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## Changes in surface CO<sub>2</sub> and ocean pH in ICES shelf sea ecosystems

Editors

Liam Fernand  
Peter Brewer

Contributors

James Barry • Richard Bellerby • Jerry Blackford  
Knut Børsheim • Nick Dulvy • Jean-Pierre Gattuso  
Frederic Gazeau • Stefan Hain • Nick Hardman-Mountford  
David Hydes • Judith Kildow • Silke Kröger  
Ian Laing • Nikos Leonardos • Francesca Marubini  
Carlos Pelejero • Hans Pörtner • Shaun Studd  
Dave Suggett • Steve Widdicombe



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## **International Council for the Exploration of the Sea Conseil International pour l'Exploration de la Mer**

H. C. Andersens Boulevard 44–46  
DK-1553 Copenhagen V  
Denmark  
Telephone (+45) 33 38 67 00  
Telefax (+45) 33 93 42 15  
[www.ices.dk](http://www.ices.dk)  
[info@ices.dk](mailto:info@ices.dk)

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## Preface

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The primary purpose of this document is to report the recommendations resulting from the ICES WORKSHOP ON THE SIGNIFICANCE OF CHANGING OCEAN CO<sub>2</sub> AND pH IN ICES SHELF SEA ECOSYSTEMS held between 2 and 4 May 2007 in London. Some excellent reports have already been published in this field, first by the Scientific Committee on Oceanic Research (SCOR; Arvidson, 2005), then by the National Oceanic and Atmospheric Administration/National Science Foundation/US Geological Survey (NOAA/NSF/USGS; Kleypas *et al.*, 2006), the Royal Society (The Royal Society, 2005), the German Advisory Council on Global Change (WBGU; WBGU, 2006), and most recently by the OSPAR Commission (OSPAR, 2006) and the Intergovernmental Panel on Climate Change (IPCC; Metz *et al.*, 2005). Cognizant of these recent efforts, the ICES Workshop set out with a slightly different aim to investigate the links between potential changes in pH and its effects on marine ecosystem components, such as plankton, fish and shellfish, and cold-water corals. To this end, the Workshop covered ground already considered by others, to provide a sound base for the prediction of likely impacts. The present report will outline those relevant issues, but the reader is advised to refer to other reports for greater detail. The novel focus of this report is the potential effects on ecosystem functions with links to fisheries, with a recommendation for work to be done to better understand the impact of this problem on the entire ecosystem, and specifically on fisheries. Most of the material used was presented at the Workshop, with Annex 1 being the most significant exception.

## Executive Summary

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Mankind is causing a global perturbation, which will likely have deleterious effects on the entire ecosystem with societal impacts; however, we still need to develop the experimental approaches, collect field data, and develop modelling approaches to quantify these effects and predict their future impacts.

—Statement by Peter Brewer made during the workshop

There is an urgent need to fund experiments and methods to quantify the extent of the problem resulting from acidification.

## 1 Key recommendations

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Recommendations fall into the following categories:

- Experimental approach
- Modelling
- Technological development
- Monitoring
- Experimental protocol

### 1.1 Experimental approach

Most of our present knowledge of the likely impacts of acidification on organisms comes from mesocosm experiments. However, present knowledge is limited and, analogous to the land-based studies on CO<sub>2</sub> where a number of study sites have been set up, many further experiments are required.

Specifically, experiments are needed that

- address the issue of long-term change. Most experiments are short term (hours to weeks). The few long-term experiments that have been undertaken have shown that some species can acclimatize over a long period, whereas other species can survive short-term exposure to low pH but suffer from long-term exposure at less reduced pH. Experiments need to target key species or groups of species that are most likely to be affected.
- include and are considered alongside other anthropogenic stress factors. The change in pH should not be dealt with in isolation. For most organisms, there will be an additional stress of increased temperature, decreased oxygen, potential changes in nutrients, and—in the case of Arctic species—increased irradiance levels caused by the melting ice.
- are geographically diverse. As the exact response of seawater to increasing CO<sub>2</sub> concentrations depends on the chemical constituents (alkalinity), there will be geographic variation in the response, particularly in shelf seas where alkalinity varies depending on the riverine inputs of DISSOLVED ORGANIC CARBON (DOC).

The above statements are true regardless of the scale. Experiments ranging from single species to experiments as large an ecosystem as is practically manageable are required. Each experiment needs to consider the importance of acidification relative to other climate change impacts, as well as considering other factors, such as overfishing and eutrophication.

### 1.2 Modelling

To assess the likely implications to the ecosystem and fisheries, an integrated approach is required, whereby models of higher trophic levels are coupled to physical and biogeochemical models. Better integration of existing modelling efforts may provide answers relevant to policy.

In relation to fishery dynamics, there are two critical issues that experiments cannot incorporate: (i) population-scale processes, such as broadcast spawning, migration, and spatial population structure, and (ii) community and ecosystem structuring processes, such as competition and predation.

It is only by increasing our understanding of these processes that the role of acidification in food supply can be assessed.

### **1.3 Technological development**

Mesocosm experiments and modelling both have severe limitations. Models require field data for validation, and mesocosm experiments can often produce results not replicated on a larger scale, perhaps owing to a lack of higher predation. Therefore, advances are required that allow current laboratory experiments to be performed *in situ*, because very different responses can be produced in the laboratory than in the wild. Such experimental strategies would include experiments in the ocean (Free Ocean CO<sub>2</sub> Enrichment (FOCE)), similar to those on land (Free Air CO<sub>2</sub> Enrichment (FACE)).

Measuring pH, partial pressure of CO<sub>2</sub>, and dissolved HCO<sub>3</sub> in seawater is not a simple process. More robust methods and cost-effective methods for use on moored buoys, ships of opportunity, and research vessels need to be developed.

### **1.4 Monitoring**

There is an urgent need for the development of highly resolved monitoring of atmospheric and surface-water pCO<sub>2</sub>, carbonate, alkalinity, and pH at spatial and temporal scales over long periods of time (>10 years) in order to validate predictions and provide the basis for macroecological analysis of the potential impacts of acidification on ecosystems and dependent services, such as fisheries. These observations would be used to assess the extent of the problem and to validate the models. Specifically, these should have broad geographic coverage to monitor response over a range of salinities and alkalinities. Continued monitoring is also required to assess the impact of any remediation measures.

### **1.5 Experimental protocol**

Currently, several barriers exist to undertaking experiments and performing an effective intercomparison. The issues raised below will deal with some of these barriers.

There is a need to change regulations pertaining to experiments and the use of CO<sub>2</sub>. Currently, experimental use of CO<sub>2</sub> is banned by the London Convention (despite the millions of tonnes being emitted by industries, etc.).

It is necessary to measure pH using a consistent approach. Attention has to be given to methodologies such as reference electrode drift.

Protocols for other chemical parameters, especially dissolved inorganic carbon, need to be adhered to and widely propagated.

Experiments need to be developed, as an example of best practice, containing a suite of measurements with full access to reference documents.

## **2 Workshop Terms of Reference (ToR)**

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The following ToRs were specified by ICES Oceanography Committee (OCC).

- review the current state of knowledge and identify future research directions stated in the Terms of Reference;
- review the spatial and temporal variability of the surface ocean pH and CO<sub>2</sub>-carbonate system in shelf seas in the ICES region;
- predict the rates of change and to understand how these can be measured;
- review the effects of pH and the CO<sub>2</sub>-carbonate system on nutrient chemistry that are important in ecosystem processes relevant to shelf seas;
- review the effects of pH and the CO<sub>2</sub>-carbonate system on contaminants in the shelf seas environments;
- review the links between potential changes in pH and its effects on marine ecosystem components, such as plankton, fish and shellfish, and cold-water corals.



### 3 Main outcomes

#### 3.1 The problem

The oceans are one of the major buffers of anthropogenic CO<sub>2</sub> emissions. Oceanic uptake of CO<sub>2</sub> has led to a perturbation of the chemical environment, primarily in ocean surface waters associated with the increase in DISSOLVED INORGANIC CARBON (DIC). The increase in atmospheric CO<sub>2</sub> from about 280 μatm 200 years ago to 370 μatm today has caused an average decrease across the surface of the oceans of about 0.08 pH units and a decrease in CO<sub>3</sub><sup>2-</sup> of about 20 μmol kg<sup>-1</sup> (Kheshgi, 1995). There could be a further drop in pH of 0.5 units by the year 2100 if CO<sub>2</sub> emissions are not regulated (The Royal Society, 2005; Caldeira and Wickett, 2003). A recent study of potential change in the North Sea (Blackford and Gilbert, 2007) suggests that pH change this century may exceed its natural variability in most of the North Sea. Impacts of acidity-induced change are likely, but their exact nature remains largely unknown and may occur across the range of ecosystem processes. Most work has concentrated on open-ocean systems, with little applied to the complex systems found in shelf sea environments.

**Table 1. The evolving chemistry of surface seawater under “business as usual” water (Brewer, 1997).**

YEAR	PCO <sub>2</sub> μATM	TOTAL CO <sub>2</sub> μMOL KG <sup>-1</sup>	PH	HCO <sub>3</sub> <sup>-</sup> μMOL KG <sup>-1</sup>	CO <sub>3</sub> <sup>2-</sup> μMOL KG <sup>-1</sup>	H <sub>2</sub> CO <sub>3</sub> μMOL KG <sup>-1</sup>
1800	280	2 017	8.191	1 789	217	10.5
1996	360	2 067	8.101	1 869	184	13.5
2020	440	2 105	8.028	1 928	161	16.5
2040	510	2 131	7.972	1 968	144	19.1
2060	600	2 158	7.911	2 008	128	22.5
2080	700	2 182	7.851	2 043	113	26.2
2100	850	2 212	7.775	2 083	97	31.8

#### 3.2 The evidence for pH change in the water column

There are a small number of long-term (>10 years) observatories that have recorded pCO<sub>2</sub> in both the atmosphere and the water column. A minimum of ten years is required because the variability is relatively great compared with the signal. These stations are quite rare with limited geographic coverage. The principal ones are the Bermuda Atlantic Time-series (BATS), the European Station for Time-series in the Ocean, Canary Islands (ESTOC), and the Hawaii Ocean Time-series (HOT). Other series exist, but are shorter than ten years, e.g. Dynamics of Fluxes in the Mediterranean (DYFAMED) in the Mediterranean and Kyodo North Pacific Ocean Time-series (KNOT) in the North Pacific. The series demonstrate that pH is decreasing, but that the natural signal is apparently variable. It is not necessary to measure pH directly to prove that this property is changing, because it is directly calculable from accurate measurement of the mass properties of total CO<sub>2</sub> and alkalinity, of which global surveys are now available. Early direct measurements of oceanic pH did yield results of insufficient quality to observe the fields with the required accuracy (Takahashi *et al.*, 1970). Although this problem has now been solved, measurement of total CO<sub>2</sub> and alkalinity remains the preferred approach for expedition work today.

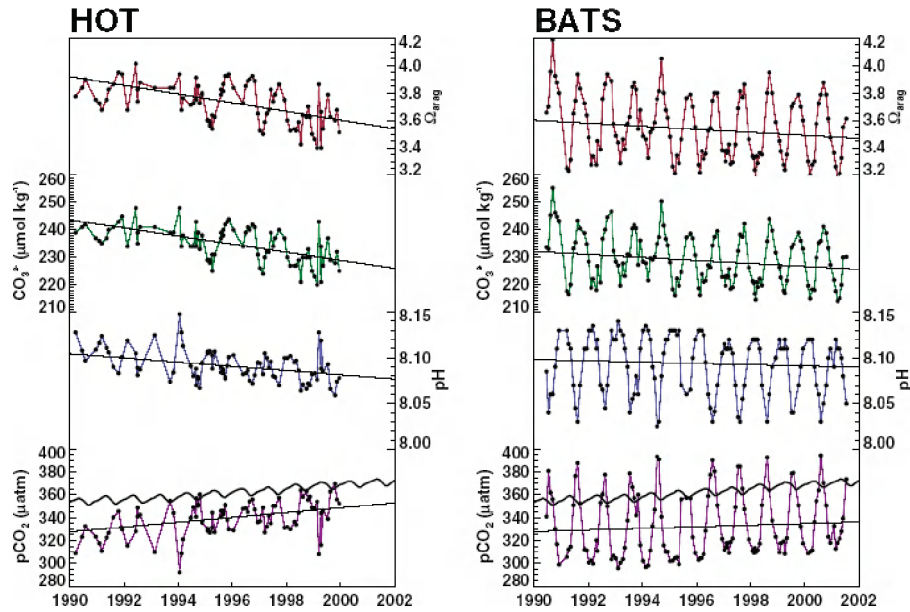


Figure 1. Time-series of the change in pH and pCO<sub>2</sub>. Hawaii Ocean Time-series (HOT) and Bermuda Atlantic Time-series (BATS; Kleypas *et al.*, 2006).

In the deep ocean, the natural pH range, and the likely subsequent change, is a function of depth, with the greatest range in the surface. In shelf seas, because they are well mixed in winter, benthic organisms are exposed to a full range of pH variation and experience the increased levels of atmospheric CO<sub>2</sub> immediately.

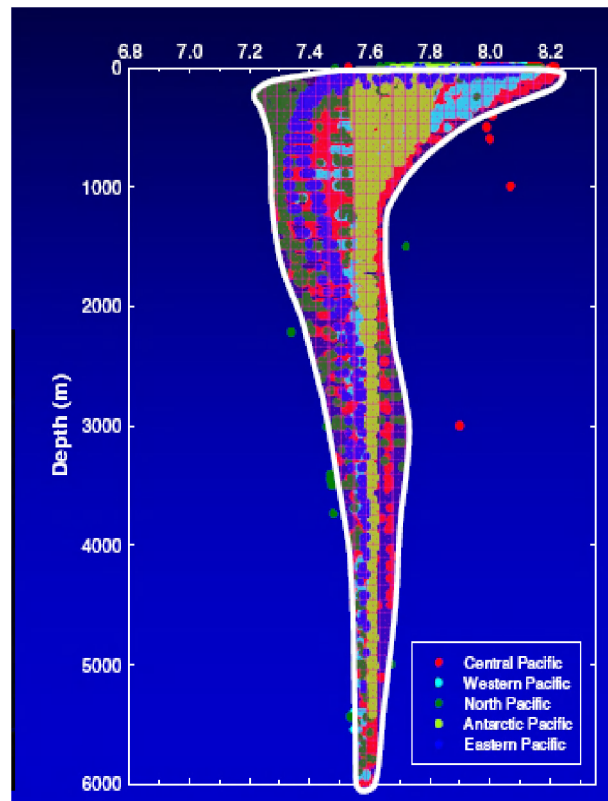


Figure 2. The range of pH exhibited in vertical profiles in the major ocean basins. In surface waters, the range extends from a pH of about 8.2 in the Central Pacific to about 7.2 in the low-oxygen waters of the Northeast Pacific (courtesy J. Barry).

### 3.3 The historical context to the change in ocean pH

Through the use of boron isotopes, cores can be used to construct proxy records of paleo-ocean pH. The results shown in Figure 3 are estimates of the changes believed to have occurred in surface ocean waters over the past 650 000 years. The left vertical axis shows only the preindustrial value of the modern Earth; today, the  $p\text{CO}_2$  far exceeds the scale range shown. This record reveals that the change in pH over the past 650 000 years has been cyclical and associated with the glacial periods, with the transition from low to high values occurring every 50 000 years. From an historical perspective, the current levels of  $\text{CO}_2$  are already high, and anthropogenic emissions are exacerbating this issue. The primary planetary restoring force for high  $p\text{CO}_2$  levels is the alkaline flux from the weathering of silicate rocks; this operates on a time-scale of hundreds of thousands of years.

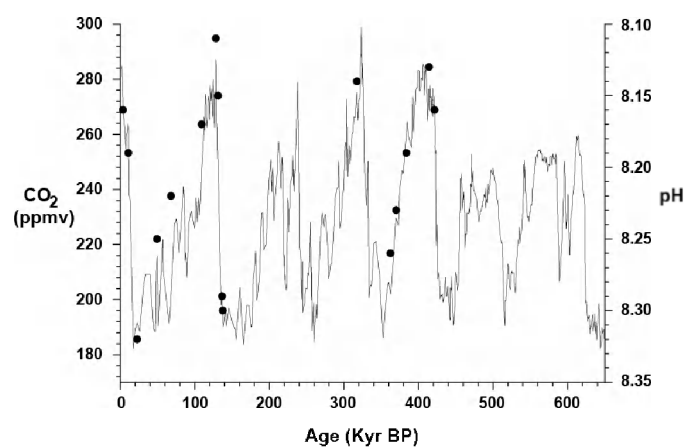


Figure 3. Record of sea surface pH (solid circles) reconstructed using boron isotopes in planktonic foraminifera from a sediment core retrieved in the eastern equatorial Atlantic (ODP668B; Hönisch and Hemming, 2005) superimposed on the record of atmospheric  $\text{CO}_2$  concentration during the past 650 000 years (solid line), inferred from the composition of air bubbles trapped in Antarctic ice cores (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005). Redrawn from Pelejero and Calvo, in press.

Over shorter and more recent time-scales, another study, also based on boron isotopes, suggests the existence of interdecadal, natural cycles of seawater pH in coral reefs, which have the potential to enhance or mitigate the vulnerability of marine organisms to future ocean acidification (Pelejero *et al.*, 2005).

Although there is possibly no exact past analogue of present  $\text{CO}_2$  emissions, important focus has been put on the Palaeocene–Eocene Thermal Maximum, a warming event that occurred ~55 million years ago and was very likely accompanied by a significant pH decrease (Zachos *et al.*, 2005). Palaeo-reconstructions for this catastrophic event suggest that associated changes in carbonate ion concentration strongly influenced marine biota, especially benthos.

### 3.4 Impacts on water column species

#### 3.4.1 Coccolithophores

Research into water column processes has primarily focused on those organisms that calcify. This group includes the coccolithophorids, foraminifera, and pteropods. However, less extensive work has been done on the effect of pH and thermal stress on adult fish and the subsequent changes in the metabolic stress. It is this change in metabolic stress that is potentially the most relevant to fisheries.



Beachy Head, the result of many thousands of years of coccolithophore formation (photograph from Encyclopædia Britannica Online).

*Emiliana huxleyi* is numerically the most abundant coccolithophore in the ocean and became prominent during glacial periods of enhanced ocean productivity. It plays an important role in converting biogenic carbon from the oceans to a solid form and has a preponderance in the ICES region.

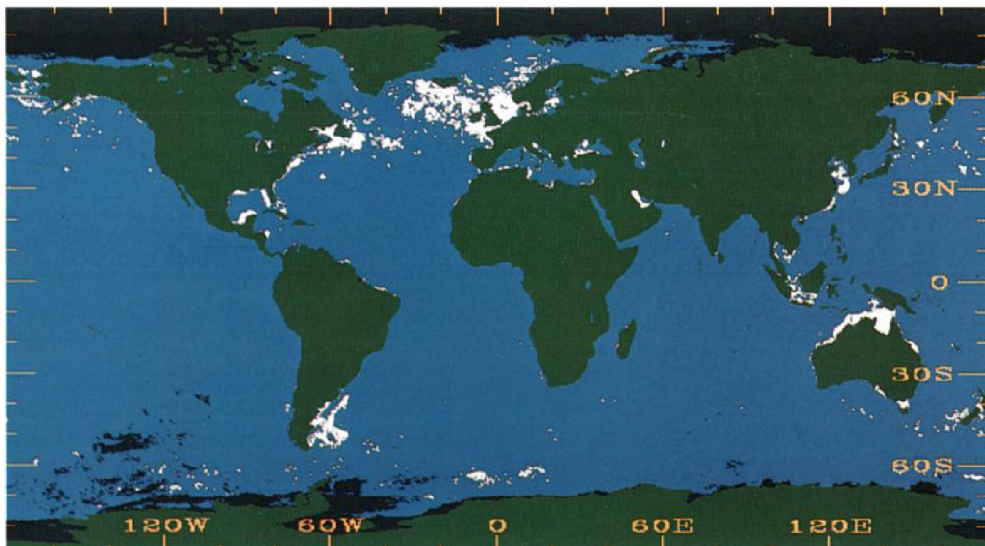


Figure 4. Distribution of *Emiliana huxleyi* (Brown and Yoder, 1994).

The first equation on the following page shows how *E. huxleyi* generates calcium carbonate, which is a major part of the carbon cycle.

The second equation shows how carbon is fixed by the process of photosynthesis.

**Coccolithophores do two major things (among others)**

They fix inorganic C.

$$2 \text{HCO}_3^- + \text{Ca}^{+2} + \text{H}^+ \xrightleftharpoons{\text{Calcification}} \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

They fix organic C by photosynthesis.

$$\text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons[\text{Respiration (energy)}]{\text{Photosynthesis (light)}} \text{CH}_2\text{O} + \text{O}_2$$

Below are experimental results demonstrating scanning electron microscope images of the structure of three different coccolithophorids when exposed to high levels of CO<sub>2</sub>.

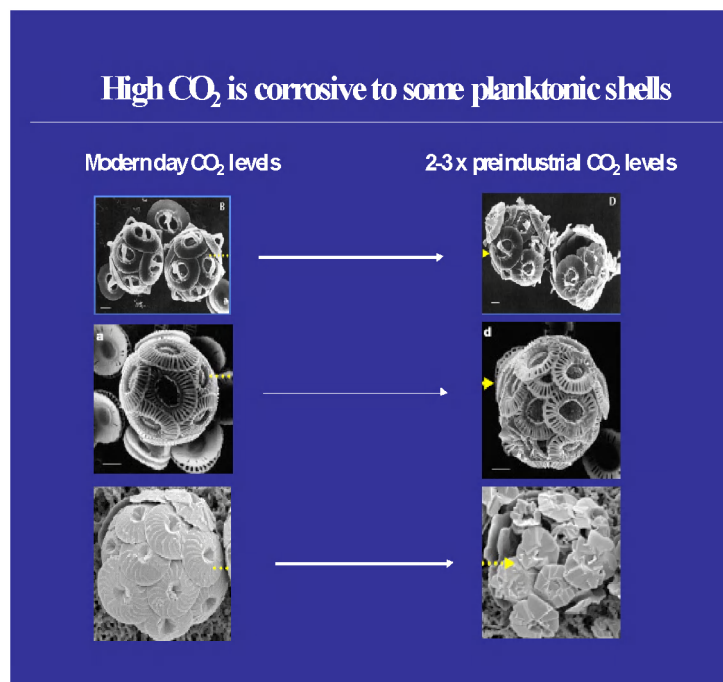


Figure 5. Scanning electron microscope images of three different coccolithophores, showing the plate-like structures (liths) at present and future CO<sub>2</sub> levels. At elevated levels of CO<sub>2</sub>, note the loss of lith order and shape (Riebesell *et al.*, 2000; Langdon *et al.*, 2000).

### 3.4.2 Pteropods

Although coccolithophores form an important part of the carbon cycle, they do not constitute a significant food source. In the Barents Sea, pteropods that calcify are a significant food source for herring. Herring are an important part of the ecosystem and a significant food source for other fish such as cod, for marine mammals, and for seabirds. As the saturation of aragonite (which constitutes most of the shell) falls below 1, the shell will corrode. Thus, by 2040, there will be notable effects on sea butterflies (pteropods) in northern waters. When saturation is <1, it will cost the organisms more to maintain their skeleton and will impose a sublethal metabolic cost.

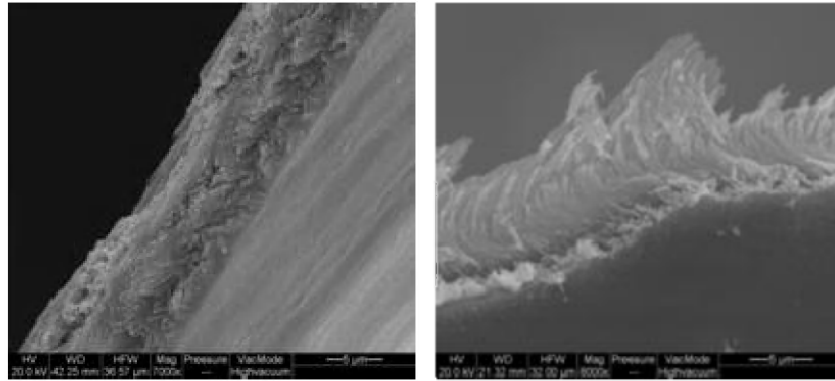


Figure 6. Electron microscope image of the shell of pteropods showing shell dissolution in a live pteropod (left) when kept in water undersaturated with respect to aragonite for 48 hours, compared with a typical shell (right). Dissolution results in etch pits and exposure of aragonite rods, and increases the surface area over which dissolution can occur (Orr *et al.*, 2005).

### 3.5 Modelling predictions

A highly useful modelling result is that of the aragonite saturation horizon produced by Orr *et al.* (2005). It demonstrates that aragonite will dissolve from shells at all depths in the southern ocean. In the ICES area, bottom-dwelling organisms will be affected, and only those in relatively shallow areas will be viable.

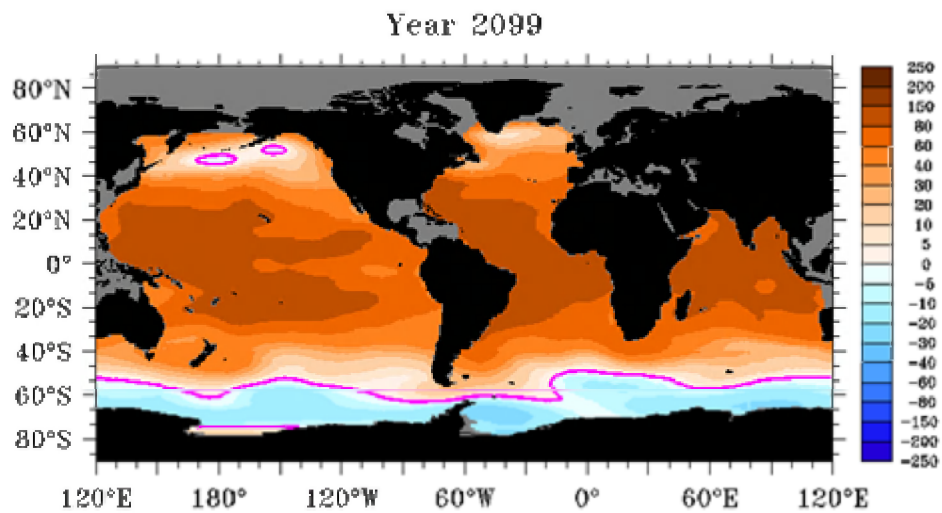


Figure 7. Map of projected surface ocean aragonite saturation levels for the year 2100 under the IPCC IS92a scenario (Orr *et al.*, 2005).

Although aragonite precipitation by marine organisms will likely be diminished and will dissolve at shallower depths, biological production of calcite and the rain of calcite particles to the sea floor will continue.

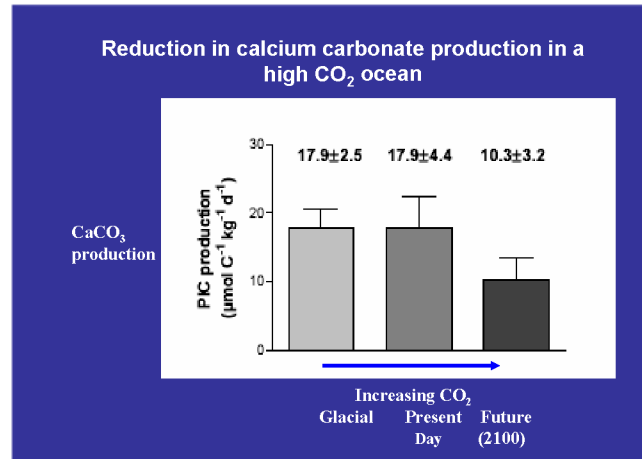


Figure 8. Reduction in calcium carbonate production for an *Emiliana huxleyi* bloom under present and future scenarios (Delille *et al.*, 2005).

### 3.6 Combined effects of climate change on larger species

The effect of changing pH is only one manifestation of the changing climate.

Temperature is the overarching signal, with reduced oxygen concentrations being another significant stress. An important concept relevant to the understanding of fish physiology is that of thermal windows, where species have developed an ecological and physiological niche to a particular environment. Stenotherms are animals that prefer a narrow temperature range and have increased energy efficiency over a narrow range that supports growth performance. One such example is cod, where the maximum growth rate spans a 5°C range. However, within a thermal window, it is oxygen consumption that limits growth. The additional decrease in CO<sub>2</sub> reduces available oxygen and adds an additional stress. It is the combined effects of these that are relevant, and dealing with one component in isolation does not reveal the whole effect.

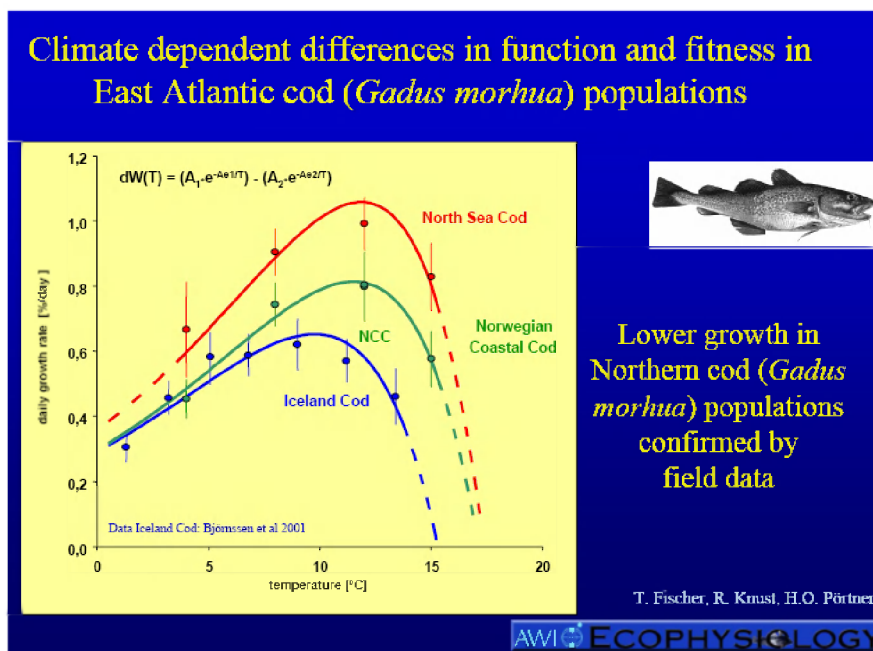


Figure 9. The daily growth rate for cod against temperature, indicating the thermal window for maximum growth (courtesy H. Pörtner).

Although experimental approaches that address all aspects of climate change are required, it is especially important to consider the following for certain species:

- CO<sub>2</sub>-dependent performance changes;
- The location of the organism in its temperature-dependent performance window, e.g. growth and fecundity;
- Seasonal shifts in performance windows;
- Climate-dependent functional specialization and temperature-dependent biogeography.

### 3.7 Effects on non-calcifying plankton and nutrient uptake

Mesocosm results demonstrate that, for increasing concentrations of atmospheric CO<sub>2</sub> and for a given nitrate concentration, more carbon is consumed. However, other studies have demonstrated that increasing the carbon:phosphate ratio reduces the growth rate of certain phytoplankton and reduces fecundity (fertility) in zooplankton.

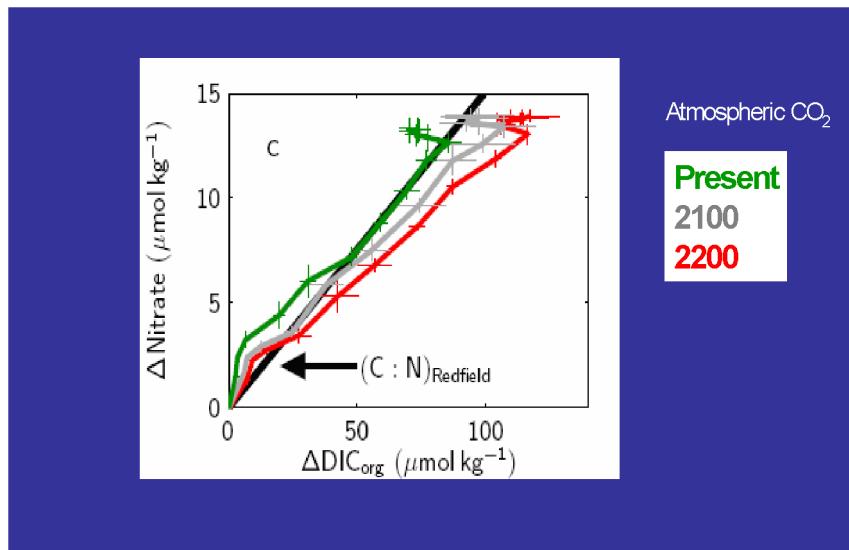


Figure 10. The increase in carbon uptake as a function of nitrate for different CO<sub>2</sub> concentrations (courtesy R. Bellerby).

### 3.8 Metals and nutrient chemistry

This topic was not considered at the Workshop, but is taken from the IPCC Special Report on Carbon Capture and Storage (Metz *et al.*, 2005) and is presented here for completeness.

Changes in the pH of marine environments affect the carbonate system, nitrification (Huesemann *et al.*, 2002), speciation of nutrients such as phosphate, silicate, and ammonia (Zeebe and Wolf-Gladrow, 2001), and speciation and uptake of essential and toxic trace elements. Observations and chemical calculations show that low pH conditions generally decrease the association of metals with particles and increase the proportion of biologically available free metals (Sadiq, 1992; Salomons and Forstner, 1984). Aquatic invertebrates take up both essential and non-essential metals, but final body concentrations of metals vary widely across invertebrates. In the case of many trace metals, enhanced bioavailability is likely to have toxicological implications, because free forms of metals are of the greatest toxicological significance (Rainbow, 2002).



### 3.9 Impacts on benthic ecosystem

Organisms can be affected by a number of mechanisms. These include:

#### Respiratory stress

Reduced pH limits oxygen binding and transport by respiratory proteins, and leads to reduced aerobic capacity.

#### Acidosis (reduced internal pH)

Disruption of acid–base balance impairs function and requires energy to restore or maintain optimal internal pH levels.

#### Reduced calcification

Depression in the carbonate saturation state increases the difficulty of carbonate deposition, with unknown metabolic consequences.

#### Metabolic depression (torpor)

Elevated CO<sub>2</sub>, reduced pH, or both can cause some animals to enter a state of reduced metabolic rate and semi-hibernation.

#### 3.9.1 Comparing *Nereis* with *Brissopsis*

Examples of these effects come from the study in tanks of two very different benthic species. *Nereis*, a burrowing polychaete worm, and *Brissopsis*, a sea urchin, were exposed to three levels of pH associated with increased CO<sub>2</sub>.



Figure 11. Two very different benthic species: *Nereis* (left; a polychaete worm) and *Brissopsis* (right; a sea urchin; courtesy S. Widdicombe).

<i>Nereis</i>	<i>Brissopsis</i>
Builds and irrigates deep burrows	Bulldozes through surface sediment
Increases uptake of nitrate	Decreases uptake of nitrate
Increased release of silicate	Increased release of silicate
No impact on phosphate	Increased release of phosphate
No impact on nitrite and ammonium flux	No impact on nitrite and ammonium flux
High tolerance to seawater acidification	Highly vulnerable to seawater acidification

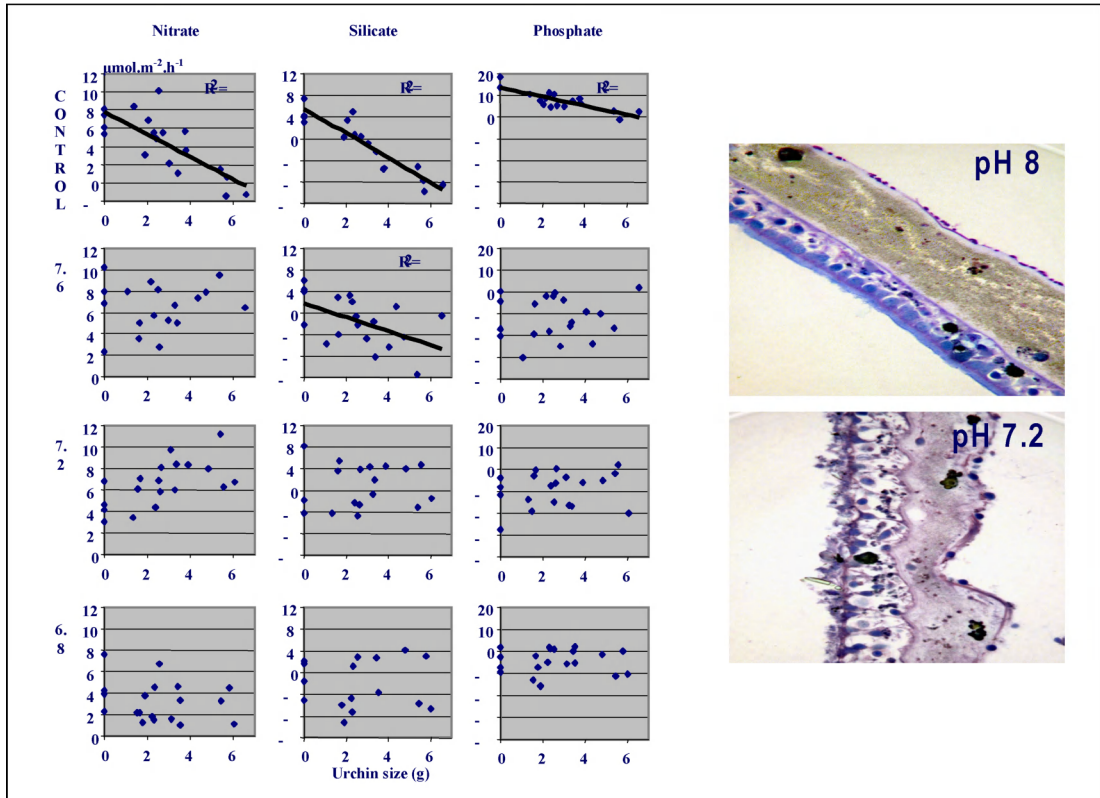


Figure 12. Impact of pH on *Brissopsis lyrifera* and nutrient flux. Left: Nutrient uptake as a function of size for different pH scenarios (S. Widdicombe). Right: *Brissopsis* tissue. Impacts have also been observed on acid–base balance, reproductive tissues, respiration rates, and meiofaunal communities.

The sea urchin is highly vulnerable because there is no impermeable membrane to isolate it from the surrounding water. As evidenced above, the control demonstrates that, under normal conditions, there is an inverse linear relationship between nutrient uptake and sea-urchin size. However, when exposed to pH values of 7.6 compared with pH = 8, this linearity was lost, indicating a change in functionality. Little further change was noticed with increasing pH. Change was also observed in the acid–base balance, reproductive tissue, and respiration rates.

### 3.10 Impacts on corals

Experimental studies on tropical shallow corals have demonstrated that biogenic calcification depends on the concentration of available carbonate ions; the lower the pH of seawater, the lower the amount of carbonate available and the lower the rate of calcification by corals. The relationship between calcification and pH is overwhelmingly consistent across species (Figure 13).

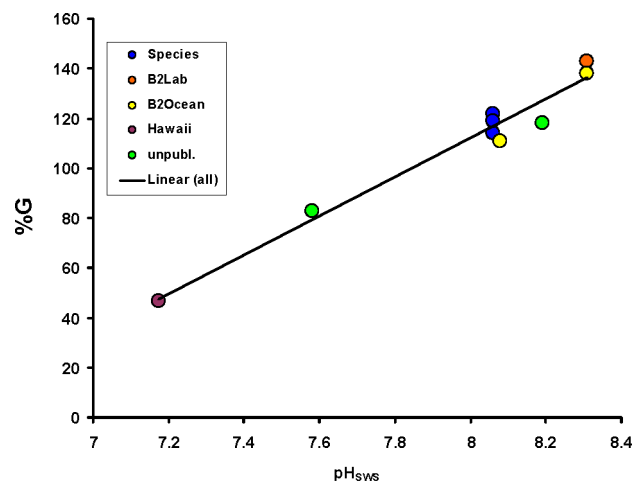


Figure 13. Calcification as a function of pH for tropical corals. Every 0.1 ↓ in pH ≈ 8% ↓ in G (G = calcification rate as weight of CaCO<sub>3</sub> deposited; courtesy F. Marubini).

Evidence of the negative effect of lower pH was also found at the microstructural level in the appearance of the growing skeletal fibres of *A. verweyi* using scanning electron microscopy (Figure 14; Marubini *et al.*, 2002).

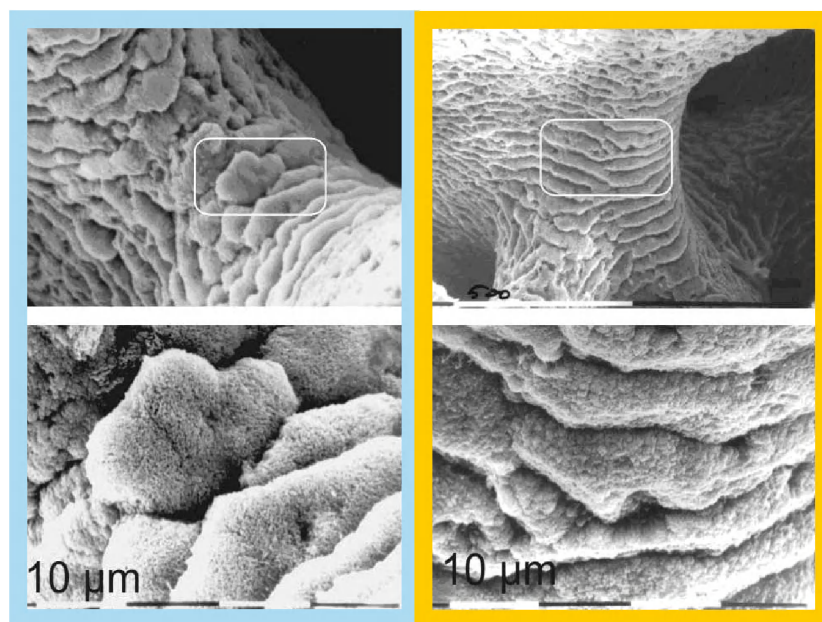


Figure 14. Skeletal microstructure of the tropical coral *Acropora verweyi*. Present day (left) vs. year 2100 (right; Marubini *et al.*, 2002).

Other work (Gattuso *et al.*, 1999) demonstrates the importance of additional factors, such as irradiance and nutrient stress, in determining calcification rates. These parameters, along with temperature, are likely to interact with pH in the future climate, and indeed their interaction requires further analysis. The North Atlantic is home to extensive coral reef frameworks built by cold-water corals. As the response of cold-water corals to pH is expected to be similar to that described above for tropical corals, concern for this highly diverse and yet little explored ecosystems of the deep sea is mounting (Roberts *et al.*, 2006).

### 3.11 Viruses

Viruses short-circuit the flow of carbon and nutrients from phytoplankton and bacteria to higher trophic levels by causing the lysis of cells and shunting the flux to the pool of dissolved and particulate organic matter (D-P-OM). As a result, more of the carbon is respired, thereby decreasing the trophic transfer efficiency of nutrients and energy through the marine foodweb. Because it is not known how pH change will affect this process, research into these effects is needed.

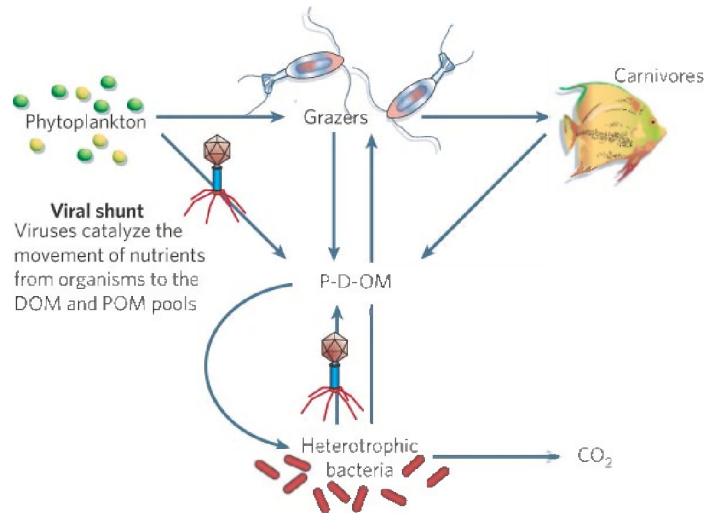


Figure 15. The role of viruses (courtesy K. Borsheim).

### 3.12 Impacts on shellfish farming

Pacific oyster (*Crassostrea gigas*) is the most cultivated species in the world and forms a significant part of the world mollusc production. There has been a 5% year<sup>-1</sup> increase worldwide in the production of mariculture for the past ten years, mostly in China and eastern Asia. This total accounts for 15–20% of the global aquaculture production, with a value of approximately US\$10 billion.

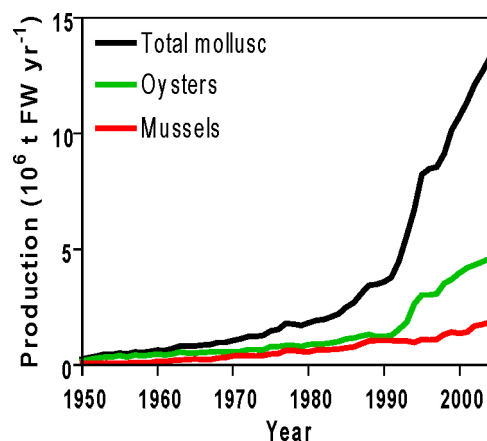


Figure 16. Worldwide shellfish production, showing the dramatic increase (FAO, 2002).

Experiments to assess the potential impact on this industry have been undertaken using incubation chambers on two of the most important farmed species. The effect on shell formation from these experiments is quite dramatic. For *Mytilus edulis*, a commonly cultivated mussel, the response is linear and exhibits a marked decrease (30%) in shell formation at pH levels likely to be reached in this century. At very high

levels of pCO<sub>2</sub> (1800 ppm by volume), the shells dissolve completely. However, the response for oysters is different with more tolerance until very high levels are reached.

One reason for this difference is the composition of the shells. Approximately 50% of a mussel shell is made from aragonite, which dissolves much more easily than calcite, which constitutes most of the oyster shells.

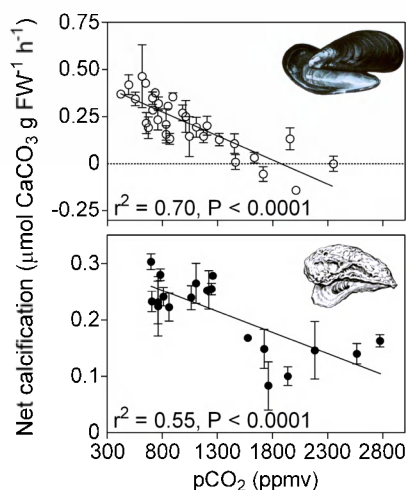


Figure 17. Calcification of mussels and oysters (courtesy F. Gazeau).

### 3.13 Impacts on finfish farming

Direct impacts on aquaculture are hard to assess, but are likely to pose a small risk. Much work has been performed previously looking at the effects of acid rain, primarily in Scandinavian lakes. These fresh-water systems are unbuffered, and the pH change experienced there is much greater than is likely to be experienced in the marine environment. Currently, most farmed finfish species experience a range of salinities and pH conditions in the wild. It is unlikely, therefore, that pH change in itself will have a noticeable effect. However, as noted previously, the combination of thermal stress and low oxygen could combine with a change in pH, with problematic results. An indirect effect may likely be from attack by different viruses or parasites, which may take advantage of different environmental conditions. Owing to a number of constraints, the industry is proposing to consider offshore sites for future development. These, however, may suffer greater relative impact than the present inshore sites.

### 3.14 Effects on fisheries

Acidification is likely to have some direct and indirect impacts on fish and fisheries. The nature and degree of such impacts is currently unknown but should be considered against a backdrop of considerable historical overfishing (Jennings and Blanchard, 2004; Piet and Rice, 2004; Dulvy *et al.*, 2005). The direct effects on fish and fisheries may be relatively limited and, most likely, will be analogous to the effects of thermal and oxygen stress outlined previously. Fish early life stages, such as eggs and larvae, are more sensitive to pH than adults (Ishimatsu *et al.*, 2004). However, mortality at the early life stages of broadcast-spawning species is typically great and highly variable, owing to natural match–mismatch and density-dependent processes in the planktonic stages (Hjort, 1914; Cushing, 1990; Goodwin *et al.*, 2006). So, it is not known whether the direct acidification effect on larval survival would be over-

whelmed by natural processes or whether it would add significantly to the natural variation, thereby appreciably increasing early life-history mortality. It is worth noting that one might predict that the larvae of calcifying species, such as sea urchins, might be most vulnerable to acidification (Kurihara and Shirayama, 2004; Shirayama and Thornton, 2005). However, contrary to this expectation, the abundance of larval urchins has risen considerably in recent years (Kirby *et al.*, 2007). Notwithstanding this absence of a likely significant effect at present, it is predicted that, for example in the North Sea, young fish will be exposed to a range of pH within the next century beyond what they have previously experienced (Blackford and Gilbert, 2007). Indirect effects are likely to be more relevant but even harder to quantify. Ocean acidification may influence the structure and productivity of primary and secondary benthic production which, in turn, may indirectly affect the productivity of fish communities and higher trophic levels. Changes in food source, e.g. Barents Sea herring feeding on pteropods (sea butterflies), may result in shifts in species distribution, lower species abundance, or diet shifts. The degree and nature of adaptation will strongly influence their availability to fisheries and their productivity. The possible effects of acidification on the timing of appearance, abundance, and quality of larval fish prey sources, such as phyto- and zooplankton, remain unknown (Edwards and Richardson, 2004). The gaps in knowledge that require addressing are extensive but could focus on key target fish species, particularly those that depend heavily on calcifying taxa as prey, e.g. pteropods. A key unknown is the relative importance of acidification for fisheries. Acidification effects have yet to be observed in shelf seas, so they are likely to be minor relative to the comparatively massive impacts of overexploitation of fisheries during the last few decades.

#### **4 Future requirements for the observation of pH and pCO<sub>2</sub>**

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Although existing quality datasets present strong evidence for the change in pH associated with the decrease in CO<sub>2</sub>, they are few and represent limited geographic types. The large-scale programmes, such as the Geochemical Ocean Section Study (GEOSECS), the World Ocean Circulation Experiment (WOCE), and the US Joint Global Ocean Flux Study (JGOFS), have given us precise and accurate descriptions of the global carbonate system, but only in series of snapshots, and these cannot be easily used to deduce the long-term trend from short-term variation. There is a need, therefore, for more long-term series of these key parameters in other areas.

Although modelling is probably the most cost-effective way to obtain worldwide estimates of pH variability and predict future pH changes, the models are only as good as the data used to validate them. There is a requirement, therefore, for a concerted data collection effort with greater spatial coverage to provide data for validation of models and to provide estimates of the rate of change in areas with differing biogeochemical response. These observational programmes are not required to avoid or delay taking preventive action but to help assess whether the mitigation undertaken is effective.

Measurements of pH and other carbonate-system parameters are currently expensive. However, recent advances in technology coupled with present observational programmes, such as the instrumented commercial vessels (FerryBox) or existing mooring networks like Smart Bouys, could increase the cost-effectiveness and feasibility of the required programmes.

This Workshop specifically endorses the Advances in Marine Ecosystem Modelling Research (AMEMR) workshop held 12–14 February 2007 in Plymouth, UK, which suggested the following recommendations for observations to support modelling.

Maximum use needs to be made of the observational data that are currently being collected; funding should be used to complement these sources.

In particular:

- A multidisciplinary approach broadening the scope of existing and planned observations should ensure that appropriate parameters are collected. Carbonate monitoring systems should be standard.
- Expanding ships of opportunity programmes both in number and in the range of measurements taken is probably one of the most efficient ways of ensuring good spatial and temporal data availability.
- Long-term time-series datasets are vital; the maintenance of these programmes requires a commitment to long-term funding.
- Coastal to offshore transects would be valuable in assessing the penetration of terrestrial signals into shelf seas.

This requires (i) international coordination and standardization (e.g. pH, DIC), and (ii) some fundamental new research on shelf seas alkalinity.

## 5 Future experimental needs

Present-day experiments fall into two broad categories: (i) those that are species-specific and occur in laboratories, and (ii) large-scale mesocosm experiments that occur in the field.

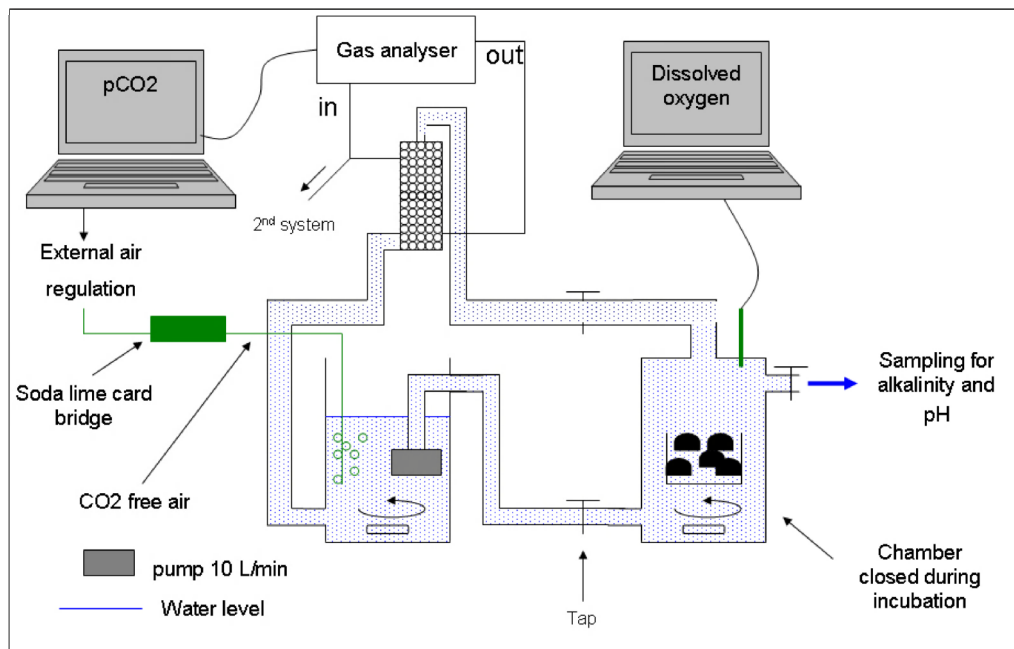


Figure 18. An example of experimental apparatus for work on mussels and oyster used by F. Gazeau.



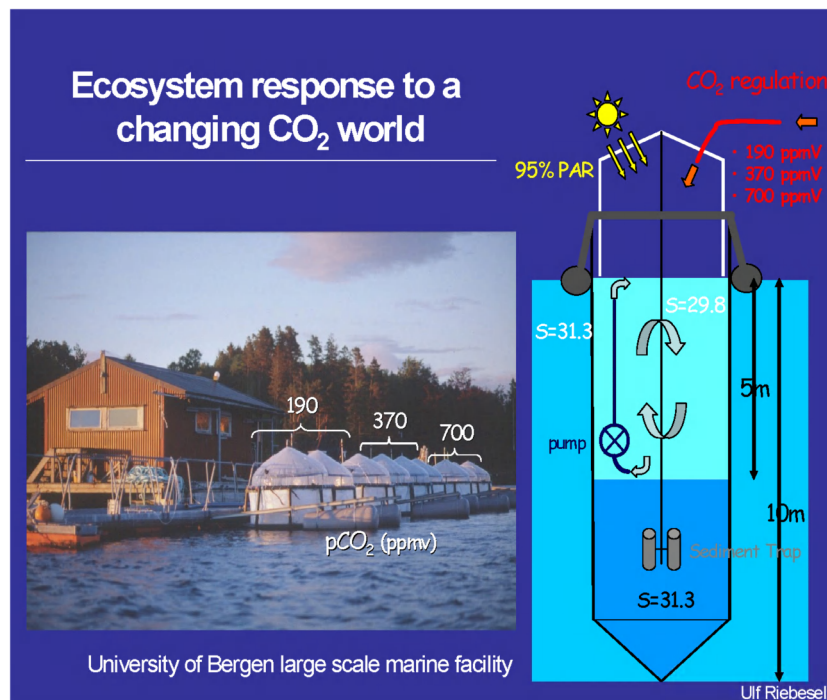


Figure 19. An example of mesocosm experiments being conducted by the University of Bergen.

The number of experimental sites is limited and needs to be increased. The level of confidence in any biological response is greatly enhanced by replication in other experiments. There is a need to perform similar mesocosm experiments in a wide variety of habitats and different water masses. As the exact response of seawater to increasing CO<sub>2</sub> depends on the chemical constituents (alkalinity), there will be geographic variation in the response.

Most experiments are currently short-term (hours to weeks). Some species can acclimatize over a long period, whereas others can survive a short-term exposure to low pH, but suffer from long-term exposure at less reduced pH.

Experiments in tanks and knowledge gained in aquaculture studies reveal that very different responses can be produced from those in the wild. There is a need, therefore, to design and conduct experiments that can manipulate the CO<sub>2</sub> field *in situ* while leaving other elements undisturbed.

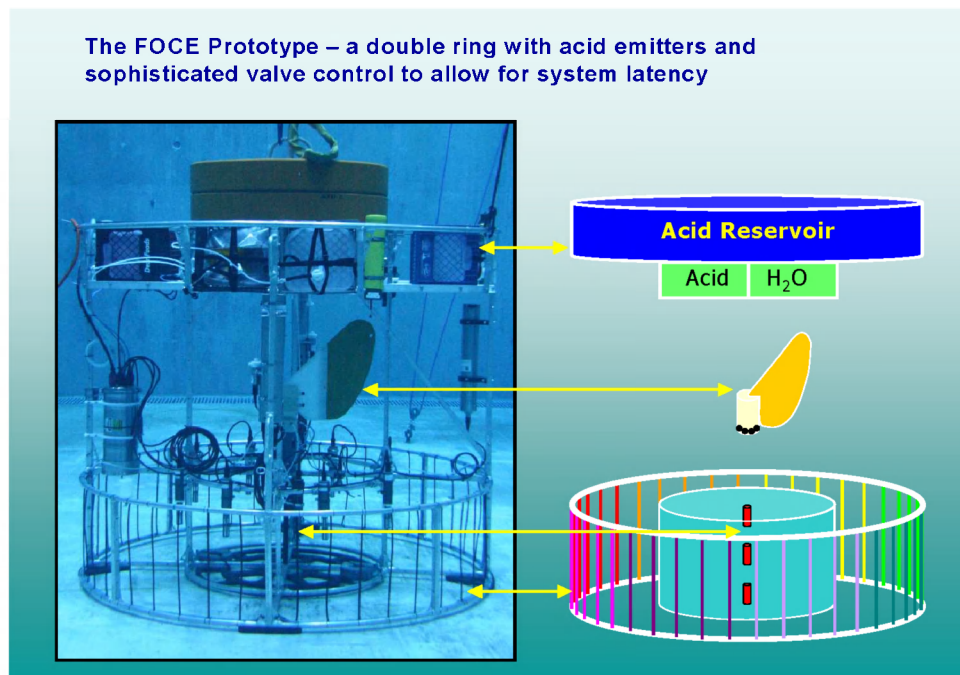
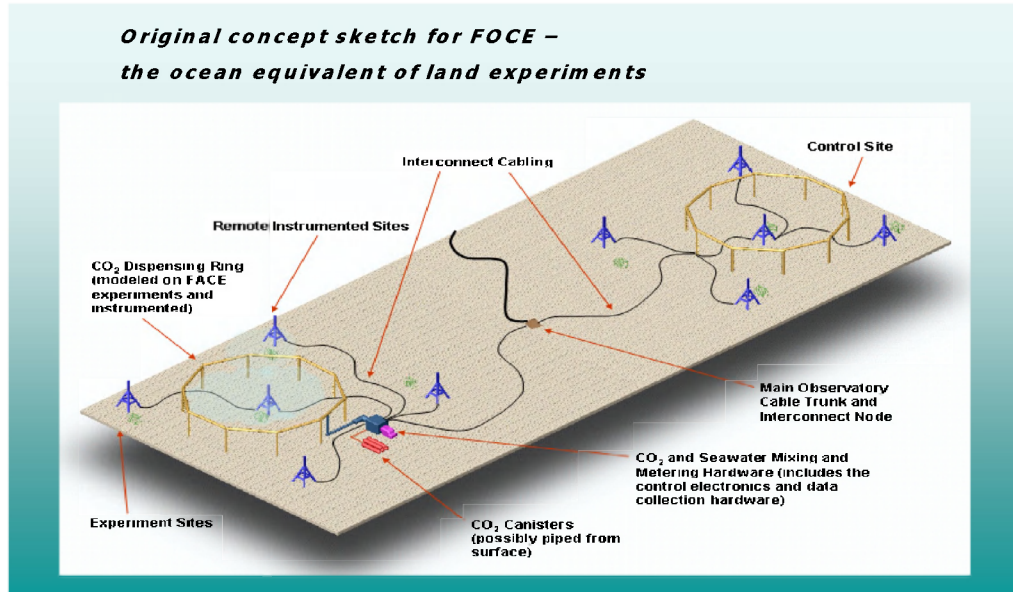


Figure 20. Concept sketch of Free Ocean CO<sub>2</sub> Enrichment Experiment (FOCE) where experiments in the seas emulate future conditions (courtesy P. Brewer).

The prototype produced by the Monterey Bay Aquarium Research Institute (MBARI) is able to provide and maintain control of a volume of fixed exposure. It works best in an area of low (but some) flow.

The access problems associated with the marine environment makes it unrealistic to expect the size and coverage that is available from the Free Air CO<sub>2</sub> Enrichment (FACE) experiments on land. Therefore, the kinds of instruments mentioned above are best used to confirm or refute results from tank experiments and more conventional mesocosm experiments.

## 6 Societal and policy implications for ocean acidification

Public awareness of the existence of the problems associated with global warming is high, but knowledge of ocean acidification, and its potential ecological and socio-economic impact, is limited. Therefore, ocean acidification needs to be brought to the attention of audiences beyond those with scientific interest and thus added to the broader climate change discussion. The United Nations Environment Programme (UNEP) is currently facilitating a television documentary to showcase the impact of ocean acidification on key marine ecosystems, such as tropical or cold-water corals and polar plankton communities. Intended for broadcast on BBC World in May 2008, this documentary will help to raise global awareness of the issue with the public and policy-makers alike.

Ocean acidification must be considered in relation to the fields of economics, politics, and culture, as well as science.

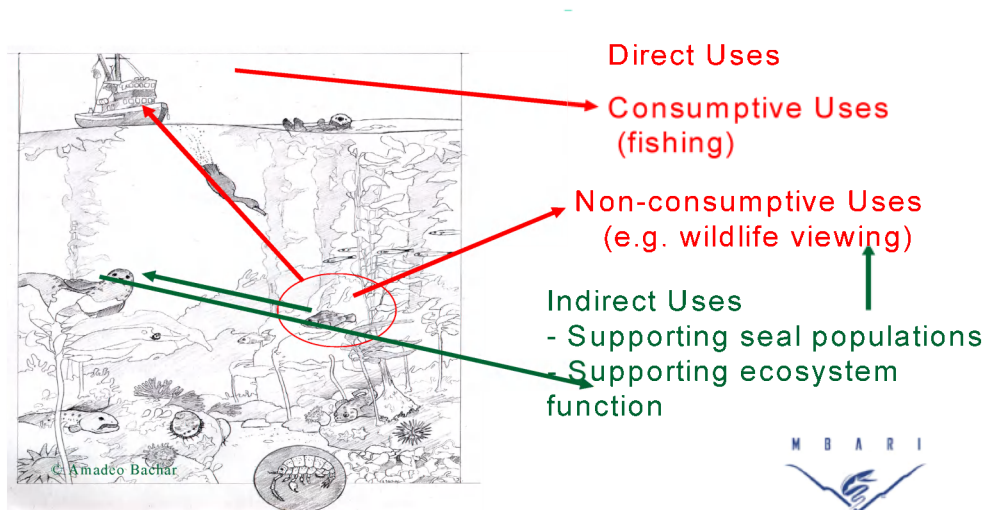


Figure 21. Understanding economic values (courtesy J. Kildow).

The economic value of fishing, tourism, and marine goods and services is substantial and relatively well known. Less clear is the impact that ocean acidification can or would have on this. Therefore, there needs to be an open policy dialogue that will increase public awareness. Scientists have an important role in ensuring that science is brought closer to policy-makers and the public, that they communicate more effectively, and that scientific needs and governmental solutions are specific.

### 6.1 Management strategy

There is a need for a management strategy at national and international levels that recognizes that a problem exists and implements action to address it.

Management goals have to be adopted, support provided for scientific research, and government actions backed by public knowledge.

A strategic plan (five-year and long-term) needs to be created with a management structure, a legal and regulatory framework, and the consideration of research priorities.

## 7 List of attendees

<b>Name</b>	<b>E-mail</b>	<b>Organization</b>
Azetsu-Scott, Kumiko	Azetsu-ScottK@mar.dfo-mpo.gc.ca	BIO, Canada
Bargeron, Charlene	cpb103@noc.soton.ac.uk	NOC, UK
Barry, James	barry@mbari.org	MBARI, USA
Barth, Hartmut	Hartmut.Barth@ec.europa.eu	EC
Bellerby, Richard	richard.bellerby@bjerknes.uib.no	Bjerknes Centre for Climate Research, Norway
Blackford, Jerry	jcb@pml.ac.uk	PML, UK
Knut, Børsheim	yngve.borsheim@imr.no	Institute of Marine Research, Norway
Brewer, Peter	brpe@mbari.org	MBARI, USA
Clemmesen, Catriona	cclemmesen@ifm-geomar.de	IFM-GEOMAR, Germany
Dulvy, Nick	nick.dulvy@cefas.co.uk	CEFAS, UK
Dalton, Sir Howard	Deceased since the Workshop	DEFRA, UK
Fernand, Liam	liam.fernand@cefas.co.uk	CEFAS, UK
Filipsson, Helena	filipsson@gvc.gu.se	University of Göteborg, Sweden
Gattuso, Jean-Pierre	gattuso@obs-vlfr.fr	CNRS , France
Gazeau, Frederic	f.gazeau@nioo.knaw.nl	Netherlands Institute of Ecology (NIOO-CEME-KNAW)
Hain, Stefan	stefan.hain@unep-wcmc.org	UNEP Coral Reef Unit
Hardman-Mountford, Nick	nhmo@pml.ac.uk	PML, UK
Hydes, David	djh@noc.soton.ac.uk	NOC, UK
Kildow, Judith	jtk@mbari.org	MBARI, USA
Kirkwood, William	kiwi@mbari.org	MBARI, USA
Kröger, Silke	silke.kroeger@cefas.co.uk	CEFAS, UK
Laing, Ian	ian.laing@cefas.co.uk	CEFAS, UK
Leedale, Andrea	a.leedale@defra.gov.uk	DEFRA,UK
Leonardos, Nikos	hernes@essex.ac.uk	University of Essex, UK
Marubini, Francesca	francesca.marubini@jncc.gov.uk	JNCC, UK
McGovern, Evin	evin.mcgovern@marine.ie	Marine Institute, Ireland
Pelejero, Carlos	pelejero@icm.cat	CSIC , Spain
Pörtner, Hans	hpoertner@awi-bremerhaven.de	AWI, Germany
Roberts, Murray	murray.roberts@sams.ac.uk	SAMS, UK
Rodriguez, Carmen	carmen@st.ieo.es	IEO, Spain
Schuster, Ute	U.Schuster@uea.ac.uk	UEA, UK
Steinke, Michael	m.steinke@essex.ac.uk	University of Essex, UK
Studd, Shaun	shaun.studd@cefas.co.uk	CEFAS, UK
Suggett, David	dsuggett@essex.ac.uk	UEA, UK
Vogt, Meike	m.vogt@uea.ac.uk	UEA, UK
Webster, Richard	not known	UEA, UK
Whiteley, Nia	n.m.whiteley@bangor.ac.uk	University of Bangor, UK
Widdicombe, Steve	swi@pml.ac.uk	PML, UK

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## Annex 1: Basic chemistry and explanation of terms

The following is taken from The Royal Society (2005)

### The meaning of pH

The term pH describes the acidity of a liquid. It is defined as:

$$\text{pH} = -\log_{10} [\text{H}^+] \quad (1)$$

This negative logarithmic dependence on hydrogen ion concentration, [H<sup>+</sup>], in moles per litre means that if [H<sup>+</sup>] increases 10-fold then pH decreases by 1 unit. The square brackets refer to the concentration of H<sup>+</sup> and subsequently to the concentration of other substances.

Water has the formula H<sub>2</sub>O. Only a small proportion of the water molecule splits up into H<sup>+</sup> and OH<sup>-</sup>. In pure water, the amounts of [H<sup>+</sup>] and [OH<sup>-</sup>] are equal and the concentration of each is 10<sup>-7</sup> in the units mole per litre. This means that a neutral solution has pH=7. Acid solutions have an excess of [H<sup>+</sup>] and a pH less than 7. Alkaline (basic) solutions have an excess of [OH<sup>-</sup>] and pH greater than 7, up to 14.

### Dissolved inorganic carbon in seawater

As CO<sub>2</sub> dissolves in seawater, it reacts with seawater to produce H<sup>+</sup> and various negatively charged forms of dissolved carbon (see Figure A). Carbon dioxide dissolved in seawater first reacts with the water molecule (H<sub>2</sub>O) to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Not all the CO<sub>2</sub> dissolved in seawater reacts to make carbonic acid and therefore seawater contains dissolved gaseous CO<sub>2</sub>; a point that is easily appreciated from a familiarity with carbonated drinks (which are solutions of carbonic acid). According to Henry's Law, in a simple aqueous solution we would expect the concentration of CO<sub>2</sub> in the air to be proportional to that in the solution of carbonic acid.

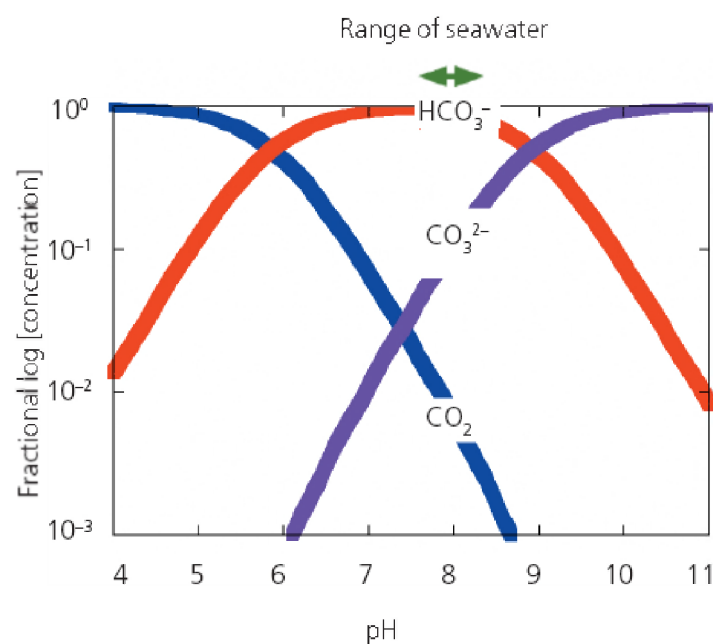


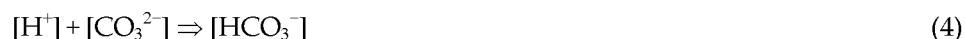
Figure A. Relative proportions of the three inorganic forms of CO<sub>2</sub> dissolved in seawater. Note the ordinate scale (vertical axis) is plotted logarithmically.



Carbonic acid is an acid because it can split up into its constituents, releasing an excess of  $H^+$  to solution and so driving pH towards lower values. Carbonic acid splits up by adding one  $H^+$  to solution along with  $HCO_3^-$  (a bicarbonate ion):



This increase in  $H^+$  causes some  $CO_3^{2-}$  (called carbonate ion) to react with  $H^+$  to become  $HCO_3^-$ :



Thus, the net effect of the dissolution of  $CO_2$  in seawater is to increase concentrations of  $H^+$ ,  $H_2CO_3$  and  $HCO_3^-$ , while decreasing concentrations of  $CO_3^{2-}$ .

The decrease in carbonate ion concentration  $[CO_3^{2-}]$  has important consequences for the chemistry of carbonate minerals commonly used by marine biota to form shells or skeletons.

The formation and dissolution of carbonate minerals can be represented as:



Because the dissolution of  $CO_2$  in seawater decreases  $[CO_3^{2-}]$ , this reaction moves to the right, impeding the formation of carbonate minerals and promoting their dissolution. Dissolution of carbonate minerals (Equation (5)) provides carbonate ions that can react to consume  $H^+$  according to Equation (4). Thus, the dissolution of carbonate minerals tends to decrease  $[H^+]$  (increase pH), counteracting some of the pH effects of added  $CO_2$  (see next below).

### The carbonate buffer and seawater pH

The term CARBONATE BUFFER is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean  $H^+$  concentration, and thus pH. If a process, such as  $CO_2$  dissolution (Equations (2) and (3)), adds  $H^+$  to seawater some of the added  $H^+$  reacts with carbonate ( $CO_3^{2-}$ ) ion to convert it to bicarbonate ( $HCO_3^-$ ; Equation (4)). Because initially most of the added  $H^+$  would be consumed in this way, the change in pH is much less than it would otherwise be. But this process also consumes some carbonate ion; therefore, this pH buffering capacity would diminish as  $CO_2$  concentrations increase. Because  $CO_2$  is absorbed at the sea surface, it is the surface oceans that are most affected.

On the longer time-scales of ocean mixing, interaction with  $CaCO_3$ -rich sediments tends further to buffer the chemistry of the seawater so that changes in pH are lessened. For example, if the deep oceans start to become more acidic such as through the addition of  $CO_2$ , which decreases concentrations of  $CO_3^{2-}$ , some carbonate ion will be dissolved from sediments (Equation (5)).

The carbonate buffer acts to stabilize the average pH of seawater at approximately pH = 8 because of the following two processes: (i) uptake of  $CO_2$  from the atmosphere (for example from volcanoes and now, importantly, from fossil fuel burning) and (ii) interaction of seawater with oceanic sediments composed of  $CaCO_3$ . Because  $CaCO_3$  is abundant in sediments, the pH of the deep oceans cannot change by large amounts over time-scales of 10 000 years. However, over historical time-scales, significant changes in surface and near-surface ocean pH can occur.

**The calcium carbonate saturation horizon**

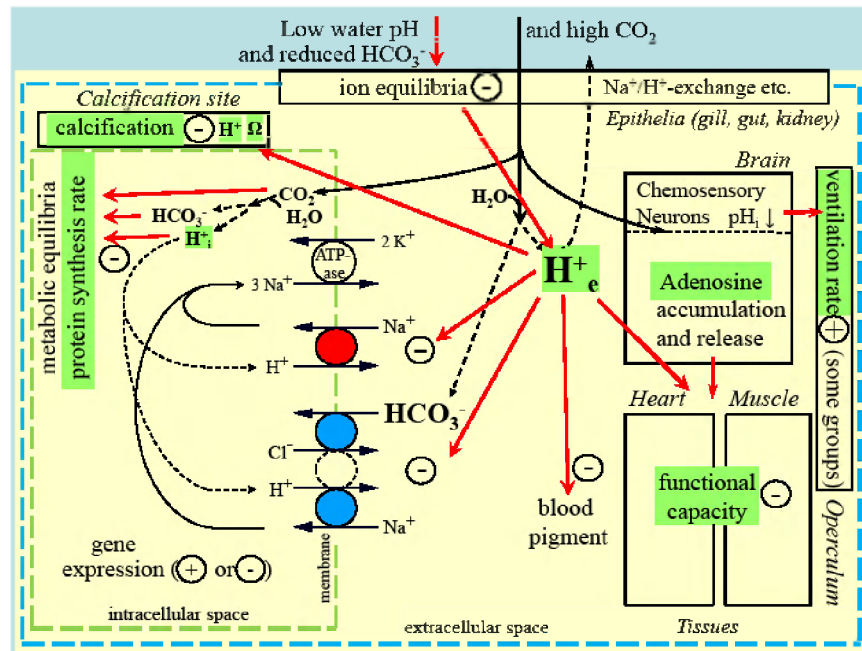
As discussed in this report, small organisms living in open ocean waters construct shells or plates of CaCO<sub>3</sub> that, on death of the organism, fall to the seabed. Their preservation in seabed sediments depends on the solubility of CaCO<sub>3</sub> in seawater and on the concentration of carbonate ions. There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which CaCO<sub>3</sub> will start to dissolve. Because CaCO<sub>3</sub> solubility increases with decreasing temperature and increasing pressure, the critical concentration occurs at a depth, the "saturation horizon", below which seawater is under saturated and CaCO<sub>3</sub> will tend to dissolve and above which seawater is supersaturated and CaCO<sub>3</sub> will tend to be preserved. Because the CaCO<sub>3</sub> mineral calcite is less soluble than the form aragonite, the aragonite saturation horizon is shallower. Because added CO<sub>2</sub> decreases the carbonate ion concentration, the saturation horizons will become shallower with increasing releases of human derived CO<sub>2</sub> to the atmosphere.

## Annex 2: Carbon Sinks

Changes to ocean chemistry and pH, estimated using the OCMIP3 models calculated from surface ocean measurements and our understanding of ocean chemistry. Note that the concentrations of bicarbonate ion ( $\text{HCO}_3^-$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ) increase with rising atmospheric concentration of  $\text{CO}_2$ , while carbonate ion ( $\text{CO}_3^{2-}$ ) decreases. The average pH of the surface ocean waters decreases with increasing atmospheric  $\text{CO}_2$  concentration. (Assumptions used in model: total alkalinity =  $2324 \text{ mol kg}^{-1}$ ; temperature =  $18^\circ\text{C}$ . All other assumptions are as per OCMIP3 (Institut Pierre Simon Laplace, 2005). Aragonite and calcite saturation is calculated as per Mucci and Morse (1990). Physical oceanographic modelling is based on Bryan (1969) and Cox (1984).

	Pre-industrial	Today	2x pre-industrial	3x pre-industrial	4x pre-industrial	5x pre-industrial	6x pre-industrial
Atmospheric concentration of $\text{CO}_2$	280 ppm	380 ppm	560 ppm	840 ppm	1 120 ppm	1 400 ppm	1 680 ppm
$\text{H}_2\text{CO}_3$ ( $\text{mol kg}^{-1}$ )	9	13	19	28	38	47	56
$\text{HCO}_3^-$ ( $\text{mol kg}^{-1}$ )	1 768	1 867	1 976	2 070	2 123	2 160	2 183
$\text{CO}_3^{2-}$ ( $\text{mol kg}^{-1}$ )	225	185	141	103	81	67	57
Total dissolved inorganic carbon ( $\text{mol kg}^{-1}$ )	2 003	2 065	2 136	2 201	2 242	2 272	2 296
Average pH of surface oceans	8.18	8.07	7.92	7.77	7.65	7.56	7.49
Calcite saturation	5.3	4.4	3.3	2.4	1.9	1.6	1.3
Aragonite saturation	3.4	2.8	2.1	1.6	1.2	1.0	0.9

### Annex 3: Overview of processes and mechanisms affected by CO<sub>2</sub> in a generalized water-breathing animal



Overview of processes and mechanisms affected by CO<sub>2</sub> in a generalized water breathing animal, emphasizing a key role for extracellular pH in defining sensitivity to ocean hypercapnia and acidification (after Pörtner *et al.*, 2005; Pörtner, 2008). As with thermal sensitivity, the first stage of hypercapnia tolerance is likely set at the level of functional capacity of whole animals and defined by tissues involved in oxygen supply. Shaded areas indicate costly processes relevant to energy budget and changes in growth and behaviours, including the capacity to collect and digest food.

## **Annex 4: Agenda**

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### **ICES WORKSHOP ON THE SIGNIFICANCE OF CHANGING OCEAN CO<sub>2</sub> AND PH IN SHELF SEA ECOSYSTEMS**

#### **2–4 May 2007**

The workshop will focus on the shelf seas of Europe and North America. It will review the current state of knowledge and identify future research directions, stating the knowns and unknowns. Talks are informal; they exist to stimulate and aid discussion.

#### **Wednesday 2 May – The mostly knowns day**

- 09:30 Registration and coffee
- 10:00 Opening Address, Sir Howard Dalton, chief scientific adviser to DEFRA (10 minutes)
- “Themes and challenges” Peter Brewer, Chair (30 minutes)
- 10:40 Session 1: The spatial and temporal variability of the surface ocean pH and CO<sub>2</sub> carbonate system in the shelf seas
- Proxy records, output from previous workshops
- “Palaeo-reconstructions of seawater pH: An overview of findings so far” Carles Pelejero (20 minutes)
- “Summary of shelf seas observations of pCO<sub>2</sub> and pH and projections for the future” Liam Fernand (15 minutes)
- “Synthesis of Plymouth AMEMR workshop on modelling ecosystem response” Jerry Blackford (20 minutes)
- Discussion (25 minutes)
- “Documentary on acidification issues” Stephen Hain (15 minutes)
- 12:30–13:30 Lunch
- 13:30 Session 2: Monitoring systems
- “Monitoring of CO<sub>2</sub>: an operational UK air–sea carbon flux observation capability” Nick Hardman-Mountford (20 minutes)
- “A system to monitor pH in shelf seas” David Hydes (20 minutes)
- Discussion (20 minutes)
- 14:30 Session 3: Examine the effects of pH and the CO<sub>2</sub>–carbonate system on nutrients and calcification
- “Calcification and nutrient uptake stoichiometry” Richard Bellerby (20 minutes)
- “pH variability and CO<sub>2</sub> induced acidification in the North Sea, relating to nutrients and plankton” Jerry Blackford (20 minutes)
- Discussion (20 minutes)
- 15:40–16:00 Coffee
- 16:00–17:00 Summary and discussion

**Thursday 3 May – Ecosystem day, many unknowns**

09:00 Session 4: Ecosystem effects: explore the links between potential changes in pH and pCO<sub>2</sub> and its effects on marine ecosystems

“Role of CO<sub>2</sub> in climate change effects in marine ecosystems “ Hans Pörtner (40 minutes)

“Experimental results on the pH, CO<sub>2</sub>, and light dependencies of photosynthesis and calcification in *Emiliana huxleyi*” Dave Sugget (20 minutes)

Discussion (20 minutes)

10:20–10:30 Coffee

10:30 Session 5: Benthic systems

“Impact of elevated pCO<sub>2</sub> on coastal benthic organisms and communities” Jean Pierre Gattuso (30 minutes)

“The effects of elevated pCO<sub>2</sub> on mussels and oysters” Frederic Gazeau (20 minutes)

“The change in pH in context of the natural variability in the sediment” Steve Widdicombe (20 minutes)

“Effects on cold-water corals” Francesca Marubini (20 minutes)

Discussion (30 minutes)

12:30–13:30 Lunch

13:30 Session 6: Overall implication to ecosystem, fisheries, shellfish, and aquaculture

“Ocean acidification effects on fisheries and marine ecosystems” Nick Dulvy (20 minutes)

“Relevance to aquaculture” Ian Laing (20 minutes)

Discussion (20 minutes)

14:30–16:00 Breakout groups: to ask or answer specific questions

16:00–16:15 Coffee

16:15–16:30 Summary of breakout groups

**Friday 4 May – How/what are we going to do about it day**

09:00 Session 7: Experimental strategies

“Results from experiments on *Emiliana huxleyi* in a high CO<sub>2</sub> environment” Nikos Leonardos (20 minutes)

“Future experimental needs” Bill Kirkwood (20 minutes)

“Experimental strategies by MBARI” James Barry (20 minutes)

Discussion (30 minutes)

10:30–10:50 Coffee

10:50 Session 8: Broader outreach—consequences of and implications to government and national policies.

“The economic context and the need for management” Judith Kildow (20 minutes)

12:30–13:30 Lunch

13:30 Agreeing on recommendation: bringing together sections of the report

15:00 Close

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