebe R.E. (2002) Impact of the ocean carbonate chemistry on living foraminiferal shell weight: comment on the 'Carbonate ion concentration in glacial age deepwaters of the Caribbean Sea' by W.S. Broecker and E Clarke, Geochemistry, Geophysics, Geosystems 3: 1064

Bindoff N.L., Willebrand J., Artale V. Cazenave A., Gregory J., Gulev S., Hanawa K., Le Quéré C., Levitus S., Nojiri Y., Shum C.K., Talle, L.D., Unnikrishnan A. (2007). Observations: Oceanic Climate Change and Sea Level. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Bown P., Pearson P. (2009) Calcareous plankton evolution and the Paleocene/Eocene thermal maximum event: New evidence from Tanzania. Marine Micropaleontology 71: 60-70

Breitbarth E., Bellerby R. J., Neill C. C., Ardelan M. V., Meyerhöfer M., Zöllner E., Croot P. L., Riebesell U. (2009) Ocean Acidification affects iron speciation in seawater. Biogeosciences Discussions., 6, 6781–6802

Brennan S.T., Lowenstein T.K., Horita J. (2004) Seawater chemistry and the advent of biocalcification. Geology 32: 473-476

Brewer P.G., Goyet C., Friederich G. (1997) Direct observation of the oceanic CO_2 increase revisited. Proceeds of the National Academy of Sciences, USA 94: 8308-8318

Browne, R., Deegan, B. Watson, L. Mac Giolla Bhríde, D, Norman, M. ó Cinnedie, M, Jackson, D., O'Carroll, T. (2008) Status of Irish Aquaculture 2007. Report prepared by MERC Consultants on behalf of Marine Institute, Bord Iascaigh Mhara and Taighde Mara Teo 142 pp

Burns W.C.G. (2008) Anthropogenic carbon dioxide emissions and ocean acidification. In Saving Biological Diversity: Balancing protection of endangered species and ecosystems Eds. Askins R.A., Dreyer G.D., Visgilio G.R., Whitelaw D.M. Springer 190-196 pp

Caldeira K., Wickett M.E. (2003) Anthropogenic carbon and ocean pH. Nature 425: 365

Caldeira K., Wickett M.E. (2005) Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. Journal Geophysical Research doi:10.1029/2004JC002671

Cannaby H., Hüsrevoğlu Y.S. (2009) Low frequency variability and long term trends in Irish Sea surface temperature records. ICES Journal of Marine Science 66, doi:10.1093/icesjms/fsp062

Canadell J.G., Le Quéré C., Raupach M.R., Field C.B., Buitenhuis E.T., Ciais P., Conway T.J., Nathan P.G., Houghton R.A., Marland G. (2007) Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks. Proceeds of the National Academy of Science 104 (47): 18866-18870

Cao L., Caldeira K. Atmospheric CO_2 stabilization and ocean acidification. 2008 Geophysical Research Letters L19609 doi: 1029/2008GL035072

Cecchini S., Saroglia M., Caricato G., Terrova G., Sileo L. (2001) Effects of graded environmental hypercapnia on sea bass (*Dicentrarchus labrax* L.) feed intake and acid-base balance. Aquaculture Research 32: 499-502

Chen G.T., Millero F.J. (1979) Gradual increase of oceanic CO_2. Nature 277: 205-206

Childress J.J., Seibel B.A. (1998) Life at stable low oxygen levels: adaptations of animals to oceanic oxygen minimum layers. Journal of Experimental Biology 201: 1223-1232

Chung S.N., Lee K., Feely R.A., Sabine C.L., Millero F.J., Wanninkhof R., Bullister J.L., Key R.M., Peng T.-H. (2003) Calcium carbonate budget in the Atlantic Ocean based on water column inorganic carbon chemistry. Global Biogeochemical Cycles 17:1093 doi:10.1029/2002GB002001, 2003

Chung S.N., Park G.H., Lee K., Key R.M., Millero F.J., Feely R.A>, Sabine C.L., Falkowski P.G. (2004) Post-industrial enhancement of aragonite undersaturation in the upper tropical and subtropical Atlantic Ocean: the role of fossil fuel CO_2. Limnology and Oceanography 49:315–21

Coffin R.B., Montgomery M.T., Boyd T.J., Maustani S.M. (2004) Influence of ocean CO_2 sequestration on bacterial production. Energy 29: 1511-1520

Cooley S.R., Doney S.C. (2009a) Economic vulnerability assessment of U.S. fishery revenues to ocean acidification. Environmental Research letters 4(2) doi: 10.1088/1748-9326/4/2/024007

Cooley S.R., Doney S.C. (2009b) Anticipating ocean acidification's economic consequences on commercial fisheries. The Journal of Marine Education 25: 15-19

De'Ath, G., Lough, J.M., Sabricius, K.E. (2009) Declining coral calcification on the Great Barrier Reef. Science 323: 116-119

De Baar, H.J.W., Gerringa, L.J.A. (2009) Effects of Ocean Acidification on the physical-chemical speciation of nutrients and trace metals. Report to the European Program on Ocean Acidification (EPOCA) 73 pp

De Grave S., Fazakerley H., Kelly L., Guiry M.D., Ryan M., Walshe J. (2000) A study of selected maërl beds in Irish waters and their potential for sustainable extraction. Marine Institute, Galway, Ireland. 46 pp

Delille B., Harlay J., Zondervan I., Jacquet S., Chou L. Wollast R., Bellerby R.G.J., Frankignoullr M., Borges A.V., Riebesell U., Gattuso J.-P. (2005) Response of primary production and calcification to changes in pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi*. Global Biogeochemical Cycles 19:GB2023 doi:10.1029/2004GB002318

Dickson, A.G, Sabine, C.L, Christian, J.R. (2007) Guide to best practices for ocean CO_2 measurements, PICES Special Report 3/IOCCP Report No. 8

Doney, S.C., Mahowald N., Lima I., Feely R.A., Mackenzie F.T., Lamarque J.F., Rasch P.J. (2007) Impact of anthropogenic atmospheric nitrogen and sulphur deposition on Ocean Acidification and the inorganic carbon system. Proceeds National Academy of Science, USA 104 (37): 14580-14585

Doney, S.C., Tilbrook, B., Roy, S., Metzl, N., Corinne, Le Quéré, C., Hood, M., Feely, R.A., Bakker, D. (2009a) Surface-ocean CO_2 variability and vulnerability. Deep Sea Research II 56: 504-511

Doney S.C., Fabry V.J., Feely R.A., Kleypas J.A. (2009b) Ocean acidification: The other CO_2 problem. Annual Review of Marine Science 1: 169-192

D'Onghia G., Maiorano P., Sion L., Giove A., Capezzuto F., Carlucci R., Tursi A. (2009) Effects of deep-water coral banks on the abundance and size structure of the megafauna in the Mediterranean sea. Deep Sea Research II. doi: 10.1016/j.dsr2.2009.08.022

Dore J.E., Lukas R., Sadler D.W., Church M.J., Karl D.M. (2009) Physical and biogeochemical modulation of Ocean Acidification in the central North Pacific. Proceeds National Academy of Science, USA 106: 12235-12240

Ehlers A., Worm B., Reusch T.B.H. (2008) Importance of genetic diversity in eelgrass *Zostera marina* for its resilience to global warming. Marine Ecology Progress Series 355: 1-7

Engel A., Zondervan I., Aerts K., Beaufort L., Benthien A., Chou L., Delille B., Gattuso J.-P., Harlay J., Heeman C., Hoffman L., Jacquet S., Nejstgaard J., Pizay M.-D., Rochelle-Newell E., Schneider U., Terbrueggen A., Riebesell U. (2005) Testing the direct effect of CO_2 concentration on a bloom of the coccolithophorid *Emiliania huxleyi* in mesocosm experiments. Limnology and Oceanography. 50(2): 493-507

Eppley R.W., Peterson B.J. (1979) Particulate organic matter flux and planktonic new production in the deep ocean. Nature 282:677-680

European Science Foundation Policy Briefing 37 (2009) Impacts of Ocean Acidification 11 pp

Fabry V.J., Seibel B.A., Feely R.A., Orr J.C. (2008) Impacts of Ocean Acidification on marine fauna andecosystem processes. ICES Journal of Marine Science 65: 414-432

Feely R.A., Sabine C.L., Lee K., Millero F.J., Lamb M.F., Greeley D., Bullister J.L., Key R.M., Peng T.H., Kozyr A., Ono T., Wong C.S. (2002) In situ calcium carbonate dissolution in the Pacific Ocean. Global Biogeochemical Cycles 16(4): 1144, doi:10.1029/2002GB001866

Feely R.A., Sabine C.L., Lee Kitack, Berelson W., Kleypas J., Fabry V.J., Millero F.J. (2004) Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science 305**:** 362–366

Feely R.A., Sabine C.L., Fabry V.J. (2006) Carbon dioxide and our ocean legacy. The Pew Charitable Trust Science Brief

Feely R.A., Sabine C.L., Hernandez-Ayon J.M., Ianson D., Hales B. (2008) Evidence for upwelling of corrosive "acidified" water onto the Continental Shelf. Science, 320: 1490–1492

Field C.B., Behrenfeld M.J., Randerson J.T., Falkowski P. (1998) Primary production of the biosphere: Integrating terrestrial and oceanic components. Science 281: 237–240

Fine M., Tchernov D. (2007) Scleractinian coral species survive and recover from decalcification. Science 315: 1811

Food and Agriculture Organisation (FAO) of the United Nations (2007) The state of world fisheries and aquaculture, 2006. FAI: Rome

Forster P., Ramaswamy V., Artaxo P., Berntsen T., Betts R., Fahey D.W., Haywood J., Lean J., Lowe D.C., Myhre G., Nganga J., Prinn R., Raga bG., Schulz M., Van Dorland R. (2007). Changes in atmospheric constituents and in radiative forcing. In Climate Change 2007: the Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, pp. 129–234. Ed. by S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, H.L. Miller, Cambridge University Press, Cambridge United Kingdom and New York, NY, USA

Fosså J.H., Bellerby R., Jakobsen T. (2008) Consequences of Ocean Acidification for fisheries. Second Symposium on the Ocean in a High-CO_2 World, Monaco

Foster M.S. (2001) Rhodoliths: between rocks and soft places. Journal of Phycology 37: 1-9.

Friedlingstein P., Cox P., Betts R., Bopp L., von Bloh W., Brovkin V., Cadule P., Doney S., Eby M., Fung I., Bala G., John J., Jones C., Joos F., Kato T., Kawamiya M., Knorr W., Lindsay K., Matthews H.D., Raddatz T., Rayner P., Reick C., Roeckner E., Schnitzler K.-G., Schnur R., Straussmann K., Weaver A.J., Yoshikawa C., Zeng N. (2006) Climate–Carbon Cycle Feedback Analysis: Results from the C4MIP Model Intercomparison' Journal of Climate 19: 3337-3353

Gattuso J.-P, Frankignoulle M., Bourge I., Romaine S., Buddemeier R.W.(1998) Effect of calcium carbonate saturation of seawater on coral calcification. Global Planetary Change 18: 37-46

Gattuso J.-P. (2008) Impact of Ocean Acidification on benthic organisms, Second Symposium on the Ocean in a High-CO_2 World, Monaco

Gattuso J.-P. (2009) Ocean acidification: impact on key organisms of oceanic fauna. Press Release CNRS http://www2.cnrs.fr/presse/communique/1660.htm?&debut=8

Gazeau F., Quiblier C., Jansen J.M., Gattuso J.-P., Middelburg J.J., Heip C.H.R. (2007) Impact of elevated CO_2 on shellfish calcification. Geophysical Research Letters 34: LO7602 doi:10.1029/2006GL028554

Green M.A., Jones M.E., Boudreau C.L., Moore R.L., Westman B.A. (2004) Dissolution mortality of juvenile bivalves in coastal marine deposits. Limnology and Oceanography 49(3): 727-734

Greenblatt J.B., Sarmiento J.L. (2004) Variability and climate feedback mechanisms in ocean uptake of CO_2 In. (Eds) Field CB, Raupach MR. The carbon cycle of the oceans: Integrating humans, climate and the natural world p 257-275Guinotte J.M., Orr J., Cairns S., Freiwald A., Morgan L., George R. (2006) Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Frontiers in Ecology and the Environment 4(3): 141-146

Guinotte J.M., Fabry V.J. (2008) Ocean Acidification and its potential effects on marine ecosystems. Annals of the New York Academy of Sciences 1134: 320-343

Gutiérrez J.L., Jones C.G., Strayer D.L., Iribarne, O.O. (2003) Mollusks as ecosystem engineers: the role of shell production in aquatic habitats. Oikos 101: 79–90

Hall-Spencer J.M., Moore P.G., 2000. Scallop dredging has profound, long-term impacts on maerl habitats. ICES J. Mar. Sci. 57 (5), 1407–1415

Hall-Spencer J.M., Allain V., Fossa J.H. (2002) Trawling damage to Northeast Atlantic ancient coral reefs. Proceedings of the Royal Society London, B. 269, 507-511

Hall-Spencer J.M., Grall J., Moore P.G., Atkinson R.J.A. (2003) Bivalve fishing and maerl-bed conservation in France and the UK-retrospect and prospect. Aquat. Cons.: Marine and Freshwater Ecosystems 13 (Suppl.), 33–41

Hall-Spencer J.M., Rodolfo-Metalpa R., Martin S., Ransome E., Fine M., Turner S.M., Rowley S.J., Tedesco D., Buia M.C. (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature 454: 96-99

Hansen J., Sato Mki., Ruedy R., Kharecha P., Lacis A., Miller R.L., Nazarenko L., Lo K., Schmidt G.A., Russell G., Aleinov I., Bauer S., Baum E., Cairns B., Canuto V., Chandler M., Cheng Y., Cohen A., Del Genio A., Faluvegi G., Fleming E., Friend A., Hall T., Jackman C., Jonas J., Kelley M., Kiang N.Y., Koch D., Labow G., Lerner J., Menon S., Novakov T., Oinas V., Perlwitz Ja., Perlwitz Ju., Rind D., Romanou A., Schmunk R., Shindell D., Stone P., Sun S., Streets D., Tausnev N., Thresher D., Unger N., Yao M., Zhang S., (2007): Dangerous human-made interference with climate: A GISS model study. Atmospheric Chemistry and Physics 7: 2287-2312

Harley C.D.G., Randall Hughes A., Hultgren K.M., Miner B.G., Sorte C.J.B., Thornber C.S., Rodriguez L.F., Tomanek L., Williams S.L. (2006) The impacts of climate change in coastal marine systems. Ecology Letters 9: 228-241

Heinze C. (2004) Simulating oceanic $CaCO_3$ export production in the greenhouse, Geophysical Research Letters 31, L16308, doi:10.1029/2004GL020613

Hession C., Guiry M.D., McGarvey S., Joyce D., (1998) Mapping and assessment of the seaweed resources (*Ascophyllum nodosum*, Laminaria spp.) off the west coast of Ireland 84 pp Marine Institute Resource Series. No. 5. Marine Institute, Dublin

Hester K.C., Peltzer E.T., Kirjwood W.J., Brewer P.G. (2008) Unanticipated consequences of ocean acidification: A noisier ocean at lower pH. Geophysical Research Letters 35 L19601

The Nature Conservancy (2008) The Honolulu Declaration on Ocean Acidification and Reef Management. Ocean Acidification Workshop, Hawaii

Houghton J. T., Ding Y., Griggs D.J., Noquer M., van der Linden P.J., Dau X., Maskell K., Johnson C.A. (2001) Climate Change 2001: The Scientific Basis Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change Cambridge Univ. Press, Cambridge, UK

Howard E., Tilbrook, B. (2008) Ocean Acidification: Australian Impacts in the Global Context. Australian Department of Climate Change and the Antarctic Climate and Ecosystems CRC

Huesemann M.H., Skillman A.D., Crecelius E.A. (2002) The inhibition of marine nitrification by ocean disposal of carbon dioxide. Marine Pollution Bulletin 44(2): 142-148

Husebo A., Nøttestad L., Fosså J.H., Furevik D.M., Jørgensen S.B. (2002) Distribution and abundance of fish in deep-sea coral habitats. Hydrobiologia 471: 91–99

Hutchins D.A., Fu F.X., Zhang Y., Warner M.E., Feng Y., Portune K., Berhardt P.M., Mulholland M.R. (2007) CO_2 control of *Trichodesmium* N_2 fixation, photosynthesis, growth rates, and elemental ratios: implications for past, present, and future ocean biogeochemistry. Limnology and Oceanography 52: 1293-1304

IAP (2009) Statement on Ocean Acidification. The Inter-academy Panel on International Issues. http://www.interacademies.net/Object.File/Master/9/075/Statement_RS1579_IAP_05.09final2.pdf

ICES (2008) Changes in surface CO_2 and ocean pH in ICES shelf sea ecosystems.Cooperative Research Report No. 290. Fernand L., and Brewer P. (Eds.) 35 pp. International Council for the Exploration of the Sea, Copenhagen http://www.ices.dk/pubs/crr/crr290/CRR290.pdf

Iglesias-Rodriguez M.D., Armstrong R., Feely R., Hood R., Kleypas J., Milliman J.D., Sabine C., Sarmiento J. (2002) Calcium carbonate in a changing ocean: Implications for the marine carbon cycle, carbonate producing organisms, and global climate. Eos, Transactions, American Geophysical Union 83: 365-375

IPCC (2001). The Third assessment report of the Intergovernmental Panel on Climate Change (IPCC). Cambridge University Press: Cambridge, UK, and New York, USA

IPCC (2005) IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp

IPCC (2007) Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [B. Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds)], Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC (2007): Summary for Policymakers. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA

Ishimatsu A., Kikkawa T., Hayashi M., Lee K., Kita J. (2004) Effects of CO_2 in marine fish: larvae and adults. Journal of Oceanography 60: 731-741

Ishimatsu A., Hayashi M., Kikkawa T. (2008) Fishes in high-CO_2, acidified oceans. Marine Ecology Progress Series 373: 295-302

Joos F. and Spahni R. (2008) Rates of change in natural and anthropogenic radiative forcing over the past 20,000 years, PNAS, 105 (5): 1425-1430

Kamenos N.A., Moore P.G., Hall-Spencer J.M. (2004) Maerl grounds provide both refuge and high growth potential for juvenile queen scallops (*Aequipecten opercularis* L.). Journal of Experimental Marine Biology and Ecology 313 (2): 241–254

Keller A.A., Klein-MacPhee G. (2000) Impact of elevated temperature on the growth, survival, and trophic dynamics of winter flounder larvae: a mesocosm study. Canadian Journal of Aquatic Science 57: 2382-2392

Kikkawa T., Kita J., Ishimatsu A. (2004) Comparison of the lethal effect of CO_2 and acidification on red sea bream (*Pagrus major*) during the early development stages. Marine Pollution Bulletin 48: 108-110

Kikkawa T., Sata T., Kita J., Ishimatsu A. (2006) Acute toxicity of temporally varying seawater CO_2 conditions on juveniles of Japanse sillago (*Sillago japonica*). Marine Pollution Bulletin 52: 621-625

Kite-Powell H.L. (2009) A global perspective on the economics of ocean acidification. The Journal of Marine Education 25: 25-29

Kleypas J.A., Feely R.A., Fabry V.J., Langdon C., Sabine C.L., and Robbins L.L. (2006). Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: A Guide for Future Research, report of a workshop held 18–20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey, 88 pp

Kuffner I.B., Andersson A.J., Jokiel P.L., Rodgers K.S., MacKenzie F.T. (2008) Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geoscience 1: 114-117

Kump L.R., Bralower T.J., Ridgwell, A. (2009) Ocean Acidification in deep time. Oceanography 22: 94-107

Kurihara H., Shirayama Y. (2004) Effects of increased atmospheric CO_2 on sea urchin early development. Marine Ecology Progress Series 274: 161-169

Kurihara H., Kato S., Ishimatsu A. (2007) Effects of increased seawater pCO_2 on early development. Marine Ecology Progress Series 274: 161-169

Kurihara H., (2008) Effects of CO_2-driven ocean acidification on the early developmental stages of invertebrates. Marine Ecology Progress Series 373: 275–284

Lacque F.L. (1975) Marine Corrosion: causes and prevention. John Wiley: New York, USA

Lalli C.M., Gilmer R.W. (1989) Pelagic snails: The biology of holoplankton gastropod mollusks. Standford University Press, Standford, CA, USA

LeBrasseur R.J. (1966) Stomach contents of salmon and steelhead trout in the northeastern Pacific Ocean. J. Fish. Res. Board Can. 23(1): 85-100

Levi R., Varona P., Arshavsky Y. I., Rabinovich M. I. Selverston A. I. (2004) Dual Sensory-Motor Function for a Molluskan Statocyst Network Neurophysiol 91: 336-345

Langer M.R., Geisen M., Baumann K.H., Kläs J., Riebesell U., Thomas S., Young J.R. (2006) Species-specific responses to calcifying algae to changing seawater carbonate chemistry. Geochemistry Geophysics Geosystems 7: Q09006 doi:10.1029/2005GC001227

Lacque F.L. (1975) Marine Corrosion: causes and prevention. John Wiley: New York, USA

Lenton A., Codron F., Bopp L., Metzl N., Cadule P., Tagliabue A., Le Sommer, J. (2009) Stratospheric ozone depletion reduces the ocean carbon uptake and enhances ocean acidification. Geophysical Research letters 36: L12606 doi:10.1029/2009GL038227

Loukos H., Monfray P., Bopp L., Lehodey P. (2003) Potential changes in skipjack tuna (*Katsuwonus pelamis*) habitat from a global warming scenario: modelling approach and preliminary results. Fisheries Oceanography 12: 474-482

Lowenstam H.A., Weiner S. (1989) On biomineralization. Oxford University Press, Oxford. 324 pp

Maier C., Hegeman J., Weinbauer M.G., Gattuso J.-P. (2009) Calcification of the cold-water coral *Lophelia pertusa* under ambient and reduced pH. Biogeosciences Discussion 6: 1875-1905

Marine Institute (2009) Atlas of the commercial fisheries around Ireland. Marine Institute, Galway

Martin S., Gattuso J.-P. (2009) Response of Mediterranean coralline algae to ocean acidification and elevated temperature. Global Change Biology 15: 2089-2100

MCCIP (2008) Marine Climate Change Impacts Annual Report Card 2007–2008. (Eds. Baxter JM, Buckley PJ and Wallace CJ) Summary Report, MCCIP, Lowestoft, 8pp. Marine Climate Change Impacts partnership, UK http://www.mccip.org.uk/arc/2007/PDF/ARC2007.pdf

MCCIP (2006) Marine Climate Change Impacts Annual Report Card 2006. (Eds. Buckley, P.J., Dye, S.R. and Baxter, J.M.) Marine Climate Change Impacts partnership, UK http://www.mccip.org.uk/arc/2006/default.htm

McGrane P.B. (2007) Extant coccolithophores in Irish shelf waters of the Northeast Atlantic. Ph.D thesis. National University of Ireland, Galway 359 pp

McKim J.M. (1977) Evaluation of tests with early life stages of fish for predicting long- term toxicity. Journal of Fisheries Research Board Can. 34: 1148-1154

Meehl G.A., Stocker T.F, Collins W.D., Friedlingstein P., Gaye A.T., Gregory J.M., Kitoh A., Knutti R., Murphy J.M., Noda A., Raper S.C.B., Watterson I.G., Weaver A.J. and Zhao Z.-C. (2007): Global Climate Projections. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon S., Qin D., Manning M., Chen Z., Marquis M., Averyt K.B., Tignor M.and Miller H.L. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA

Melzner F., Göbel S., Langenbuch M., Gutowska M.A., Pörtner, H.-O., Lucassen M. (2009) Swimming performance in Atlantic Cod (*Gadus morhua*) following long-term (4-12 months) acclimation to elevated seawater pCO_2. Aquatic Toxicology 92: 30-37

Michaelidis B, Spring A, Pörtner HO (2007) Effects of long-term acclimation to environmental hypercapnia on extracellular acid-base status and metabolic capacity on Mediterranean fish *Sparus aurata*. Marine Biology 150: 1417-1429

Miles E.L., Bradbury J. (2009) What can be done to address Ocean Acidification through U.S. policy and governance. Journal of Marine Education 25: 30-32

Miller A.W., Reynolds A.C., Sobrino C., Riedel G.F. (2009) Shellfish face uncertainty in High CO_2 world: Influence of acidification on oyster larvae calcification and growth in Estuaries. PLoS ONE 4(5): e5661. doi:10.1371/journal.pone.0005661

Milliman J.D., Droxler A.W. (1996) Neritic and pelagic carbonate sedimentation in the marine environment: Ignorance is not bliss Global Biogeochemical Cycles 18: GB4028

Monaco Declaration (2008) Second International Symposium on the ocean in a high CO_2 world

Moore S.K., Trainer V.L., Mantua N.J., Parker M.S., Laws E.A., Backer L.C., Fleming L.E. (2008). Impacts of climate variability and future climate change on harmful algal blooms and human health. Environmental Health 7: doi:10.1186/1476-069X-7-S2-S4

Moy A., Howard W.R., Bray S., Trull T. (2009) The reduced calcification in modern Southern Ocean planktonic foraminifera. Nature Geosciences 2: 276-280

Mucci A. (1983) The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. American Journal of Science 283:780–99

Munday P.L., Dixson D.L., Donelson J.M., Jones G.P., Pratchett M.S., Devitsina G.V., Døving K.B. (2009) Ocean Acidification impairs olfactory discrimination an homing ability of a marine fish. Proceedings of the National Academy of Sciences of the United States 106: 1848-1852

O'Donnell M.J., Hannond L.M., Hofmann G.E. (2009) Predicted impact of Ocean Acidification on a marine invertebrate: elevated CO_2 alters response to thermal stress in sea urchin larvae. Marine Biology 156: 439-446

Olafsson J., Oplafsdottir S.R., Benoit-Cattin A., Danielsen M., Takahashi T. (2008) Current rates of change in pH and calcium carbonate saturation in the high-latitude North Atlantic Ocean, Second Symposium on the Ocean in a High-CO_2 World, Monaco

Orr J.C., Fabry V.J., Aumont O., Bopp L., Doney S.C., Feely R.A., Gnanadesikan A., Gruber N., Ishida A., Joos F., Key R.M., Lindsay K., Maier-Reimer E., Matear R., Monfray P., Mouchet A., Najjar R.G., Plattner G.-K., Rodgers K.B., Sabine C.L., Sarmiento J.L., Schlitzer R., Slater R.D, Totterdell I.J., Weirig M.F., Yamanaka Y., Yool A. (2005) Anthropogenic Ocean Acidification over the twenty-first century and its impact on calcifying organisms. Nature 437: 681-686

Orr J.C., Caldeira K., Fabry V., Gattuso J.-P., Haugan P., Lehodey P., Pantoja S., Pörtner H.-O., Riebesell U., Trull T., Hood M., Urban E., Broadgate W. (2009) Research Priorities for Ocean Acidification, report from the Second Symposium on the Ocean in a High- CO_2 World, Monaco, October 6-9, 2008, convened by SCOR, IOC-UNESCO, IAEA, and IGBP, 23 pp

Oschlies A., Schulz K.G., Riebesell U., Schmittner, A. (2008) Simulated 21st century's increase in oceanic suboxia by CO_2 enhanced biotic carbon export. Global Biogeochemical Cycles 22: GB1013, doi:10.1029/2007BG002953

OSPAR (2006) Effects on the marine environment of Ocean Acidification resulting from elevated levels of CO_2 in the atmosphere. Biodiversity Series No. 285/2006

Palacios S., Zimmerman R.C. (2007) Response of eelgrass *Zostera marina* to CO_2 enrichment: possible impacts of climate change and potential remediation of coastal habitats. Marine Ecology Progress Series 344: 1-13

Pane L., Feletti M., Francomacaro B., Mariottini G.L. (2004) Summer coastal zooplankton biomass and copepod community structure near the Italian Terra Nova Base (Terra Nova Bay, Ross Sea, Antarctica). Journal of Plankton Research 26: 1479-1488

Parker L. M., Ross P. M. & O'Connor W. A., (2009). The effect of ocean acidification and temperature on the fertilization and embryonic development of the Sydney rock oyster *Saccostrea glomerata* (Gould 1850). Global Change Biology 15: 2123-2136

Pörtner H.-O.(2008). Ecosystem effects of ocean acidification in times of ocean warming: a physiologist's view. Marine Ecology Progress Series, 373, 203-217

Raupach M. R., Marland G., Ciais P., Le Quéré C., Canadell J.G., Klepper G., Field C.B. (2007) Global and regional drivers of accelerating CO_2 emissions. Proceedings of the National Academy of Science USA. 104:10288–10293

Raven J.A., Johnston A.M. (1991) Mechanisms of inorganic-carbon acquisition in marine phytoplankton and their implications for the use of other resources. Limnology and Oceanography 36: 1701–1714

Raven J., Caldeira K., Elderfield H., Hoegh-Guldberg O., Liss P., Riebesell U., Shepherd J., Turley C., and Watson A. (2005): Ocean Acidification due to Increasing Atmospheric Carbon Dioxide. Policy Document 12/05. The Royal Society, London, 59 pp

Rees S.A., Opdyke B.N., Wilson P.A., Henstock T.J. (2007) Significance of *Halimeda* bioherms to the global carbonate budget based on a geological sediment budget for the Northern Great Barrier Reef, Australia. Coral Reefs 26: 177-188

Richardson A.J., Shoeman D.S. (2004) Climate impact on plankton ecosystems in the Northeast Atlantic. Science 305: 1609-1612

Richardson W., Greene C., Malme C., Thomson D. (1998) Marine mammals and noise. Academic Press. 576 pp.

Riebesell U., Zondervan I., Rost B., Tortell P.D., Zeebe R.E., Morel F.M.M. (2000) Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature 407: 364-367

Riebesell U. (2004) Effects of CO_2 enrichment on marine phytoplankton. Journal of Oceanography 60: 719-729

Riebesell U., Schulz K.G., Bellerby R.G.J., Botros M., Fritsche P., Meyerhofer M., Neill C., Nondal G., Oschlies A., Wohlers J., Zöllner E. (2007) Enhanced biological carbon consumption in a high CO_2 ocean. Nature 450: 545-549

Ries, J. B., Cohen, A. L, McCorkle, D. C. (2009) Marine calcifiers exhibit mixed responses to CO_2-induced ocean acidification, Geology 37 (12): 1057-1152

Roberts J.M., Gage J.D. and the ACES party. (2003) Assessing biodiversity associated with cold-water coral reefs: Pleasures and pitfalls. Erlanger Geologische Abhandlungen 4: 73

Roberts D., Howard W.R., Moy A.D., Roberts J.L., Trull T.W., Bray S.G., Hopcroft R.R. (2008) Interannual variability of pteropod shell weights in the high-CO_2 Southern Ocean. Biogeosciences Discuss 5(6): 4453-4480

Rost B., Zondervan I., Wolf-Gladrow D. (2008) Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. Marine Ecology Progress Series 373:277-237

Sabine C.L., Feely R.A., Gruber N., Key R.M., Lee K., Bullister J.L., Wanninkhof R., Wong C.S., Wallace D.W.R., Tilbrook B., Millero F.J., Peng T.H., Kozyr A., Ono T., Rios A.F. (2004) The oceanic sink for anthropogenic CO_2. Science, 305: 367–371

Sabine C.L., Feely R.A., Key R.M., Bullister J.L., Millero F.J., Lee K., Peng T.H., Tilbrook B., Ono T., Wong C.S. (2002) Distribution of anthropogenic CO_2 in the Pacific Ocean Global Biogeochemical Cycles 16 (4): 1083, doi:10.1029/2001GB001639

Safefood (2006) Consumer focused review of the finfish food chain. Safefood, Cork http://www.safefood.eu/en/Publication/Research-reports/Finfish/

Santana-Casiano, J.M., González-Dávila M., Rueda M., Llinás O., González-Dávila E.F. (2007) The interannual variability of oceanic CO_2 parameters in the northeast Atlantic subtropical gyre at the ESTOC site. Global Biogeochemical Cycles 21: 16pp doi:10.10292006GB002788

Salisbury J., Green M., Hunt C. & Campbell J., (2008). Coastal acidification by rivers: A new threat to shellfish? Eos, Transactions, American Geophysical Union 89(50):513

Schippers P., Lürling M., Scheffer M. (2004) Increase of atmospheric CO_2 promotes phytoplankton productivity. Ecology Letters 7: 446-451

Schubert R., Schellnhuber H.J., Buchmann N., Epiney A., Grießhammer R., Kulessa M., Rahmstorf S., Schmid J. (2006) The future oceans- Warming up, rising high, turning sour. Special Report by the German Advisory Council on Global Change (WBGU). 123 pp

Schulz K.G., Zondervan I., Gerringa L.J.A., Timmermans K.R., Veldhuis M.J.W., Riebesell U. (2004) Effect of trace metal availability on coccolithophorid calcification. Nature 430: 673-676

Sciandra A., Harlat J., Lefevre D., Lemee R., Rimmelin P., Denis M., Gattuso J.P. (2003) Response of coccolithophorid *Emiliania huxleyi* to elevated partial pressure of CO_2 under nitrogen limitation. Marine Ecology Progress Series 261: 111-122

Secretariat of the Convention on Biological Diversity (2009). Scientic Synthesis of the Impacts of Ocean Acidification on Marine Biodiversity. Montreal, Technical Series No. 46, 61 pp.

Seibel B.A., Walsh P.J. (2003) Biological impacts of deep-sea carbon dioxide injection inferred from indices of physiological performance The Journal of Experimental Biology 206, 641-650

Shirayama Y., Thorton H. (2005) Effect of increased atmospheric CO_2 on shallow marine benthos. Journal of Geophysical Research. 110: 7pp CO9S08

Sims D.W., Wearmouth V.J., Genner M.J., Southward D.J., Hawkins S.J. (2004) Low-temperature-driven early spawning migration of a temperate marine fish. Journal of Animal Ecology 73: 333-341

Solomon S., Qin D., Manning M., Alley R.B., Berntsen T., Bindoff N.L., Chen Z., Chidthaisong A., Gregory J.M., Hegerl G.C., Heimann M., Hewitson B., Hoskins B.J., Joos F., Jouzel J., Kattsov V., Lohmann U., Matsuno T., Molina M., Nicholls N., Overpeck J., Raga G., Ramaswamy V., Ren J., Rusticucci M., Somerville R., Stocker T.F., Whetton P., Wood R.A. and Wratt D. 2007 Technical Summary. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA

Spero H.J., Lea S.W. (1993) Intraspecific stable isotope cariability in the planktonic forminifera *Globigerinodies sacculifer*: results from laboratory experiments. Marine Micropaleontology, 22: 221-234

Spicer J.I., Raffo A., Widdicombe S. (2007) Influence of CO_2-related seawater acidification on extracellular acid-base balance in the velvet swimming crab, *Necora puber*. Marine Biology 151:1117-1125

Stanley G.D., Fautin D.G. (2001) The origins of modern corals. Science 291: 1913-1914

Stanley G.D. Jr. (2006) Photosymbiosis and the evolution of modern coral reefs. Science 312: 857-858

Steinacher M., Joos F., Frölicher T.L., Plattner G.-K., Doney S.C. (2009) Imminent Ocean Acidification in the Arctic projected with the NCAR global coupled carbon cycle0climate model. Biogeosciences 6: 515-533

Turley C.M., Roberts J.M., Guinotte J.M. (2007) Corals in deep-water: will the unseen hand of Ocean Acidification destroy cold-water ecosystems? Coral Reefs 26: 445-448

Turley C., Blackford J.C., Widdicombe S., Lowe D., Nightingale P.D., Rees A.P. (2006) Reviewing the impact of increased atmospheric CO_2 on Ocean pH and the Marine Ecosystems. Joachin Schellnhubered. Avoiding dangerous climate change 67

Tyrell T., Holligan P.M., Mobley C.D. (1999) Optical impacts of oceanic coccolithophore blooms. Journal of Geophysical Research 104: 3223-3241

Tyrrell T., Shepherd J.G., Castle S. (2007) The long-term legacy of fossil fuels. Tellus B 59 (4): 664-672

Van Oevelen, D., Duineveld, G., Lavaleye, M., Mienis, F., Soetaert, K., Heip, C.H.R. (2009) The cold-water coral community as a hot spot for carbon cycling on continental margins: A food-web analysis from Rockall Bank (northeast Atlantic). Limnology and Oceanography 54(6): 1829-1844

Veron J.E.N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27: 459-472

Vézina A.F., Hoegh-Guldberg O. (2008) Introduction: Effects of Ocean Acidification on marine ecosystems. Marine Ecology Progress Series 373: 199-201

Warren B., (2009) The Big Seven: Acidification risks and opportunities for the seafood industry. The Journal of Marine Education 25: 20-24

Weiss I.M., Tuross N., Addai L., Weiner S. (2002) Mollusc larval shell formation: amorphous calcium carbonate is the precursor phase for aragonite. Journal of Experimental Biology 293: 478-491

Wells E., Wilkinson M. (2001) Intertidal seaweed biodiversity in relation to environmental factors – a case study from Northern Ireland. In: Marine Biodiversity in Ireland and adjacent waters. Proceedings of a conference 26-27 April 2001. Ed: J.D.Nunn. Ulster Museum. 15-26

Wilson S., Blake C., Berges J.A., Maggs C.A., (2004) Environmental tolerances of free-living coralline algae (maerl): implications for European marine conservation. Biological Conservation 120: 283–293

Wootton J.T., Pfister C.A., Forester J.D. (2008) Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset. Proceeds of the National Academy of Science 105 (48) doi_10.1073_pnas.0810079105

Wolf-Gladrow D.A., Riebesell U., Burkhardt S., Bijma J. (1999) Direct effects of CO_2 concentration on growth an isotopic composition of marine plankton. Tellus B Chemical and Physical Meteorology 51: 461-476

Wright S., Davidson A. (2006) Ocean Acidification: a newly recognised threat. Australian Antarctic Magazine 10: 26-27

Young J.R., Geisen M., Probert I. (2005) A review of selected aspects of coccolithophore biology with implications for paleobiodiversity estimation. Micropeleontology 51: 267-288

Zachos J.C. (2005) Rapid acidification of the ocean during the Paleocene-Eocene Thermal Maximum. Science 308: 1611-1615

Zeebe R.E., Wolf-Gladrow D. (2001) CO_2 in seawater: Equilibrium, kinetics, isotopes. Elsevier Oceanographic Series 65. Elsevier. 346 pp

Zeebe R.E., Zachos J.C., Calderia K., Tyrrel T. (2008) Carbon emissions and acidification. Science 321: 51-52

Zimmerman R.C., Kohrs D.G., Steller D.L., Alberte R.S. (1997) Impacts of CO_2-enrichment on productivity and light requirements of eelgrass. Plant Physiology 115: 599-607

Zondervan I., Zeebe R.E., Rost B., Riebesell U, (2001) Decreasing marine biogenic calcification: A negative feedback on rising atmospheric pCO_2. Global Biogeochemical Cycles 15: 507-516

Zondervan I., Rost B., Riebesell U. (2002) Effect of CO_2 concentration on the PIC/POC ratio in the coccolithophore *Emiliania huxleyi* grown under light-limiting conditions and different daylengths. Journal of experimental Marine Biology and Ecology 272: 55-70

ANNEX 1: RESEARCH PROJECTS RELATING TO CLIMATE CHANGE AND OCEAN ACIDIFICATION

NATIONAL PROJECTS:

Marine Climate Change Programme (2007-09): This programme, under the SSTI (Strategy for Science, Technology and Innovation) and Sea Change Strategies, was funded under the NDP Marine Research Sub-programme 2007-2013. As an element of this the 'Impact of increased atmospheric CO_2 on ocean chemistry and ecosystems' is a 2 year project led by Physics at NUI Galway (see box 6).

BioChange: This EPA funded project is an integrative, multi-disciplinary research framework to support national and local biodiversity policy in Ireland. Within this framework, work package 4 (**Natural resource exploitation and global change** - the need for improved sustainable management to protect biodiversity) has an overall aim to assess the effects of climate change on a model keystone organism (*A. nodosum*), with the development of standardized monitoring protocols that in the future will allow a fast and reliable assessment of biodiversity change as a consequence of global change. This package is led by Botany and Plant Science at NUI Galway.

Exchange at the air-sea interface: *air quality and climate impacts:* EPA funded project under Climate Change Research projects. This is lead by Physics at NUI Galway.

UK PROJECTS:

Carbon-ops: An operational UK air-sea carbon flux observation capability. This is a UK project currently funded under NERC Knowledge Transfer initiative (2007-2009), which aims to develop an automated supply chain of ocean surface and atmospheric carbon dioxide measurements from selected UK research ships to operational end-users.

CASIX: The centre for observation of Air-Sea Interactions and fluxes is a NERC centre of excellence in Earth Observation. The scientific focus is on advancing the science of air-sea interactions and reducing the errors in the prediction of climate change. The primary goal is to quantify accurately the global air-sea fluxes of carbon dioxide (CO_2).

NERC: The Natural Environment Research Council and the Department for Environment, Food & Rural Affairs are developing a collaborative 5 year research programme on ocean acidification of approximately £12m. A call for proposals is expected to be announced in April - May 2009. The £7m initiative will shed light on areas including the effects of more acid oceans on vulnerable ecosystems, and how these effects will interact with other expected global changes, such as higher temperatures.

INTERNATIONAL PROJECTS:

EPOCA: The European Project on ocean acidification is a 4-year project funded by the European Commission. The overall objective of this study is to advance understanding of the biological, ecological, biogeochemical, and societal consequences of ocean acidification. The EPOCA project brings together 28 partner institutes, including 105 principle investigators and will coordinate national and international projects and programs.

IOCCP: The International Ocean Carbon Coordination Project coordinates information on ocean carbon measurements and brings together experts on a regular basis to determine if the existing network is sufficient to meet research goals. The IOCCP is co-sponsored by the Intergovernmental Oceanographic Commission of UNESCO and the Scientific Committee on Oceanic Research (SCOR).

SOLAS: Surface Ocean-Lower Atmosphere study. This project is an international research initiative comprising of over 1500 scientists in 23 countries. Its main objective is to *'*achieve quantitative understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and atmosphere, and of how this coupled system affects and is affected by climate and environmental change.*'*

IMBER: Integrated Biochemistry and Ecosystem Research is an IGBP (International geosphere-biosphere programme)-SCOR (Scientific Committee on Oceanic Research) project focusing on ocean biogeochemical cycles and ecosystems. In particular the 'Carbon Research' working group is focused on seamless implementation of ocean carbon research in SOLAS and IMBER. Two major scientific emphases have been identified: (i) carbon inventories, fluxes and transports, and (ii) sensitivities of carbon-relevant processes to changes occurring in the ocean. This group will work in coordination with IOCCP.

CARBOOCEAN: Marine carbon sources and sinks assessment. This European Commission funded project consists of 47 international groups that have started an integrated research activity on the marine carbon cycle. www.carboocean.org

EUR-OCEANS: Consortium for European Research on Ocean Ecosystems under Anthropogenic and Natural Forcings. While the Euro-oceans project has officially ended from 1st January 2009, the **"EUR-OCEANS Consortium"** will ensure the continuity and further integration of Member Organisations presently involved in the EUR-OCEANS Network of Excellence.

HERMES: Hotspot Ecosystem research on the Margins of European Seas. An integrated EU research project designed to gain new insights into the biodiversity, structure, function and dynamics of ecosystems along Europe's deep-ocean margin.

PAGES: The Past Global Change project is an international effort to coordinate and promote past global change research. The primary objective is to improve our understanding of past changes in the Earth System in order to improve projections of future climate, environment and sustainability. The project is funded by the U.S. and Swiss National Science Foundations, and the National Oceanic and Atmospheric Administration (NOAA). Over 3800 scientists in more than 100 countries around the world currently subscribe to PAGES.

MARBEF: European Network of Excellence for Marine Biodiversity and Ecosystem Functioning. This network of excellence is funded by the European Union and consists of 94 European marine institutes. It is a platform to integrate and disseminate knowledge and expertise on marine biodiversity.

DYNAMITE: Understanding the Dynamics of the Coupled Climate System Specific Targeted Research Project (STREP) Specifically, DYNAMITE will advance the understanding of strongly and weakly coupled processes underlying the natural variability of ENSO and NAO/AO; it will evaluate the representation of the coupled processes underlying ENSO and the NAO in state-of-the-art models used to predict climate change; it will advance understanding of the response of ENSO and NAO/AO to climate change; and it will assess the role of ocean biology in the variability of the tropical coupled climate system, including ENSO.

US Development of an Integrated Science Strategy for Ocean Acidification Monitoring, Research, and Impacts Assessment. This US National Academies project will examine the anticipated consequences of ocean acidification due to rising atmospheric carbon dioxide levels on fisheries, protected species, coral reefs, and other natural resources in the United States and internationally. The committee will recommend priorities for a national research, monitoring, and assessment plan to advance understanding of the biogeochemistry of carbon dioxide uptake in the ocean and the relationship to atmospheric levels of CO_2, and to reduce uncertainties in projections of increasing ocean acidification and the potential effects on living marine resources and ocean ecosystems.

LOICZ: Land-ocean interactions in the coastal zone. LOICZ is a core project of the International Geosphere-Biosphere Programme (IGBP) and the International Human Dimensions Programme on Global Environmental Change (IHDP). LOICZ aims to provide science that contributes towards understanding the Earth system in order to inform, educate and contribute to the sustainability of the world's coastal zone.

BOOM: Biodiversity of Open Ocean Microcalcifiers. This is a French ANR funded pluri-disciplinary research program (10 teams from 4 countries) aimed at unravelling the biological and physiological diversities within coccolithophores.

PEECE: Pelagic ecosystem CO_2 enrichment study. The objective of this project is to examine effects of ocean acidification on natural marine plankton communities. Partners are involved from a number of European countries.

BIOACID: A German research initiative to investigate the biological impacts of ocean acidification.

ACRONYMS AND ABBREVIATIONS

Ω	Saturation state of calcium carbonate
Ca^{2+}	Calcium ions
CCS	Carbon Capture and Storage
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ions
DIC	Dissolved Inorganic Carbon
DMS	Dimethyl sulfide
ESTOC	European Station for Time Series in the Ocean at the Canary Islands
GtC	Gigatonnes carbon (109 tonnes)
H^+	Hydrogen ions
H_2CO_3	Carbonic acid
H_2SO_4	Sulfuric acid
HNO_3	Nitric Acid
HCO-	bicarbonate
ICES	International Council for the Exploration of the Seas, Copenhagen
IPCC	Intergovernmental Panel on Climate Change
kHz	kilohertz
kPa	kilopascals
MSFD	Marine Strategy Framework Directive (European Directive 2008/56/EC)
NH_3	Ammonia
NUI Galway	National University of Ireland, Galway
OSPAR	OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic (1992)
pCO_2	partial pressure of carbon dioxide (in seawater)
pH	- log10 [H+] where [H+] is the concentration of the hydrogen ion
ppmv	parts per million volume
PtC	Petatonnes carbon (1015 tonnes)
SSTI	Strategy for Science Technology and Innovation
TA	Total Alkalinity
TAC	Total Allowable Catch
TEP	Transparent exopolymeric particles
µatm	micro atmosphere
UK	United Kingdom
yr^{-1}	per year

Marine Environment & Food Safety Services

Marine Institute
Foras na Mara

www.marine.ie

HEADQUARTERS

MARINE INSTITUTE
Rinville
Oranmore
Galway
Tel: +353 91 387 200
Fax: +353 91 387 201
Email: institute.mail@marine.ie

MARINE INSTITUTE REGIONAL OFFICES & LABORATORIES

MARINE INSTITUTE
80 Harcourt Street
Dublin 2
Tel: +353 1 4766500
Fax: +353 1 4784988

MARINE INSTITUTE
Furnace
Newport
Co. Mayo
Tel: +353 98 42300
Fax: +353 98 42340

MARINE INSTITUTE
Snugboro Road
Abbottstown
Dublin 15
Tel: +353 1 822 8200
Fax: +353 1 820 5078