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Report of the Workshop on the Significance of Changing Ocean CO₂ and pH in Shelf Sea Ecosystems

2-4th May London

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Preface

The primary purpose of this document is to report the recommendations resulting from the ICES workshop on the “Significance of Changing Ocean CO₂ and pH in ICES Shelf Sea Ecosystems” held 2-4th May, in London. There are some excellent reports already published in this field firstly by SCOR¹ and then by NOAA/NSF/USGS², the Royal Society³, WGBU⁴ and more recently by OSPAR⁵ and the IPCC. Cognisant of these recent efforts, this 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 this workshop covered ground already considered by others to give it a sound base for the predictions of likely impacts, this report will outline those relevant issues but the reader is advised to refer to other reports, if greater depth is required. The novel focus of this report is the potential effects on ecosystem function with links to fisheries. This report makes recommendations for work associated with understanding this problem to the entire ecosystem and specifically for the understanding of this problem to fisheries. Most of the material used was presented at the workshop, appendix I being the most significant exception.

Executive Summary

“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.”

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

Key recommendations

Recommendations fall into the following categories,

- **Experiments**
- **Technology development**
- **Modelling**
- **Monitoring**
- **Experimental protocol development and applications**

Experimental approach

Most of our present knowledge on the likely impacts of acidification on organisms comes from mesocosm experiments. However, present knowledge is limited and in analogy to the land based studies on CO₂ where a number of study sites have been set up, many further experiments are required.

Specifically experiments are needed that ;

- address the issue of longterm change: most experiments are short-term (hours to weeks), the few long term experiments that have been undertaken have shown that some species can acclimatise over a long period, where as other species can survive a 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 stresses. 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 due to the melting ice.
- are geographically diverse. As the exact response of the sea water to increasing CO₂ 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 DOC (Dissolved Organic Carbon).

The above statements are true for all scales of experiments, experiments are required on all scales from a single species to as large an ecosystem as practical. Each experiment also needs to consider the relative importance of acidification compared to other climate change impacts, as well as other factors such as over fishing and eutrophication.

Modeling

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

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

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

Technological Development

Mesocosm experiments and modelling both have severe limitations. Models require field data to validate them and mesocosm experiments can often produce results not replicated at a higher scale, perhaps due to a lack of higher predation. Advances are therefore required so that experiments currently performed in the lab can be performed in-situ as very different responses can be produced in the lab than in the wild. Such experimental strategies would include experiments in the ocean (FOCE) similar to those which occur on land (FACE).

Measuring pH, partial pressure of CO₂ and dissolved HCO₃ in seawater is not a simple process and more robust methods and cost effective methods for use on moored buoys, ships of opportunity and research vessels needs to be developed

Monitoring

There is an urgent need for the development of spatially and temporally highly resolved monitoring of atmospheric and surface water pCO₂, carbonate, alkalinity and pH over long periods of time (>10 years) in order to validate predictions and to provide the basis for macroecological analysis of the potential impacts of acidification for ecosystems and dependent services, such as fisheries. These observations would be used to assess the extent of the problem and for the validation of 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 that have been undertaken.

Experimental protocol

At present there are several barriers to the undertaking of experiments and to the effective inter comparison of experiments. The issues raised below will deal with some of these barriers.

There is a need to change permitting associated with experiments and the use of CO₂, at present it is banned by the London convention (despite the millions of tons being out gassed)

pH needs to be measured using a consistent approach. Attention has to be paid to methodology such as reference electrode drift.

Protocols for the other chemical parameters, especially Dissolved Inorganic Carbon need to be adhered to and widely propagated.

An experiment(s) need to be set up as an example of best practice, containing a suite of measurements with full access to reference documents.

The terms of reference (TOR) for the workshop

These TORs were specified by the OCC (Oceanography committee).

To review the current state of knowledge and identify future research directions stated in the Terms of Reference:

- The spatial and temporal variability of the surface ocean pH and CO₂ – carbonate system in shelf seas in the ICES region;
- To predict the rates of change and to understand how these can be measured;
- The effects of pH and the CO₂–carbonate system on nutrient chemistry that are important in ecosystem processes relevant to shelf seas;
- The effects of pH and the CO₂–carbonate system on contaminants in the shelf seas environments;
- The links between potential changes in pH and its effects on marine ecosystem components such as plankton, fish and shellfish and cold water corals.

Main outcomes

The problem

The oceans are one of the major buffer of anthropogenic CO₂ emissions. Oceanic uptake of CO₂ has led to a perturbation of the chemical environment primarily in ocean surface waters associated the increase in dissolved inorganic carbon (DIC): The increase in atmospheric CO₂ from about 280 μatm 200 years ago to 370 μatm

Table 1. The evolving chemistry of surface sea water under “Business as Usual” water

Time	pCO₂	Total CO₂	pH	HCO₃⁻	CO₃²⁻	H₂CO₃
yr.	μatm	μmol kg ⁻¹		μmol kg ⁻¹	μmol kg ⁻¹	μmol kg ⁻¹
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851	2043	113	26.2
2100	850	2212	7.775	2083	97	31.8

today has caused an average decrease across the surface of the oceans of about 0.08 pH units and a decrease in CO₃²⁻ of about 20 μmol/kg (Kheshgi 1995). It could drop by a further 0.5 units by the year 2100 if CO₂ emissions are not regulated (Royal Soc, 2005; Caldera and Wickett, 2003). A recent study of potential change in the North Sea

(Blackford and Gilbert, 2006) 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.

The evidence for pH change in the water column

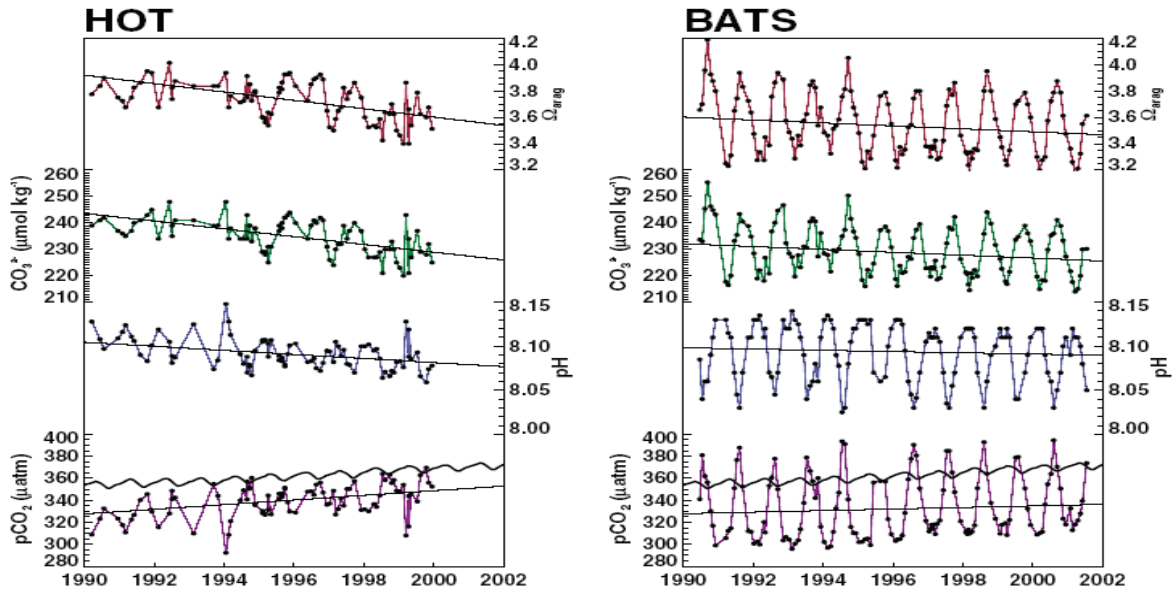
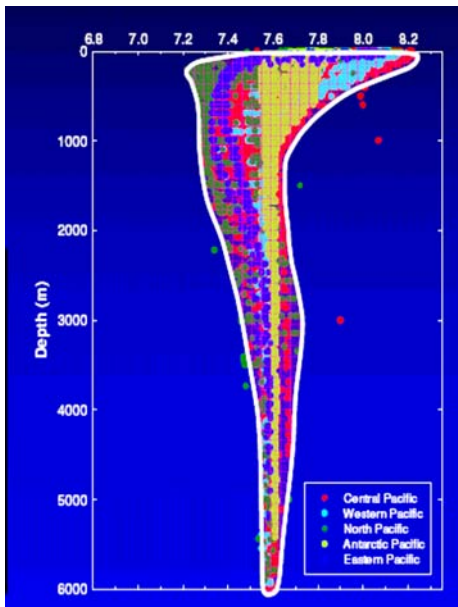


Figure 1 Time series of the change in pH, pCO_2 Hawaiian Ocean Times Series and Bermuda Atlantic time series Kleypass *et al.*, 2006

There does exist a small number of long term (>10 years) observatories which have recorded pCO_2 in both the atmosphere and water column. A minimum of 10 years is required because the variability is quite large compared to the signal. These stations are relatively rare with limited geographic coverage. The principal ones are The Bermuda Atlantic Ocean time series ([bats](#)), the Estoc ([ESTOC](#)) series off the Canary Islands and the Hawaiian Ocean times series (HOTS), other series exist, but are shorter than 10 years e.g. [DYFAMED](#) in the Mediterranean, KNOT Kyodo in the north pacific. The series demonstrate that the pH is decreasing, but that the natural signal is apparently variable. Because the measurement of pH in seawater requires a different approach to that in freshwater, historical values of pH (prior to 1970s) are suspect and not reliable.



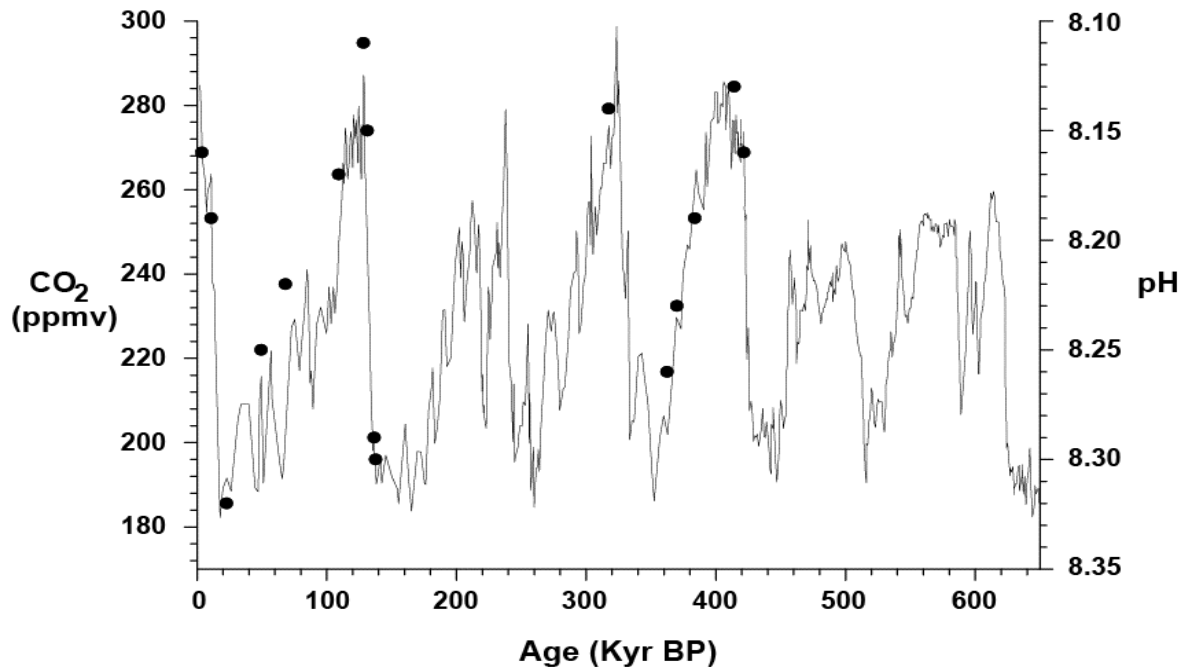
Care has to be taken in using existing data sets as sampling bias and geographic variation can lead to erroneous interpretations. In the deep ocean the natural pH range and subsequent likely change is a function of depth, with the greatest range in the surface. In shelf seas because they are well mixed in the winter months, benthic organisms are exposed to a full range of pH variation and immediately experience the increased levels of atmospheric CO_2 .

Figure 2 The variation of pH in the vertical courtesy J Barry

The historical context to the change in ocean pH

Through the use of boron isotopes cores can be used to construct past records of pH. This record shows the change in pH over the last 650,000 thousand years, there has been a cyclical change in pH associated with the glacial periods. The present day values of pH are comparable with the lowest values recorded in the past with transition from low pH to high pH occurring in 50k years. From an historic perspective the present levels of CO₂ are already high and anthropogenic emissions are exacerbating this issue.

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 to the record of atmospheric CO₂ concentration during the last 650,000 years (solid line) inferred from the composition of air bubbles trapped in Antarctica ice cores (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005). Redrawn from Pelejero and Calvo, in press.



-Natural cycles in seawater pH could enhance or mitigate the vulnerability of marine organisms to future ocean acidification. The catastrophic events in the past suggest that issues of saturation state were important, additionally the record suggests that high pCO₂ perturbation will last long (thousands to hundred thousand years).

Impacts on water column species

Coccolithophores



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

Beachy Head." Online Photograph. Encyclopædia Britannica. The result of many thousands of years of coccolithophore formation

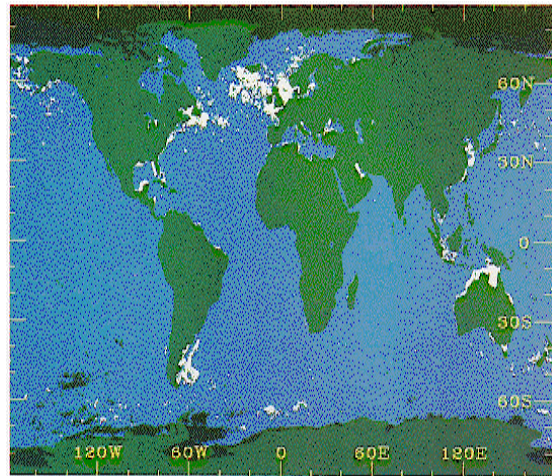


Figure 4 Distribution of *Emiliana Huxleyi* (Brown and Yoder, 1994, © AGU)

Emiliana Huxleyi is numerically the most abundant, the most abundant coccolithophore in the ocean and became prominent during glacial periods of enhanced ocean productivity. It is a major sink of Carbon and has a preponderance in the ICES region. Below the first equation shows how *E. Huxleyi* generates Calcium Carbonate which is a major part of the carbon cycle.

The 2nd equation shows how carbon is fixed by the process of photosynthesis.

Coccolithophores do two (among other) major things :

a) They fix inorganic C

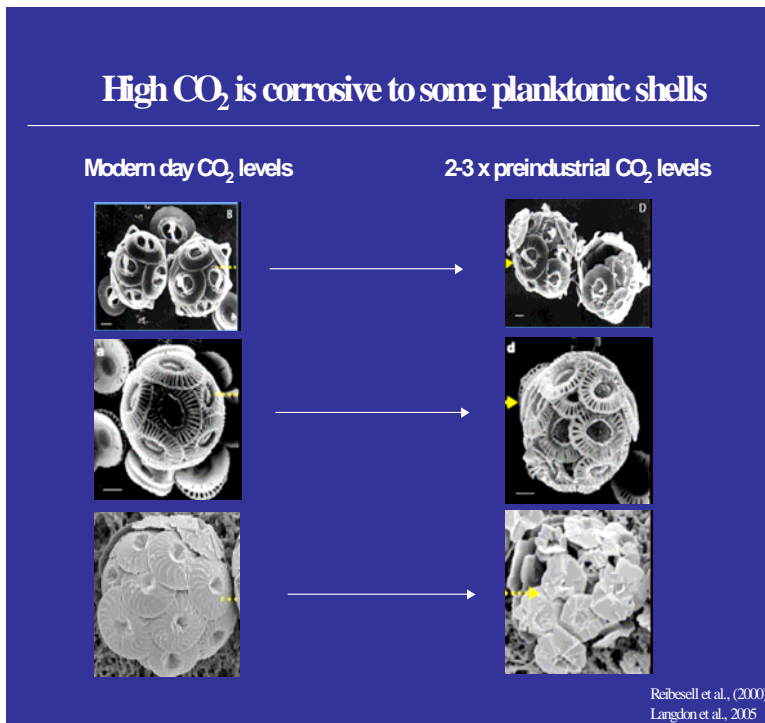


(which eventually finds itself at the bottom of the sea)

b) They fix organic C by photosynthesis:



However, the increased CO_2 will lead to dissolution of liths (Appendix I), left are experimental results



experimental results showing scanning electron microscope images of the structure for three different coccolithoporoids, when exposed to high levels of CO_2 .

Figure 5 Effect of high CO_2 on coccolithophores. Reibesell *et al.* 2000, ©Nature

Pteropods

However while Coccolithophores form an important part of the carbon cycle they do not constitute a significant food source. In the

Barents Sea pteropods which do calcify are a significant food source for herring. Herring are an important part of the ecosystem and are a significant food source for fish such as cod, for marine mammals and sea birds. As the saturation of aragonite (which constitutes most of the shell) becomes below 1 then 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 its skeleton and impose a sub-lethal metabolic cost rather than cause sudden death as is the case with some present deep water cold corals.

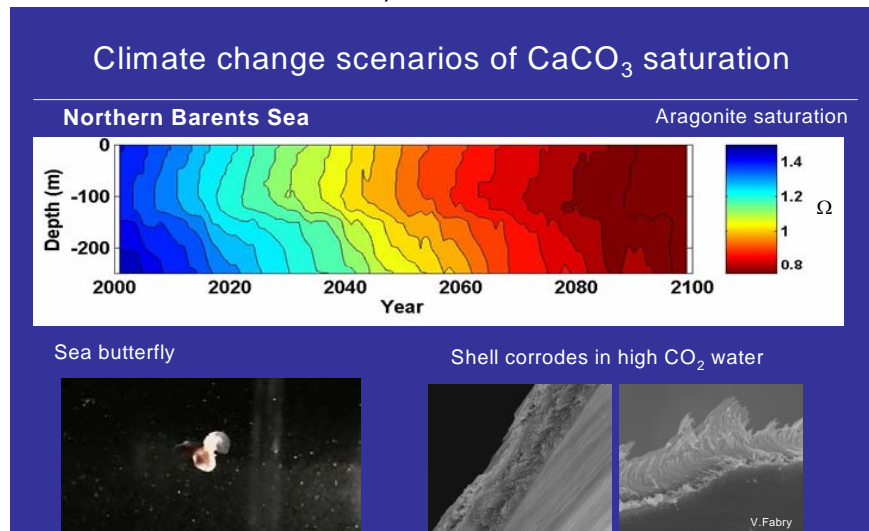
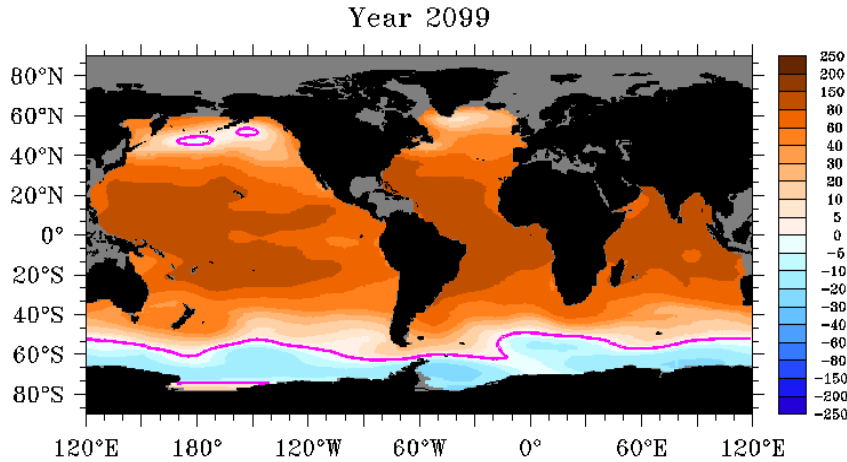


Fig 6. Aragonite Saturation in the Northern Seas Redrawn from Orr *et al.*, 2005 © Nature

Modelling predictions

A highly useful modelling result is that of the Aragonite saturation horizon produced by Orr *et al.*, 2004. It demonstrates that in the southern ocean

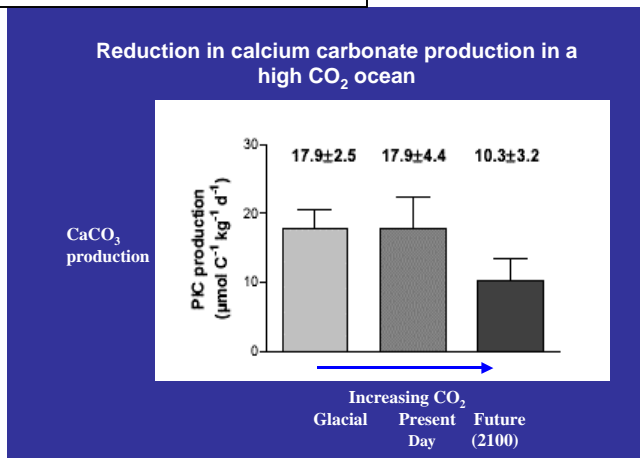


Aragonite will dissolve from shells at all depths. While in the ICES area bottom dwelling organisms will be affected and only those in relatively shallow areas will be viable.

Figure 7 Global Aragonite Saturation 2099 Orr *et al.*, 2005 © Nature

However while aragonite will dissolve particulate inorganic production due primarily to calcite production is likely to still occur in the future however at a reduced rate compared to the present day.

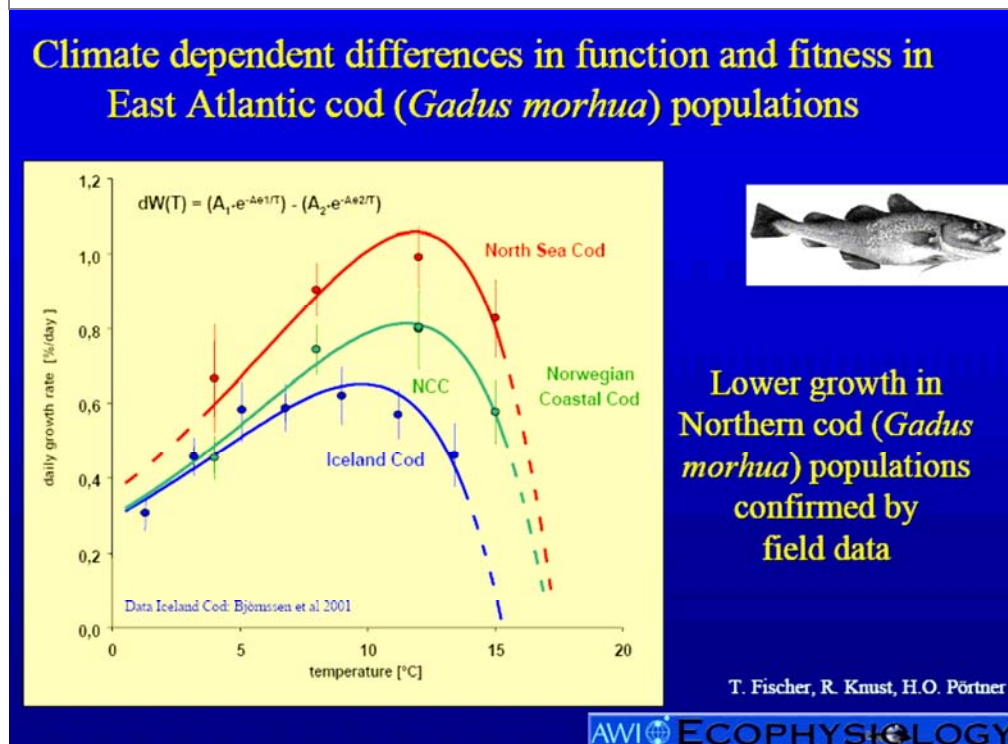
Figure 8 Reduction in calcium carbonate production for an Emilian Huxleyi bloom under present and future scenarios. Delille *et al.*, 2005.



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 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 an increased energy efficiency over a narrow range supports growth performance. One such example is that of cod where the maximum growth rate lies over a 5° C range. However, within a thermal window it is the oxygen consumption that limits growth. The additional draw down of CO₂ 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 give the whole effect.

Figure 9 The daily growth rate for Cod against temperature, indicating the thermal window for maximum growth. Courtesy H. Portner

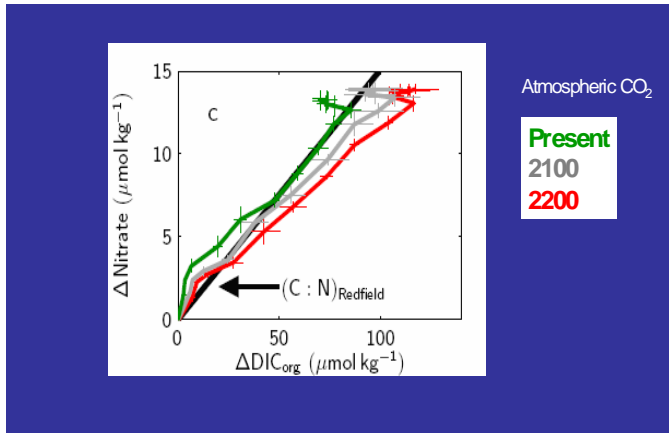


Experimental approaches are required which consider all aspects of climate change but need to consider the following on certain species;

- CO₂ dependent performance changes
- where the organism is in its temperature dependent performance window, e.g growth and fecundity
- seasonal shifts in performance windows
- climate dependent functional specialization and temperature dependent biogeography

Effects on non calcifying plankton and nutrient uptake

Figure 10, The increase in Carbon uptake as a function of Nitrate for different CO₂ concentrations (courtesy R Bellerby)



Mescosm results show that for increasing concentrations of atmospheric CO₂ then for a given nitrate concentration more Carbon is consumed. However, other studies have shown that increasing the Carbon:Phosphate ratio, reduces the growth rate of certain photo plankton and reduces fecundity (fertility) in zooplankton.

Metals and nutrient chemistry

(This was not presented at the work shop and is taken from the IPCC, special report on Carbon Capture and Storage⁶ it is presented here for completeness). The cycling of nitrogen from particulate organic forms to form nitrate *via* ammonium and nitrite in marine systems is known as marine nitrification. Studies of the potential impact of pH reduction on this process showed that it was significantly reduced (by around 50%) as pH fell from 8 to 7. At a pH of 6, nitrification was almost completely inhibited. (Huesemann *et al*, 2002), leading the authors to speculate that similar impacts in natural systems could result in unpredictable eutrophication phenomena. Reduced pH values could affect uptake of trace metals and nutrients by marine organisms. All aquatic invertebrates take up both essential and non-essential metals, with a wide variability in final body concentration with respect to individual metals and to the invertebrate taxa involved (Rainbow, 2002). Low pH will affect the speciation and bioavailability of many trace metals (both biologically essential and non-essential) and of nutrients in the ocean. Decreases in ambient water pH generally increase the proportion of free metals and decrease the level of metals associated with particulates. Free metals are the generally more bioavailable forms (Sadiq, 1992). Speciation/dissolution processes will be highly dependent upon, for example, sediment geochemistry. Prediction of metal behaviour under conditions of reduced pH should be possible in simple chemical terms (Salomons and Forstner 1984). In the case of many trace metals, enhanced bioavailability is likely to have toxicological implications, since free forms of metals are of the greatest toxicological significance (Rainbow 2002). The behaviour of other nutrients may also be influenced by depression of pH values. Speciation of phosphate, silicate and ammonia are pH dependent (Zeebe and Wolfe-Gladrow 2001). To date no systematic evaluation of the likely scale of any pH related changes in metal or nutrient speciation or of concomitant changes in biological

systems has been carried out and it is unclear whether such effects reach the same order of magnitude as direct CO₂ effects.

Impacts on benthic ecosystem

There a number of mechanisms by which organisms can be affected. These include

Respiratory Stress

Reduced pH limits oxygen-binding and transport by respiratory proteins, leading 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 carbonate saturation state increases the difficulty of carbonate deposition, with unknown metabolic consequences.

Metabolic Depression (Torpor)

Elevated CO₂, reduced pH, or both can cause some animals to enter a state of reduced metabolic rate and semi-hibernation.

Examples of these effects come from the study in tanks on two very different benthic species, *Nereis* a burrowing worm and *Brissopsis* a sea urchin were exposed to three levels of pH associated with increased CO₂.

Comparison of *Nereis* v *Brissopsis*



Figure 11 Two very different benthic species *Nereis* (a worm) and *Brissopsis* (a sea urchin, courtesy S. Widdicombe)

Builds and irrigates deep burrows
Increases uptake of nitrate
Increased release of silicate
No impact on phosphate
No Impact on nitrite and ammonium flux
High tolerance to seawater acidification

Bulldozes through surface sediment
Decreases uptake of nitrate
Increased release of silicate
Increased release of phosphate
No impact on nitrite and ammonium flux
Highly vulnerable to seawater acidification

Figure 12 Impact of Brissopsis and nutrient flux

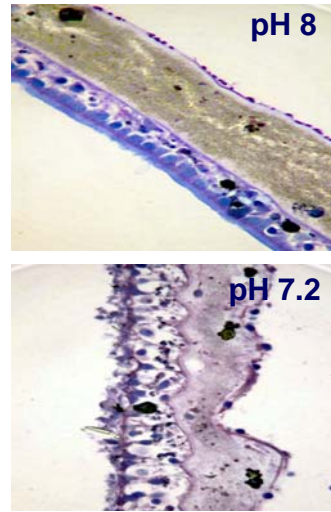
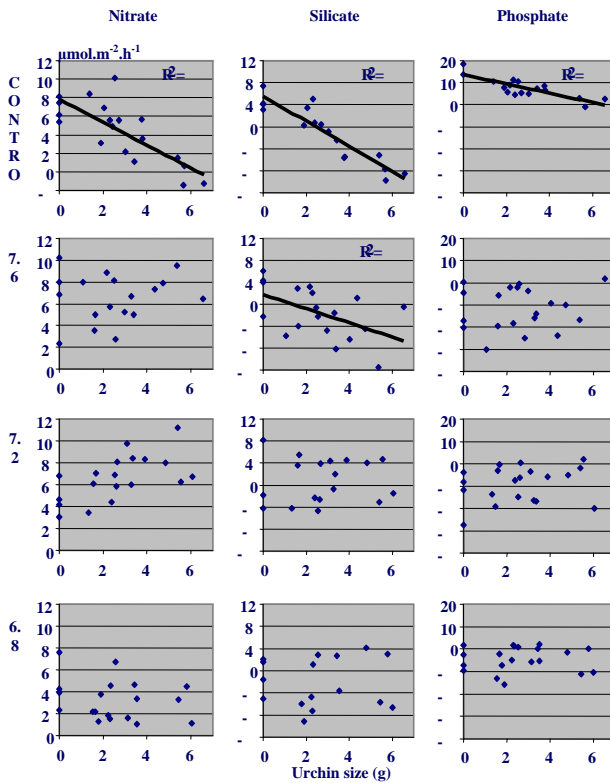


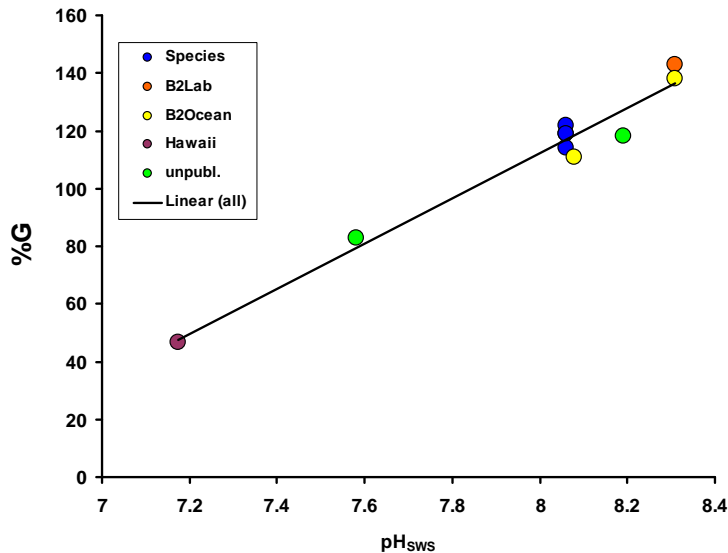
Fig 12. b Brissopsis tissue

Fig 12a Nutrient uptake as a function of size for different pH scenario(S. Widdicombe)

The sea urchin is highly vulnerable as 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 to pH 8, this linearity was lost indicating a change in functionality. Little further change was noticed with increasing pH. There was also observed change in the acid-base balance, reproductive tissue and respiration rates.

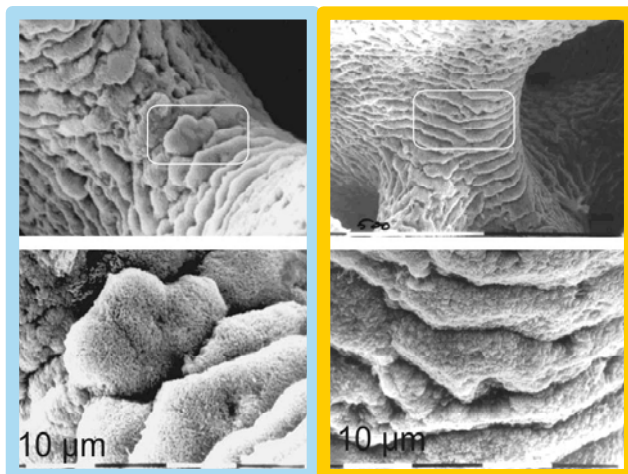
Impacts on Corals.

Figure 13 Calcification (G growth rate) as a function of pH for tropical corals. For every 0.1 ↓ in pH ≈ 8% ↓ in G. Courtesy F. Marubini.



In the ICES shelf region there are both warm water corals in the Mediterranean and also cold water corals. Gaffected by the reduction in calcification rates (Marubini 2002). Studies on tropical corals show a direct relation between pH and calcification. These results while from a relatively limited number of studies do show the response to be surprinsgly linear.

The images form a scanning electron microscope of a coral (*A. verweyi*) at a pH of present day levels and at a decreased level in the future of 7.76 show the size of formations has decreased.



Other work (Gattuso *et al.*, 1999) demonstrates the importance of additional factors such as irradiance and nutrient stress in determing calcification rates. These parameters along with temperature are likely to interact with pH in the future climate.

Figure 14 Skeletal microstructure of *A.verweyi* (a coral)courtesy J.P.Cuif, Present Day vs. Year 2100

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). The result is that more of the carbon is respired, thereby decreasing the trophic transfer efficiency of nutrients and energy through the marine foodweb.

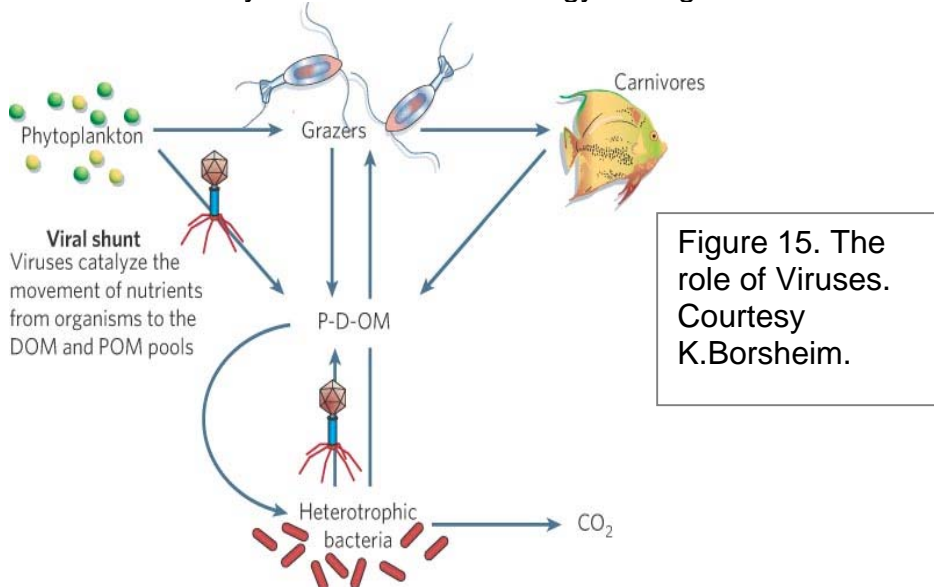


Figure 15. The role of Viruses. Courtesy K.Borsheim.

However it is not known how pH change will affect this process, research into these effects is therefore needed.

Impacts on Shellfish farming

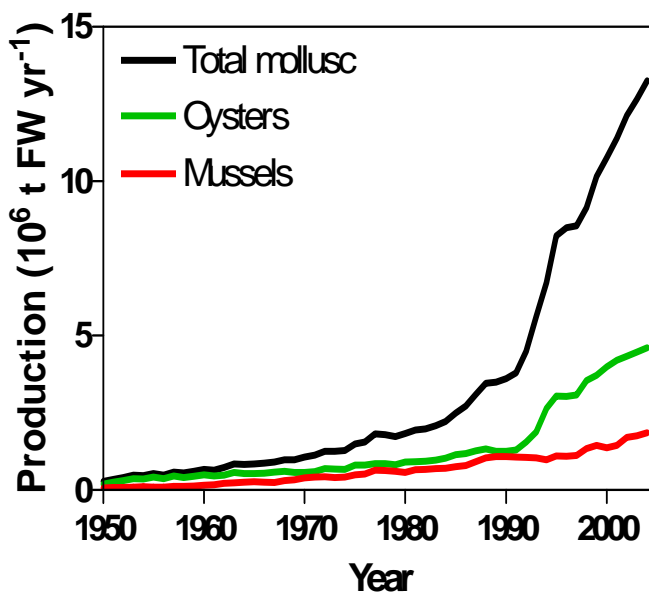


Figure 16 World wide shellfish production, showing the dramatic increase. Source FAO2004⁷

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 an increase in world wide the production of mariculture 5% yr⁻¹ for the last ten years, mostly in far China and East Asia. This total accounts for 15 – 20% of global aquaculture economic and a value of approx 10 billion US\$

Experiments to assess the potential impact on this industry have been undertaken using incubation chambers, on the 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 shows a marked decrease (30%) in shell formation at pH levels likely to be reached in this century. At very high levels of pCO₂ (1800 ppm by vol) then 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, approx 50% of a mussel shell is made from Aragonite, which dissolves much more easily than calcite, which constitutes most of the oyster shells.

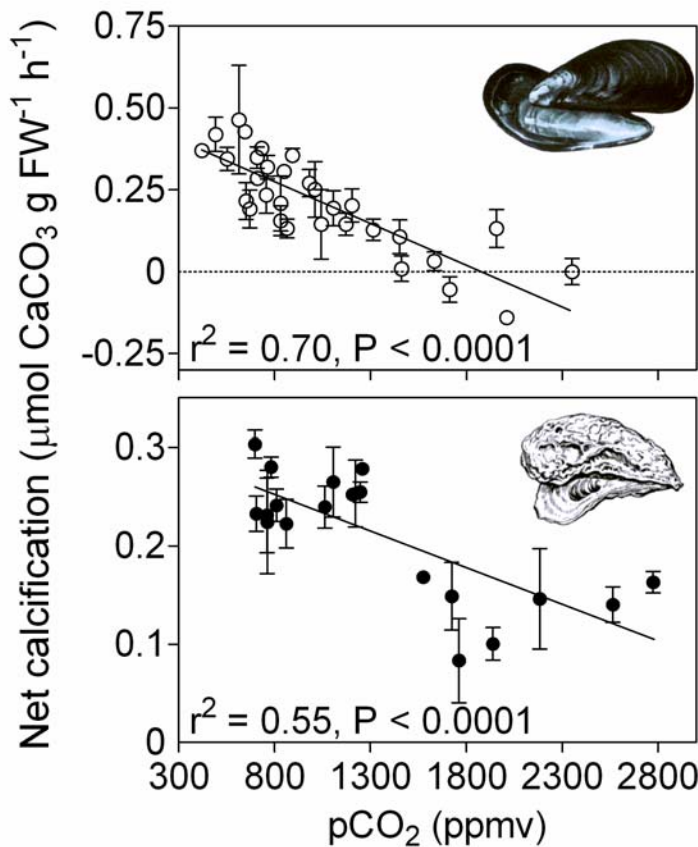


Figure 17 Calcification of mussels and oysters. Courtesy F. Gazeau

most of the oyster shells.

Impacts on Finfish farming

Direct impacts on aquaculture are hard to assess but are likely to be of low risk. Much work has been performed previously looking at the effects of acid rain in, primarily, Scandinavian lakes. These freshwater systems are unbuffered and the pH change experienced there is much greater than likely to be experienced in the marine environment. At present most farmed finfish species, experience a range of salinities and pH conditions in the wild, it is therefore unlikely that pH change in itself is likely to have a noticeable effect. However, as noted previously the combination of thermal stress and low oxygen could combine with a change in pH to cause problems. An indirect effect may likely be from attack by different viruses or parasites, which may take advantage of different environmental conditions. The proposed future for this industry is to look at offshore sites which may suffer greater relative impact than the present inshore sites.

Effects on fisheries

Acidification is likely to have some direct and indirect impacts on fish and fisheries, the nature and degree of impact is currently unknown, but should be

considered against a backdrop of considerable historic overfishing (Jennings & Blanchard 2004; Piet & Rice 2004; Dulvy *et al.* 2005). The likely direct effects on fish and fisheries may be relatively limited and mostly likely to 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 compared to adults (Ishimatsu *et al.* 2004). However, mortality at the early life stages of broadcast spawning species is typically high and highly variable due 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 swamped by natural processes or whether it would add significantly to the natural variation 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 & Shirayama 2004; Shirayama & 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 outside that they have previously experienced within the next century (Blackford & 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 distributions, lower species abundance or diet shifts. The degree and nature of adaptation will strongly influence availability to fisheries and 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 & Richardson 2004). The gaps in knowledge that require addressing are extensive, but could focus on key target fishery species, particularly those that are heavily dependent 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 are likely to be minor relative to the comparatively massive impacts of overexploitation over the last few decades.

Future requirements for the observation of pH and pCO₂

While the quality data sets that do exist present strong evidence for the change in pH associated with draw down of CO₂ they are few and represent limited geographic types. While modelling is probably the best way to get world wide estimates of pH variability and predict future pH changes, the models are only as good as the data used to validate them. There is therefore a requirement for a concerted data collection effort with a greater spatial coverage to validate models and provide estimates of the rate of change in areas with differing bio geochemical response. More extensive observational

programs are required not to avoid taking preventative action, but to help assess if mitigation undertaken is effective.

Thus placing appropriate sensors on existing platforms, research vessels, buoys and ships of opportunity e.g. Ferry Box would yield a good return for the investment.

This workshop specifically endorses the AMEMR workshop 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 multi-disciplinary approach broadening the scope of existing / planned observations should ensure that appropriate parameters are collected. Carbonate monitoring systems should be standard.
- Expanding ships of opportunity programs both in number and in terms of 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.
- So this requires (i) international coordination and standardisation [e.g. pH, DIC], (ii) some fundamental new research on shelf seas alkalinity

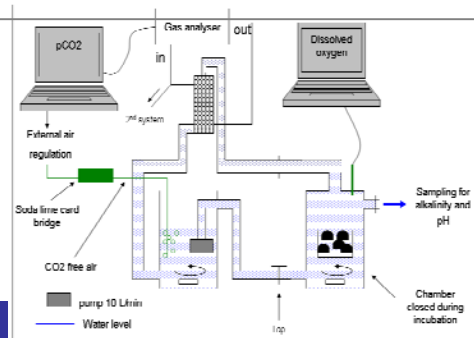
Future experimental needs



Fig 19 Example of mesocosm experiments being conducted by University of Bergen (below)

Present day experiments fall into two broad categories, those which are species specific and occur in laboratories and large scale mesocosm experiments, which occur in the field.

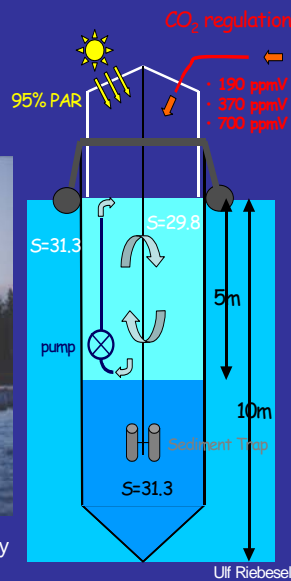
Figure 18. Left and below is an example of experimental apparatus for work on mussels and Oyster used by F Gazeau.



Ecosystem response to a changing CO₂ world



University of Bergen large scale marine facility



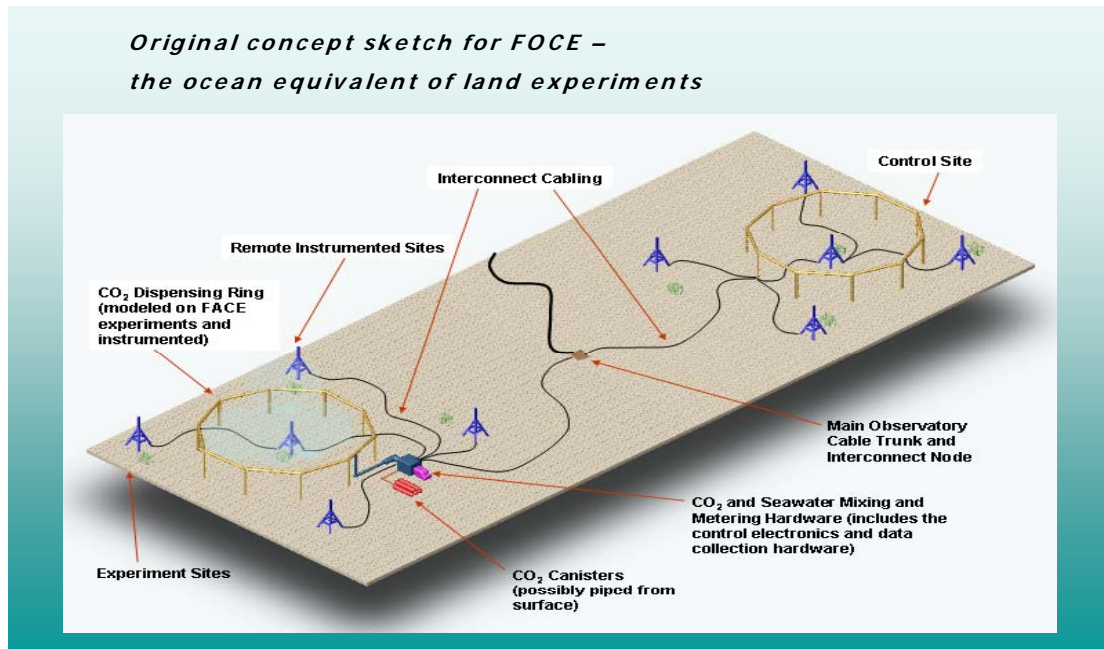
The number of these sites is limited and needs to be increased. The level of confidence in any biological response is greatly enhanced by replication in other experiments. There is a need to perform similar mesocosm experiments in a wide a variety of habitats and different waters masses. As the exact response of the sea water to increasing CO₂ depends on the chemical constituents (alkalinity) there will be geographic variation

in the response.

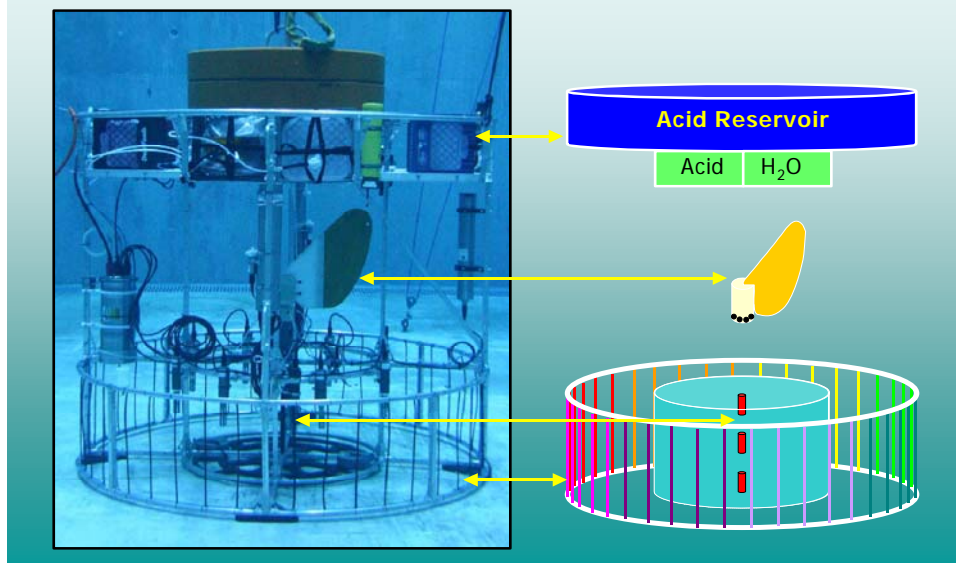
Presently most experiments: are short-term (hours to weeks), some species can acclimatise over a long period, where as others can survive a short term exposure to low pH but suffer from long term exposure at less reduced pH.

The history of experiments in tanks, from knowledge gained in aqua culture studies show that very different responses can be produced from those in the wild. There is therefore a need to produce experiments which can manipulate the CO₂ field in situ whilst leaving other elements undisturbed.

Figure 20 Concept sketch of FOCE , Free Ocean CO₂ Enrichment Experiment, where experiments in the seas emulate future conditions. (courtesy P.Brewer)



The FOCE Prototype – a double ring with acid emitters and sophisticated valve control to allow for system latency

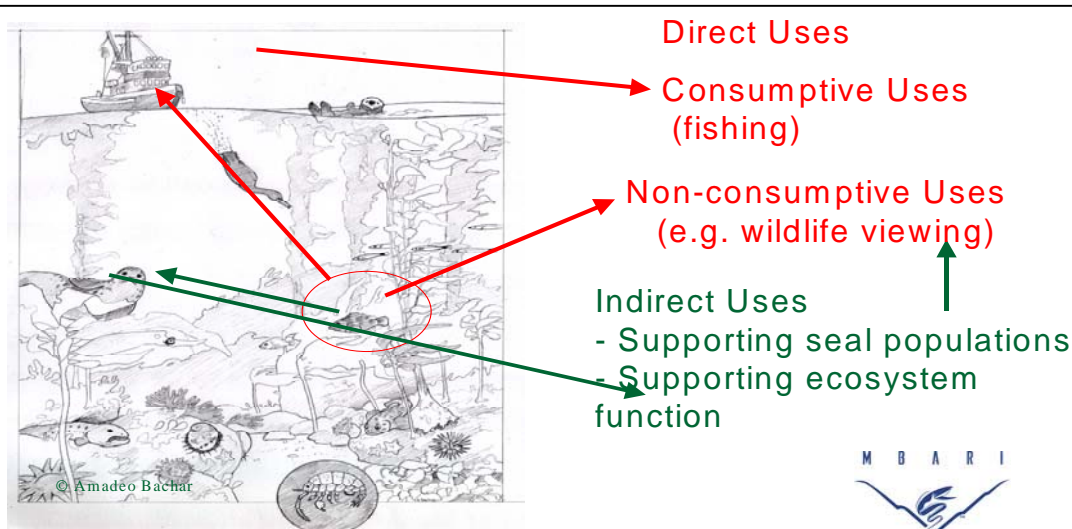


The prototype produced by MBARI is able to provide and maintain a control a volume of fixed exposure. It works best in an area of low (but some) flow. The access problems associated with the marine environment mean that it is unrealistic to expect the size and coverage that is available from the FACE experiments on land. However these kinds of instruments could be best used to confirm or refute results from tank and more conventional mesocosm experiments.

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 added to the climate change discussion to audiences beyond those of scientific interest. UNEP (United Nations Environment Program) is currently facilitating a television documentary to showcase the impact of ocean acidification on key marine ecosystems such as tropical / cold-water corals and polar plankton communities. Intended for broadcast on BBC World in May 2008, this documentary helps to raise the global awareness of the issue with the public and policy makers alike. Topics that Ocean Acidification will need to consider are 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 good and services are substantial and relatively well known, less clear is the impact that ocean acidification can or would have on this. There needs to be an open policy dialogue which will therefore increase public awareness. Scientist have an important role in insuring that; Science is brought closer to policy makers and the public, that they communicate more effectively and that the science needs and the governmental solutions are specific.

Management Strategy

There is a need for a management strategy at national and international level. It would recognize that there is a problem and implement action to address it. Management goals would have to be adopted, there would need to be support for scientific research, with government actions backed by public knowledge.

A strategic plan (5 year and long term) needs to be created which would have a management structure, a Legal and regulatory framework and would consider research priorities.

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Appendix I

Basic Chemistry and explanation of terms
(From Royal Society Report)

The meaning of pH

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

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

This negative logarithmic dependence on hydrogen ion concentration, $[\text{H}^+]$, in moles per litre means that if $[\text{H}^+]$ increases 10-fold then pH decreases by 1 unit. The square brackets refer to the concentration of H^+ and subsequently for the concentration of other substances.

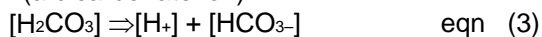
Water has the formula H_2O . Only a small proportion of the water molecule splits up into H^+ and OH^- . In pure water, the amounts of $[\text{H}^+]$ and $[\text{OH}^-]$ are equal and the concentration of each is 10^{-7} in the units mole per litre. This means that a neutral solution has $\text{pH} = 7$. Acid solutions have an excess of $[\text{H}^+]$ and a pH less than 7. Alkaline (basic) solutions have an excess of $[\text{OH}^-]$ and pH greater than 7, up to 14.

Dissolved inorganic carbon in seawater

As CO_2 dissolves in seawater, it reacts with seawater to produce H^+ and various negatively charged forms of dissolved carbon (see Figure A). Carbon dioxide dissolved in seawater first reacts with the water molecule (H_2O) to form carbonic acid (H_2CO_3). Not all the CO_2 dissolved in seawater reacts to make carbonic acid and therefore seawater contains dissolved gaseous CO_2 ; 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_2 in the air to be proportional to that in the solution of carbonic acid.



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^- :

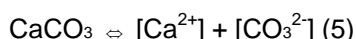


Thus, the net effect of the dissolution of CO_2 in seawater

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 $[\text{CO}_3^{2-}]$ 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:

< mineral formation



dissolution>

Calcification dependent on $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$

Because the dissolution of CO_2 in seawater decreases $[\text{CO}_3^{2-}]$, 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 $[\text{H}^+]$ (increase pH), counteracting some of the pH effects of added CO_2 (see next below).

The carbonate buffer and seawater pH

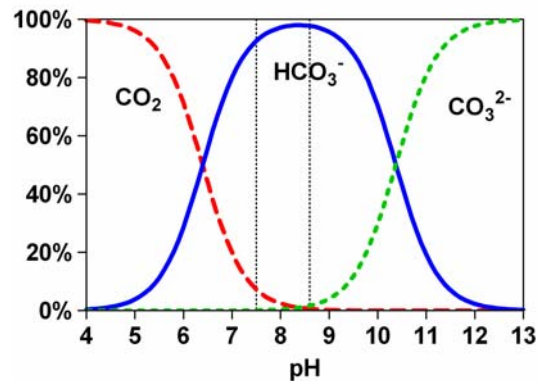
The term 'carbonate buffer' is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean H^+ concentration, and thus pH. If a process, such as CO_2 dissolution (Equations 2 and 3), adds H^+ to seawater some of the added H^+ reacts with carbonate (CO_3^{2-}) 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 stabilise the average pH of seawater at approximately pH = 8 because of the following two processes: (i) uptake of CO₂ from the atmosphere (for example from volcanoes and now, importantly, from fossil fuel burning) and (ii) interaction of seawater with oceanic sediments composed of CaCO₃. Because CaCO₃ is abundant in sediments, the pH of the deep oceans cannot change by large amounts over timescales of 10 000 years. However, over historical timescales, 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 CaCO₃ that, on death of the organism, fall to the sea floor. Their preservation in sea floor sediments depends on the solubility of CaCO₃ in seawater and on the concentration of carbonate ions. There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which CaCO₃ will start to dissolve. Because CaCO₃ solubility increases with decreasing temperature and increasing pressure, the critical concentration occurs at a depth, the 'saturation horizon', below which seawater is undersaturated and CaCO₃ will tend to dissolve and above which seawater is supersaturated and CaCO₃ will tend to be preserved. Because the CaCO₃ mineral calcite is less soluble than the form aragonite, the aragonite saturation horizon is shallower. Because added CO₂ decreases the

carbonate ion concentration, the saturation horizons will become shallower with increasing releases of human derived CO₂ to the atmosphere.



Saturation state : $\Omega = [\text{CO}_3^{2-}] [\text{Ca}^{2+}] / K_s$

K_s is the solubility product of calcite or aragonite

- $\Omega > 1 \rightarrow$ supersaturation \rightarrow precipitation
- $\Omega < 1 \rightarrow$ undersaturation \rightarrow dissolution

$[\text{Ca}^{2+}]$ at constant salinity is \sim constant

TA = Total Alkalinity

$$\text{TA} = 2 [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+]$$

$$\Delta\text{CaCO}_3 = -0.5 \times (\text{TA}_{\text{final}} - \text{TA}_{\text{initial}})$$

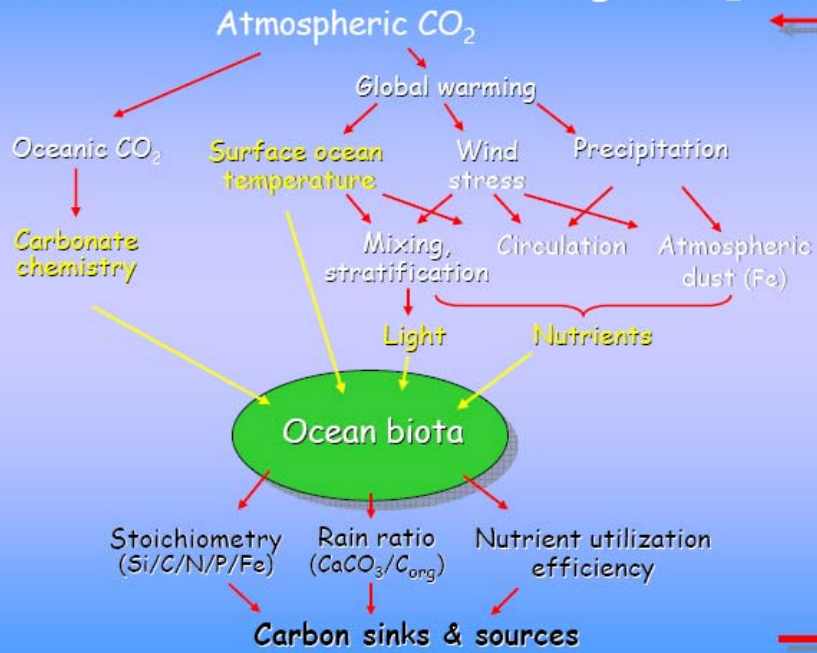
- $\Delta\text{TA} < 0 \rightarrow$ net calcification
- $\Delta\text{TA} > 0 \rightarrow$ net dissolution

Appendix II – Carbon Sinks

Table 1. 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 concentration of bicarbonate ion (HCO₃⁻) and carbonic acid (H₂CO₃) increase with rising atmospheric concentration of CO₂ while carbonate ion (CO₃²⁻) decreases. The average pH of the surface ocean waters decreases with increasing atmospheric CO₂ concentration. (Assumptions used in model: Total alkalinity = 2324 mol/kg, temperature = 18° C. All other assumptions as per OCMIP3 (Institut Pierre Simon Laplace 2005). Aragonite and calcite saturation calculated as per Mucci & Morse (1990). Physical oceanographic modelling is based on Bryan (1969) and Cox (1984).

	Pre-industrial	Today	2 × pre-industrial	3 × pre-industrial	4 × pre-industrial	5 × pre-industrial	6 × pre-industrial
Atmospheric concentration of CO ₂	280 ppm	380 ppm	560 ppm	840 ppm	1120 ppm	1400 ppm	1680 ppm
H ₂ CO ₃ (mol/kg)	9	13	19	28	38	47	56
HCO ₃ ⁻ (mol/kg)	1768	1867	1976	2070	2123	2160	2183
CO ₃ ²⁻ (mol/kg)	225	185	141	103	81	67	57
Total dissolved inorganic carbon (mol/kg)	2003	2065	2136	2201	2242	2272	2296
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

Potential drivers in a future high-CO₂ world



Source: Riebesell et al., 2004.

Appendix III

Agenda for ICES Workshop on the significance of changing Ocean CO₂ and pH in shelf sea ecosystems

2-4th 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 2nd May –(The mostly knowns day)

9:30 Registration and coffee

10:00 Opening Address Sir Howard Dalton (Chief scientific advisor to DEFRA) (10mins)

“Themes and challenges” Peter Brewer (Chair) (30 mins)

10:40 Session 1: The spatial and temporal variability of the surface ocean pH and CO₂ carbonate system in the shelf seas

Proxy records, output from previous workshops

“*Paleoreconstructions of seawater pH: An overview of findings so far*”: - Carles Pelejero (20min)

“*Summary of shelf seas observations of pCO₂ and pH and projections for the future*”: - Liam Fernand (15min)

“*Synthesis of Plymouth AMEMR workshop on modelling ecosystem response*”: - Jerry Blackford” (20min)

Discussion (25mins)

“*Documentary on acidification issues*”: - Stephen Hain. (15mins)

12:30 – 13:30 Lunch

13:30 Session 2: Monitoring systems

“*Monitoring of CO₂ :- An operational UK Air – Sea carbon flux observation capability*”: - Nick Hardman-Mountford (20mins)

“*A system to Monitor pH in shelf seas* ”: -David Hydes (20min)

Discussion (20mins)

14:30 Session 3: Examine the effects of pH and the CO₂-carbonate system on nutrients and calcification

“*Calcification and nutrient uptake stoichiometry.*”: - Richard Bellerby (20mins)

“*pH Variability and CO₂ induced acidification in the North Sea, relating to Nutrients and Plankton*”: - Jerry Blackford (20mins)

Discussion (20mins)

15:40 - 16:00 Coffee

16:00 – 17:00 Summary and Discussion.

Thursday 3rd May (Ecosystem day, many unknowns)

9:00 Session 4: Ecosystem effects; Explore the links between potential changes in pH and pCO₂ and its effects on marine ecosystems

"Role of CO₂ in climate change effects in marine ecosystems": - Hans Poertner (40mins)

*"Experimental results on the pH, CO₂ and light dependencies of photosynthesis and calcification in *Emiliana huxleyi*."*: - Dave Sugget (20mins)

Discussion (20mins)

10:20 – 10:30 Coffee

10:30 Session 5: Benthic systems

"Impact of elevated pCO₂ on coastal benthic organisms and communities": - Jean Pierre Gattuso (30mins)

"The effects of elevated pCO₂ on mussels and oysters": - Gazeau Frederic (20mins)

"The change in pH in context of the natural variability in the sediment": - Steve Widdicombe (20mins)

"Effects on cold water corals": - Francesca Marubini (20mins)

Discussion (30mins)

12:30 - 13:30 Lunch

13:30 Session 7: Overall implication to ecosystem, fisheries shellfish and aquaculture

"Ocean acidification effects on fisheries and marine ecosystems": - Nick Dulvy (20mins)

"Relevance to aquaculture": - Ian Laing (20mins)

Discussion (20mins)

14:30 – 16:00 Break out groups. (To ask or answer specific questions)

16:00 – 16:15 Coffee

16:15 – 16:30 Summary of break out groups.

Friday 4th May (how/what are we going to do about it day)

09:00 Session 8: Experimental strategies

*"Results from experiments on *Emiliana Huxleyi* in a high CO₂ environment"*: - Nikos Leanardos (20mins)

"Future experimental needs": - Bill Kirkwood (20mins)

"Experimental strategies by MBARI": - James Barry (20mins)

Discussion (30mins)

10:30 – 10:50 Coffee

10:50 Session 9: Broader outreach – consequences of and implications to government and national policies.

"The economic context and the need for management": - Judith Kildow (20mins)

12:30 – 13:30 Lunch

13:30 Agreeing recommendation: - Bringing together sections of the report

15:00 End