MCCIP Ecosystem Linkages Report Card 2009
CO_2 and ocean acidification

Marine Climate Change Impacts Partnership

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EXECUTIVE SUMMARY

The oceans are an enormous store of carbon, substantially greater than on land or in the atmosphere and hence play a key role in the global carbon cycle, especially in helping regulate the amount of CO_2 in the atmosphere. The oceans are important because they have taken up around 27-34% of the CO_2 produced by humankind through the burning of fossil fuels, cement manufacturing and land use changes since the industrial revolution. Whilst this has somewhat limited the historical rise of CO_2 in the atmosphere, thereby reducing the extent of greenhouse warming and climate change caused by human activities, this has come at the price of a dramatic change to ocean chemistry. In particular, and of great concern, is the measurable change in ocean *p*H and carbonate and bicarbonate ion concentration – 'ocean acidification'. Our understanding of the impact of CO_2 on the carbonate chemistry is such that we know with very high certainty that ocean acidification will continue, tracking future CO_2 emissions to the atmosphere.

Evidence from experiments and observations indicate that ocean acidification is a serious threat to many marine organisms which may have implications to the food webs and ecosystems but these are difficult to predict especially as studies of potential adaptation have not been carried out. Also of less certainty are the scale and direction of impacts on biogeochemical cycling of carbon, nutrients and climate reactive gases and other potential feedbacks to climate. Here, ocean acidification events in the Earth's past may help interpret the future of our oceans in a world of unabated CO_2 emissions. Whilst no exact geological analogue exists for society's activities today, it seems likely that the extent of future acidification and the speed of change will destroy the habitat of some key calcifying organisms, with the possibility of adaptation of many organisms unlikely and extinctions possible. Previously in Earth's history, recovery of marine ecosystems from such an event has taken several hundreds of thousands of years. The only way of reducing the impact of ocean acidification is the urgent and substantial reduction of CO_2 emissions.

At present, the socio-economic impacts of ocean acidification are difficult to predict. However, the goods and services provided by the marine environment to the UK are important, for example, multi-million pound fisheries, fish meal and aquaculture industries employing tens of thousands of people and if impacted by ocean acidification could have a direct economic impact. Globally coral reefs have been valued at $30 billion providing food, tourism and shore protection so any threat to them will be important for the economics of some of UK's overseas territories.

1. OCEAN UPTAKE OF CO_2 AND SUBSEQUENT CHANGES TO OCEAN CHEMISTRY

1.1. The ocean carbon reservoir and changes to ocean chemistry

The oceans are a major part of the Earth's carbon cycle, with estimates of the pre-industrial ocean carbon reservoir of ~38000 PgC, compared with ~700 PgC in the atmosphere and <1170 PgC in the terrestrial biosphere (reviewed in Royal Society, 2005). Oceans act as an important carbon sink, absorbing more CO_2 than they release into the atmosphere. About a quarter of all anthropogenic CO_2 released into the atmosphere since the industrial revolution has been absorbed by the World's oceans (Sabine *et al*., 2004). Ocean uptake of anthropogenic CO_2 has therefore buffered climate change by reducing the atmospheric concentration of this greenhouse gas. However, when the CO_2 reacts with seawater the concentration of the bicarbonate ion (HCO_3^-) increases, while the amount of carbonate ions (CO_3^{2-}) and pH of the surface ocean waters decrease (Figure 1).

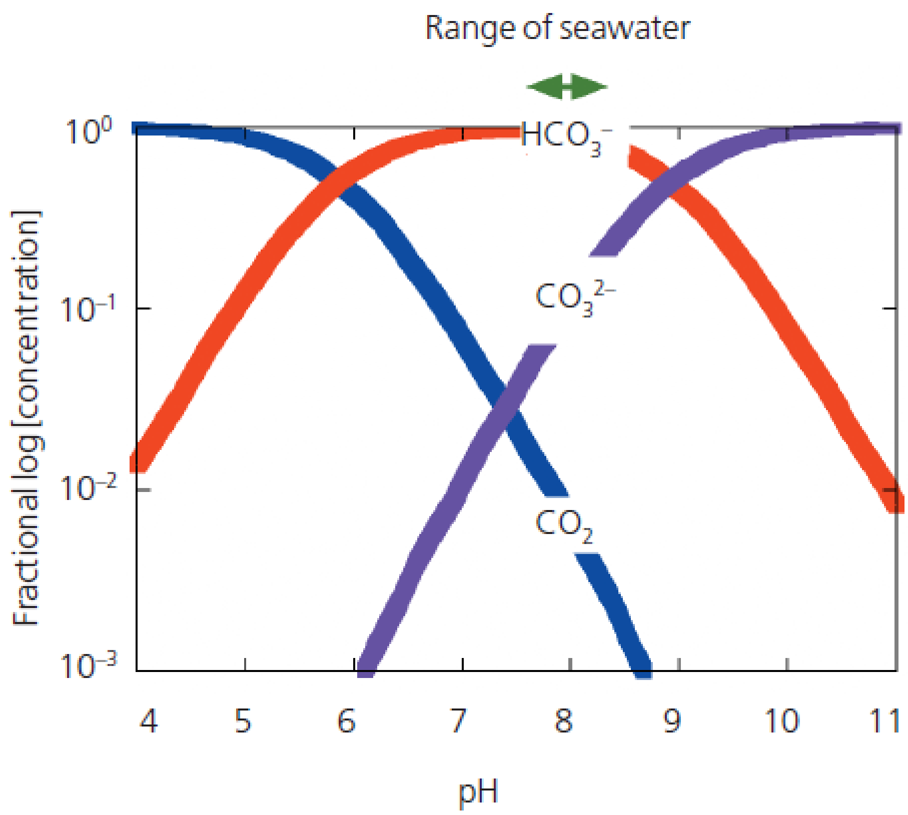

Figure 1. *Relative proportions of the three inorganic forms of CO2 dissolved in seawater. The green arrows at the top indicate the narrow range of pH (7.5–8.5) that is likely to be found in the oceans now and in the future. Note the ordinate scale (vertical axis) is plotted logarithmically. From Royal Society (2005).*

This has already had a significant impact on ocean chemistry, with estimates of mean surface ocean pH decrease of ~0.1 (equivalent to a ~30% increase in hydrogen ion (H^+) concentration), from a value of ~8.18 around the time of the industrial revolution (Caldeira & Wickett, 2003; Figure 2). This pH drop is significantly larger than the seasonal pH variability of 0.03 to 0.04 due to changes in temperature and photosynthesis (Santana-Casiano *et al*., 2007). Long term oceanographic time series stations corroborate this model and observed, after removal of seasonal variability, an annual rate of decline in surface ocean pH of 0.0019 ± 0.00025 a^{-1} over the last two decades (IPCC, 2007; Doney *et al*., 2009).

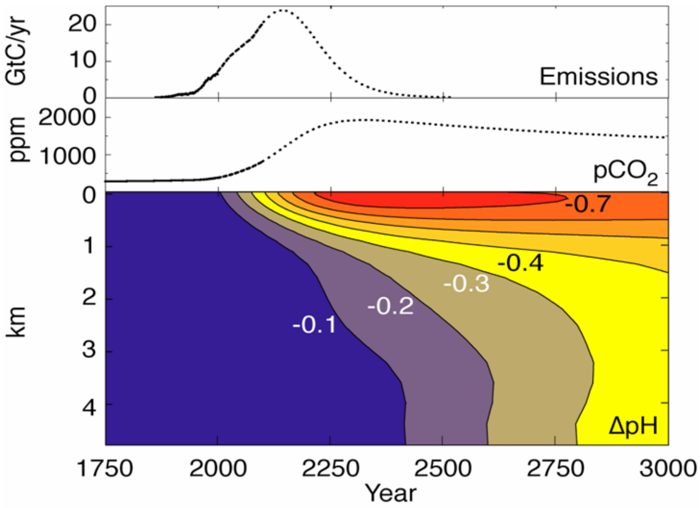

Figure 2. *Projected changes in ocean pH from a model scenario of continued use of all known fossil fuel reserves. From Caldeira & Wickett (2003).*

1.2. Changes to aragonite and calcite saturation

The concentration of CO_3^{2-} directly influences the saturation, and consequently the rate of dissolution and formation, of calcium carbonate ($CaCO_3$) minerals in the ocean. The saturation state (Ω) is used to express the degree of $CaCO_3$ saturation in seawater. The three main mineral forms of $CaCO_3$ produced by organisms are, in order of least soluble to most soluble: calcite, aragonite and magnesium-calcite, with each mineral form having a different saturation state profile because of their solubility differences. When $\Omega > 1$ seawater is supersaturated with respect to mineral $CaCO_3$ and the larger this value the more favourable the environment will be for organisms that produce $CaCO_3$ (in shells, skeletons and liths ($CaCO_3$ plates)). Where $\Omega < 1$ seawater is undersaturated and corrosive to $CaCO_3$ producing organisms. Currently the vast majority of the surface ocean is supersaturated with respect to all forms of $CaCO_3$. Increasing ocean acidification is lowering the carbonate ion concentration and hence Mg-Calcite, aragonite and calcite saturation states are all decreasing. The physiology of each organism will also be important in determining their vulnerability to decreasing saturation state (see below). Global ocean models unanimously project undersaturation with respect to aragonite occurring in polar and sub polar surface waters within decades (Orr *et al*., 2005). However there is still much uncertainty at a regional scale, as many of the models cannot resolve processes well at for example freshwater boundaries or upwelling areas, as discussed below.

1.3. Shoaling of the saturation horizons

Saturation of these minerals does not just vary from the poles to the tropics but also with water depth because solubility is dependent on temperature, salinity and pressure. The depth at which these calcium carbonate minerals stop being formed and start to dissolve is known as the saturation horizon. Aragonite is more soluble than calcite and therefore the aragonite saturation horizon (ASH) is in shallower water than the calcite saturation horizon (CSH). Due to differences in ocean chemistry, the depths of these horizons naturally vary between the ocean basins. For instance, the ASH is <600m in the North Pacific but is over 2000 m deep in the North Atlantic (Guinotte *et al.*, 2006). Continued uptake of anthropogenic CO_2 by the ocean is moving the ASH towards the surface of the ocean at a rate of >1m/a, although this varies with location and season. This means that, for example in the Southern

Ocean, under IS92a emissions scenario, the saturation horizon will have shoaled by more than 700 m by the end of the century, where it will have reached the ocean surface (Orr *et al*., 2005).

Intermediate waters from below the depth of the ASH, which are rich in CO_2, are upwelled onto the shelf seas along the western coast of all major continents. A recent study off the western coast of North America found that these undersaturated, corrosive waters with pH of 7.6 bath, the shelf from February to September (Feely *et al*., 2008). A reduction of ocean pH will extend the duration of exposure of the shelf biota to these corrosive waters. This indicates that other upwelling regions as well as high latitude waters may be particularly vulnerable to the onset of undersaturated conditions with respect to aragonite, at least earlier than that predicted by large scale General Circulation Models.

Projection of future seawater pH around UK coastal and shelf waters is generally consistent with global projections but variability and uncertainties are greater due to riverine inputs and geochemical interactions between ocean and underlying sediments (Blackford & Gilbert, 2007).

1.4. Ocean acidification and relationship to climate change mitigation options

The degree of changes to ocean chemistry, including ocean pH, will depend on the mitigation or emissions pathway society takes (Figure 3). By 2100, atmospheric CO_2 concentrations could reach >800 ppm without any mitigation of emissions causing an additional surface water pH decrease of ~0.4 pH units. Worse case scenario (continued, unabated usage of known fossil fuels reserves) estimates indicate that average surface ocean pH could fall by a maximum of 0.77 pH units by ~2300 (Calderia & Wickett, 2003: Figure 2).

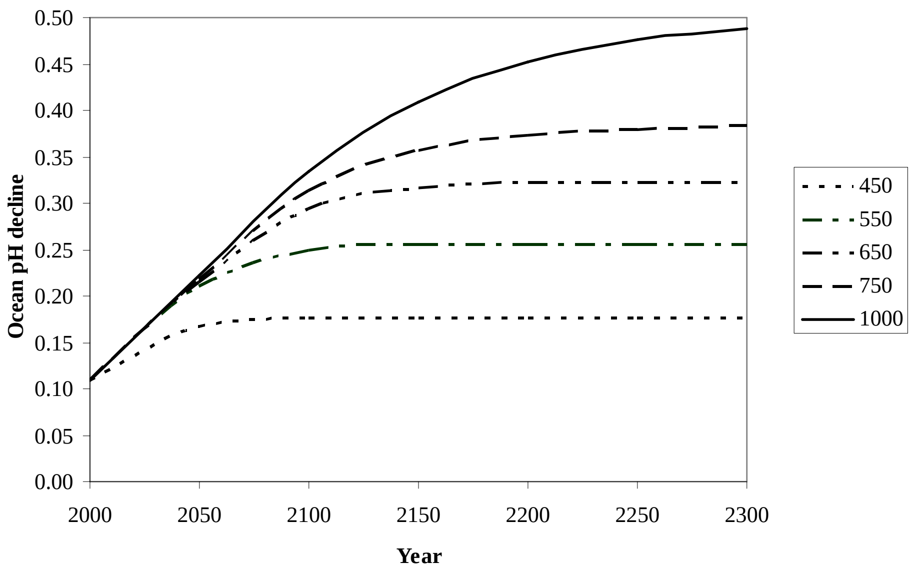

Figure 3. *Trajectories for surface ocean pH decrease calculated for different atmospheric CO_2 concentration profiles leading to stabilization from 450-1000 ppm. These were calculated from the model predictions by Caldeira & Wickett (2003). From Turley (2006).*

1.5. The long term legacy of CO_2 emissions on ocean chemistry

It will take tens of thousands of years for the changes in ocean chemistry to be buffered through neutralization by calcium carbonate from sediments and hundreds of thousands for the weathering of rocks on land to eventually restore ocean pH completely (Archer & Brovkin, 2008). The only way of reducing the impacts of ocean acidification on a global scale and in a societally-relevant time-frame is through urgent and substantial reductions in anthropogenic CO_2 emissions.

2. POTENTIAL IMPACTS TO MARINE ORGANISMS

Marine organisms use ions obtained from the surrounding seawater in a number of important biological processes, including formation of mineral structures like shells or skeletons, as well as in key physiological processes. Internal pH for marine animals is normally regulated at a particular level (e.g. haemolymph pH 7.4 – 7.9 depending on species). Organisms have adapted a number of mechanisms that can, on short timescales, buffer changes in pH thereby preventing damage to internal processes and functioning. Changes in seawater chemistry caused by ocean acidification threaten to disrupt these systems. It is unclear how long these compensation mechanisms can function, particularly as they are energetically costly. Experiments at CO_2 levels equivalent to those predicted for the next 100 to 300 years have significantly impacted survival, growth and development of many marine organisms (Fabry *et al*., 2008). Many marine organisms play important roles within ecosystems so that changes to their diversity or efficiency of function could affect the ecosystems and food webs within them (Figure 4).

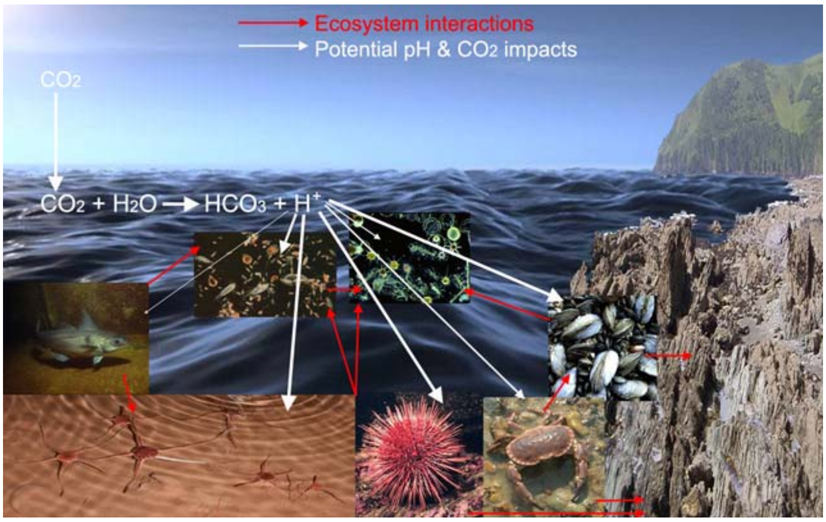

Figure 4. *Simple schematic of some ecosystem interactions between example organisms living in open water (fish, zooplankton, phytoplankton), coastal water (crabs, shellfish, urchins) and the sediment (brittlestars and urchins) together with arrows denoting the potential CO_2 impact on the organism (large width arrows denote higher vulnerability based on authors judgement from information taken from the literature).*

2.1. Calcification

Calcifying organisms are not only vulnerable through impacts to their physiology, but additionally by dissolution of their $CaCO_3$ structures. The mineralogy is species specific, and hence their susceptibility to dissolution will depend on the mineral form as well as the relative biological control that they exert on shell formation (reviewed by Kleypas *et al*., 2006). Amorphous calcite is laid down by some species, particularly in early development stages, as the basis for carbonate formation and may be particularly susceptible to dissolution, even more so than aragonite and calcite.

2.2. Sea bed dwelling organisms

The UK's regional seas provide a variety of important habitats for many benthic organisms (animals and plants that live on and in rocks, sand, mud, shingle, etc.), including commercially important species such as lobsters, crabs and shellfish. There have been limited investigations into the response of key organisms from these ecosystems to realistic future ocean acidification scenarios. Studies on sea urchins and brittlestars showed they were unable to compensate for longer-term changes in ocean acidification. Sea urchins were unable to maintain their internal pH balance for longer than seven days at pH 7.4 resulting in loss of normal body functions (Miles *et al*., 2007). In experiments at CO_2 levels just 200 ppm higher than today they exhibited reduced growth and survival rates over several months (Shiryama and Thornton, 2005). Other experiments on brittlestars showed muscle wastage in their arms as a trade-off attempt to increase their calcification at pH 7.7 (Wood *et al.*, 2008). Reduced juvenile success, fertilisation, larval growth and development, has been documented at these pH levels (Dupont *et al.,* 2008; Havenhand *et al.,* 2008). Mussels and oysters show a decrease of shell and body growth by 55% at pH 7.3 (Michaelidis *et al.,* 2005). Net calcification decreased by 25% (at 2x pre-industrial CO_2, year 2050) and 37% (at 3x pre-industrial CO_2, year 2100) in mussels and 10% (2x CO_2) and 15% (3x CO_2) in oysters (reviewed by Guinotte & Fabry, 2008). Crustaceans (crabs, lobsters, barnacles) have been shown to be somewhat more able to compensate for changes in pH (Spicer *et al.,* 2007; Pane & Barry, 2007), however, they are still subject to dissolution impacts and their early life stages are again proving vulnerable. Other organisms appear to be less vulnerable, such as sediment-dwelling organisms (*Neries* worms), which may be periodically subjected to low pH in their current environment and therefore have compensations mechanisms (Widdicombe & Needham, 2007).

These organisms are not only commercially important, but also play important roles in the cycling of nutrients between the sediment and the water column (Figure 4), and as "ecosystem engineers". Sea urchins, for example, in soft sediments are bioturbators and efficiently mix the sediments; on rocky shores they modify the habitat by grazing algae and allowing diverse communities to develop. Lowered fitness of these animals could change nutrient and carbon cycling (Fernand & Brewer, 2008), potentially altering the availability of nutrients for other organisms as well as disrupting ecosystem dynamics of rocky shores or in sediments.

Cold-water or deep-water corals are found throughout the worlds' oceans, including the European continental shelf and the UK coastline (e.g. cold-water coral, *Lophelia*). They can form large reef frameworks that persist for millennia and are biodiversity hotspots that play an important role as refuges, feeding grounds and nurseries for deep-sea organisms, including commercial fish (Guinotte *et al.,* 2006; Roberts *et al.,* 2006). Future projections of global aragonite saturation state and the depth of the ASH indicate that 70% of cold-water corals are likely to experience undersaturation this century and in some places as early as 2020 (Orr *et al.,* 2005; Guinotte *et al.,* 2006,). It is unknown whether cold-water corals will be able to calcify under these conditions, though it is likely that their aragonitic skeletons will experience dissolution in these corrosive waters, potentially leading to breakdown of reef structure and loss of habitat for other organisms (Turley *et al.,* 2007).

Warm water coral reefs do not grow around the UK, but are important in many of UK's Overseas Territories (e.g. Anguilla, British Virgin Islands, etc.) located in warm, sunlit, aragonite rich waters. Coral reefs harbour an immense biodiversity and are important for shore protection. Decreasing aragonite saturation is reducing rates of coral calcification so much so that if this continues their rate of erosion will outpace calcification resulting in loss of coral structural integrity (Kleypas *et al*., 2006 and references therein).

2.3. Pelagic organisms

Pelagic organisms, including phytoplankton, zooplankton and other organisms living in the upper water column may also be vulnerable to ocean acidification, although results so far have shown there is high species-species variability. Coccolithophores, planktonic algae which produce blooms so large they are visible from space (Figure 5), produce calcitic liths or plates. Experiments indicate that some species (e.g. *Emiliania huxleyi* and *Gephyrocapsa oceanica*) may experience decreased rates of calcification by 16% at 2x CO_2 and 30% at 3x CO_2 (Riebesell *et al.,* 2000), although other species have shown no response (Langer *et al.,* 2006) or indeed an increase in calcification (Igelezias-Rodrigeouz *et al.,* 2008). Copepods, which make up a large proportion of the zooplankton, have been found to have reduced survival in their early life stages (Kurihara *et al.,* 2004). Planktonic pteropods, important grazers in areas of the polar oceans, have been found to be highly susceptible to dissolution (Fabry, 1990).

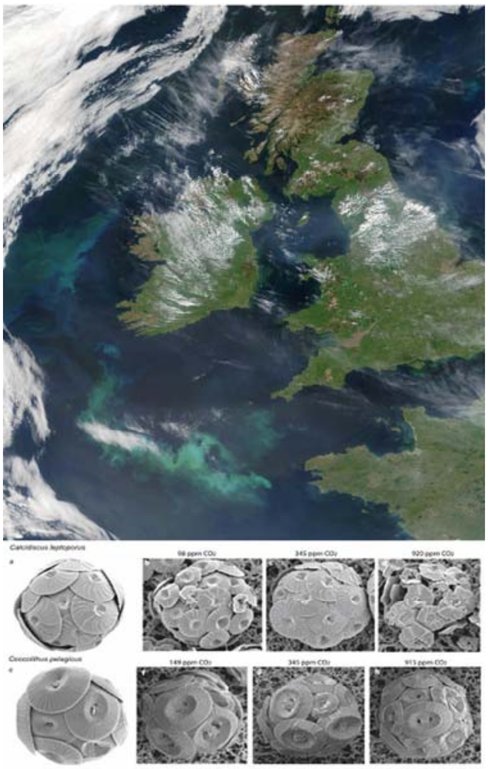

Figure 5. *MODIS Satellite image of UK regional seas showing phytoplankton and coccolithophore blooms (whitish green blue swirls). From NASA Visible Earth (visibleearth.nasa.gov/view_rec.php?id=2119) Credit: Jacques Descloitres, MODIS Land Rapid Response Team, NASA/GSFC). Two images of coccolithophores showing some of the more extreme malformations found in experiments (CO_2 concentrations were 920 ppm , equivalent to ca. year 2100 scenarios). From Langer et al (2006).*

In addition to direct impacts on marine organisms, the lower pH expected over the next hundred years could theoretically impact the speciation of biologically important nutrients (e.g. nitrogen, phosphate and silica) and micronutrients (e.g. iron, cobalt, manganese, etc). A decrease in pH of 0.3 units could reduce the fraction of ammonium by around 50% (Raven, 1986) however, at the moment there is no direct evidence for this. Nitrification has also been shown to be pH sensitive, with rates reduced by ~ 50% at pH 7 (Huesemann *et al.* 2002). This may result in a reduction of ammonia oxidation rates and an accumulation of ammonia instead of nitrate. Over a shelf sea ecosystem model this has been predicted to result in a 20% decrease in pelagic nitrification by year 2100 (Blackford & Gilbert, 2007). Laboratory results have also shown a change in nutrient sediment flux rates with decreasing pH, most likely resulting from changes to microbial communities; although these changes are less obvious at pH levels expected from ocean acidification over the next 100 years. For example, reduced pH increased the nitrate uptake into the sediment and increased ammonium release from the sediment to the overlying water column (Widdicombe & Needham, 2007). Ocean acidification may also increase the proportion of soluble iron, which might be beneficial to areas of the oceans where iron is thought to limit primary production. Additionally, the nutritional quality of plankton may also change with increasing acidification, by reducing particle size and phytoplankton community structure (Engel *et al.,* 2008), changing C:N:P stoichiometry of community production, and/or a loss of carbon (Bellerby *et al.,* 2007, Riebesell *et al*., 2007, Thingstad *et al*., 2008). Changes in phytoplanktonic assemblages either caused by changes to calcification, nutrients or to different CO_2 uptake rates by different species (Tortell *et al.* 2008) are difficult to predict but may result in a change in community structure. A loss of organic carbon or an increase in C: N ratio lowers the nutritional value of primary-produced organic matter, which in turn affects the quality of food available for zooplankton, and hence lowers growth and reproduction. The repercussion of these changes in nutrient availability and primary production quality will be felt throughout the entire food web, as there will be less energy available for larger organisms.

Unabated CO_2 emissions may result in changes to species biogeography as they track their habitat. Habitat disappearance might lead to extinction for example in high latitudes. Some species may fill the abandoned niches, changing the structure of the ecosystem. For example, non calcifiers and alien species are found instead of calcifiers in areas of low pH around the CO_2 vent in Mediterranean (Hall Spencer *et al*., 2008) and may give us a future view of the regime shifts that might occur in a future high CO_2 ocean.

2.4. Sensitivity to multiple stressors

Many organisms in coastal and shelf seas are additionally impacted by other climate factors (changing temperature, salinity, wind, waves and currents) and non-climate factors (invasion of non-native species, over-fishing, pollution (particularly acid run-off and atmospheric deposition), diseases, and nutrient and sediment load). The majority of studies so far on ocean acidification have been at ambient (and often optimal) conditions that organisms are found in. If an organism is increasingly stressed by temperature or pollution then ocean acidification could compound these impacts preventing them from adapting or recovering (see review by Pörtner *et al*., 2005).

3. LEARNING FROM OCEAN ACIDIFICATION EVENTS IN THE DEEP PAST

The rate of change of oceanic pH projected this century may be the most rapid change experienced by marine organisms for 65 million years. For example, glacial interglacial changes in CO_2 over the last 800.000 years in the order of 50 to 100 ppmv happened over thousands of years (EPICA community members, 2006) in contrast to the rapid change in atmospheric CO_2 happening at the moment. An examination of the geological record for such acidification events may give us an understanding of potential adaptation and scale of recovery.

3.1. Considering the geological record for an analogue for today's ocean acidification event

Culture and mesocosm experiments have demonstrated detrimental effects of ocean acidification on calcifying organisms (see above). These experiments use rather abrupt changes in pH and are relatively brief compared to the generation times of some of these organisms. Therefore cultures cannot fully assess adaptation potential which demands long time series covering large numbers of generations. The geological record, stored in the sediment at the bottom of the ocean, encapsulates both past records of ocean acidification and the biological reaction. The global distribution of marine sediments therefore allows the investigation of ecosystems shifts and their impact on biogeochemical cycles as well as the timescales of recovery after ocean acidification events.

No geological event could ever be a perfect analogue for future ocean acidification. Ideally, the analogue would be during a time with similar climates, configuration of continents and ecosystems. It is important to keep in mind though, that most modern organisms alive in the ocean today are likely to have never experienced such a large change in their evolutionary history. During no point in the recent Earth history did the atmospheric CO_2 reach values comparable to current ranges or predictions for the future (Siegenthaler *et al.*, 2005), nor was any of the past ocean acidification events as rapid as the projected changes happening in the next decades.

3.2. The Pliocene warmth, 3.3 to 3 million years ago

Most likely, the last time that CO_2 has been as high as that found today was during the Pliocene, three million years ago (Raymo *et al.*, 1996). The higher CO_2 led globally to a three degree warming over several millennia which regionally was amplified to twice this temperature change (Dowsett *et al.,* 1996) making it an ideal analogue for future climate (Solomon *et al*., 2007). Ecosystems during this time were very similar to present. The climate change led to poleward migration of organisms, likely as a response to the warming both on land and in the ocean, but did not cause large scale extinctions. This highlights that comparatively slow changes in CO_2, temperature and pH over several millennia did not permanently alter ecosystems. Estimates of rates of pH change during the Pliocene warmth could provide constraints for CO_2 mitigation targets but the CO_2 change is not large enough to determine adaptation potential and ecosystem responses.

3.3. The late Cretaceous, 99.6 to 65.5 million years ago

An example of a period during Earth history with CO_2 as high as the projections for non-mitigation scenarios is the late Cretaceous (Bice *et al*., 2006). Intriguingly, although CO_2 was high for millions of years during this period, the coastline of Britain, for example the White Cliffs of Dover, documents vast carbonate deposition by coccolithophores whose decedents are still important carbonate producers today and which can be affected by ocean acidification (e.g. Langer *et al.,* 2006; Riebesell *et al.*, 2000). However, there are two major differences between then and today, which make this comparison flawed. Firstly, the Cretaceous ocean had about a 2-fold higher Ca concentration, meaning that low pH and low carbonate ion concentrations could co-exist with super-saturation of the surface ocean. Secondly, gradual increases of CO_2 and decreases in pH over millions of years would have provided enough time for genetic adaptation to high CO_2 conditions. Therefore, credible analogues for future ocean acidification need to have similar rates as well as magnitudes of CO_2 change as those predicted for the next century and millennium.

3.4. The end Cretaceous meteorite impact, 65.5 million years ago

The rapid environmental change associated with the end Cretaceous meteorite impact 65 Million years ago lead to a mass-extinction, which has also been linked to ocean acidification (d'Hondt *et al*., 1994). The meteorite impacted in the Yucatan peninsula and vaporised vast amounts of carbonate and gypsum. The input of CO_2, SO_2 and NO_x into the ocean likely affected the surface water pH in an extremely short time, significantly faster than our current change. The planktonic ecosystems showed the largest extinction not in the high latitudes but amongst the highly specialised, large tropical and subtropical species (Keller, 2003) while the more opportunistic species in high latitudes were much less affected. Benthic deep sea species show no extinction (Alegret & Thomas, 2004) as do non-calcifying planktonic organisms (Hollis *et al.*, 2003). These features are very different from predictions for future impacts of ocean acidification and open the question about impact of environmental change on highly specialised versus more tolerant ecosystems. It is important to remember that the environmental change causing this mass extinction is much more complex than pure ocean acidification and has a large number of features which are very dissimilar to our current environmental change, such as mega-tsunamis, loss of sunlight, extensive wildfires (d'Hondt, 2005) also limiting the use of this time interval as an analogue.

3.5. Palaeocene-Eocene Thermal Maximum, 55.5 million years ago

The best current analogues for ocean acidification are the Palaeogene hyperthermals, a series of events between 58 and 52 millions years ago. Sediments deposited during these events (Figure 6) are characterised by very low amounts of carbonate and record a geochemical signature of a massive input of carbon associated with a transient temperature rise (Dickens *et al.*, 1995). The best studied of these events is the Palaeocene-Eocene Thermal Maximum (PETM) 55.5 million years ago.

Figure 6. *Sedimentary evidence of an ocean acidification event 55.5 million years ago (Palaeocene-Eocene boundary) from the South Atlantic (Ocean Drilling Leg 208, Walvis Ridge). The arrow indicates the boundary visible by a sharp contrast between white carbonates and red clays. The red clay shows that the carbonate saturation horizon shoaled and all carbonates in the sediment dissolved.*

The geological signature of this event is not just restricted to the deep sea but is also recorded in the North Sea and the shelf sediments of the Mediterranean (Speijer *et* *al.*, 1997). The biotic response is very different in the deep sea benthic than in the planktonic ecosystem. While planktonic organisms reacted to the environmental change with migration to higher latitudes, thereby tracking their ideal temperature, benthic organisms in the deep sea, mainly benthic unicellular organisms called foraminifers, faced extinction. The extinction is much larger amongst the calcifying benthic foraminifers than amongst those building their shells out of sand grains and organic material suggesting that the ability to calcify was severely affected. This hypothesis is further corroborated by the fact that the surviving benthic foraminifers and ostracods, small crustaceans, are small and thin-walled suggesting low saturation conditions (Thomas, 2007). The planktonic ecosystem did not experience a comparable extinction. The composition of the marine fossilised plankton changed dramatically though, the most important of which was the occurrence of a massive dinoflagellate bloom (Sluijs *et al*., 2005). Several other planktonic assemblages, such as foraminifers, radiolarians and coccolithophorids, showed major compositional changes as a reaction to changing nutrient and temperature conditions *(see Sluijs et al.*, 2007 for a review). This highlights that adaptation to these climatic changes was possible if the organism had a habitat they could track. The question arises, if the rate of change during this geological ocean acidification episode is comparable to the rate of environmental change predicted for the next 100 years? If the rate of change is comparable, future extinction of benthic calcifiers is highly likely. The other Palaeogene acidification events were of much smaller magnitude than the PETM. These led to changes in the benthic assemblages, but not to a large extinction. Therefore, quantifying the ocean acidification for a series of the events will allow us to make the link between the rate and extent of ocean acidification and the degree of ecosystem change and hence allow us to identify and quantify potential threshold of adverse ecosystem disruption in response to ocean acidification.

4. GLOBAL CARBON CYCLING AND CLIMATIC CONSEQUENCES

With the continued dissolution of anthropogenically-sourced CO_2 in surface ocean waters, the capacity of the ocean to absorb further CO_2 emissions diminishes. This is because carbonate ions in the ocean in effect scavenge $CO_{2(aq)}$ to form bicarbonate, in the reaction:

$$CO_{2(aq)} + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$$

As the carbonate ion concentration of the ocean declines, so does the capacity of seawater to buffer atmospheric CO_2, encapsulated in the ‘Revelle Factor’ (Zeebe & Wolf-Gladrow, 2001). Hence with continuing CO_2 emissions, the fraction of each mole of CO_2 emitted that is taken up by the ocean declines and a greater fraction will remain in the atmosphere, producing a positive feedback on global warming in which warming is expected to be approximately linear with cumulative CO_2 emissions (Goodwin *et al*., in press). However, the reduction in the strength of the ocean carbon sink with increasing cumulative CO_2 emissions is no more a consequence of ocean acidification, than ocean acidification is a consequence of reduced buffering – both are closely related consequences of the dissolution of CO_2 from the atmosphere and both involve decreases in carbonate ions. We thus focus here on the specific impacts of ocean acidification, but noting that the progressive weakening of the seawater CO_2 buffer is arguably the most fundamental single impact on the ocean of fossil fuel combustion.

4.1. Direct effects of ocean acidification on atmospheric CO_2

By precipitating calcium carbonate ($CaCO_3$) from seawater, marine organisms affect the global carbon cycle and climate system. In the chemical reaction for creating carbonate shells and skeletons:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_{2(aq)} + H_2O$$

Dissolved inorganic carbon in seawater in the form of HCO_3 cannot interact directly with the atmosphere, but via calcification it is converted into dissolved CO_2 ($CO_{2(aq)}$), that can leave solution and escape to the atmosphere as gaseous CO_2. Thus, ignoring questions of whether $CaCO_3$ particles are important to the fate of organic carbon ('ballasting' – see below), the process of calcification acts to increase the concentration of $CO_{2(aq)}$ at the ocean surface and acts as a brake on the transfer of fossil fuel CO_2 from the atmosphere into the ocean. Reducing the rate of calcification globally then accelerates the rate of uptake of fossil fuel CO_2 from the atmosphere – a negative feedback for climate change.

Only a few global models have so far been applied in quantifying the importance of changing pelagic carbonate production on the oceans ability to sequester CO_2. Predictions for the additional quantity of fossil fuel CO_2 taken up by the ocean by the year 2100 fall in the range 5.9 and 18 PgC (Heinze, 2004; Gehlen *et al*., 2007; Ridgwell *et al*., 2007). An alternative approach to this question is to use a single model, but run as a large ensemble of differing experiments which explicitly take into account the broad range of calcification responses observed in laboratory manipulation experiments. The uncertainty from model ensembles spans 5.4 PgC to 25.7 PgC, with an ensemble mean CO_2 uptake of 17.2 PgC (Ridgwell *et al*., 2007). This range is broadly comparable to that existing between different models, suggesting that the current uncertainty in the species calcification response in conjunction with their relative importance for carbonate production dominates the overall uncertainty in model predictions of fossil fuel CO_2 by the ocean.

Better experimentally-based understanding of acidification impacts at both the organism and ecosystem levels and how this translates to the global scale is needed for improvements to be made in model predictions of future fossil fuel CO_2 uptake. However, it should be recognised that the direct impact on atmospheric CO_2 is relatively small compared to emissions and other carbon cycle feedbacks. For instance, currently yearly emissions of CO_2 from fossil fuels and cement production of 7.2 PgC yr^{-1} (IPCC, 2007) are of a comparable magnitude to the 100-year integrated impact of reduced calcification. The year 2100 model predictions of a 5-25 PgC repartitioning of CO_2 from atmosphere to ocean is also dwarfed by the likely anthropogenic CO_2 inventories of the ocean and atmosphere, which even in 1994 stood at 118 and 165 PgC, respectively. There are also important gaps in our understanding of fundamental aspects of the workings of the marine carbon cycle (see below).

4.2. Indirect impacts of ocean acidification on atmospheric CO_2

How some of the organic matter produced by plankton at the ocean surface manages to reach the deep ocean without first being completely degraded by bacteria along the way may be sensitive to changes in calcification and thus ocean acidification (Figure 7). This is important because the continual transfer of particulate organic matter and its associated carbon to the deep sea creates a chemical gradient in the ocean with lower concentrations of dissolved CO_2 at the surface than at depth. Any reduction in the fraction of organic matter reaching the deep ocean would reduce the surface-to-deep dissolved CO_2 gradient, resulting in a higher concentration of CO_2 in the atmosphere.

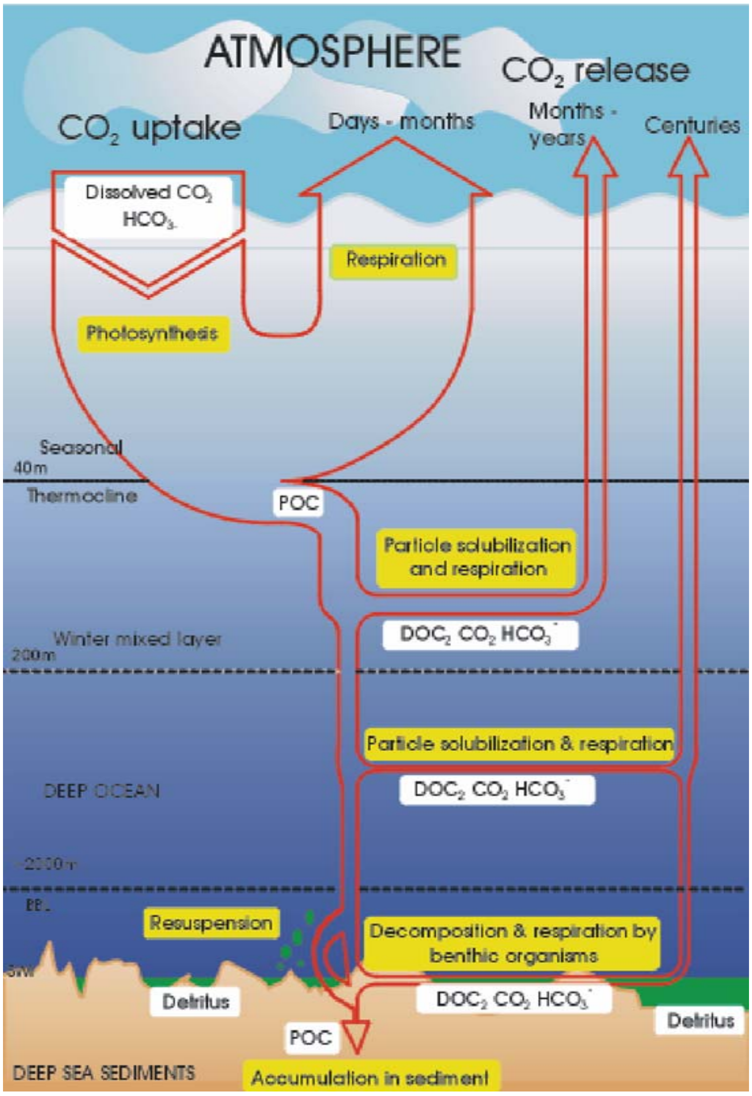

Figure 7. *Schematic diagram showing the biological pump and the flux of carbon through the oceanic water column to the deep sea sediments and approximate return times dependent on depth of remineralisation. From Turley (2000).*

Because the $CaCO_3$ shell material produced by marine calcifiers (Figure 5) is much denser than the soft body parts of plankton, its presence in aggregates with organic matter (Figure 8) may play an important role in accelerating the rate of sinking (Armstrong *et al.*, 2002). Any reduction in calcification by plankton at the ocean surface due to ocean acidification would then increase the time that organic matter was suspended in the warm upper ocean and increase the likelihood of its being consumed by bacteria. The consequence would be an increase in the rate of recycling of both nutrients and CO_2 back to the surface. While this may result in an increase in primary production by plankton due to greater nutrient availability, the faster rate of return of dissolved carbon would drive atmospheric CO_2 higher overall.

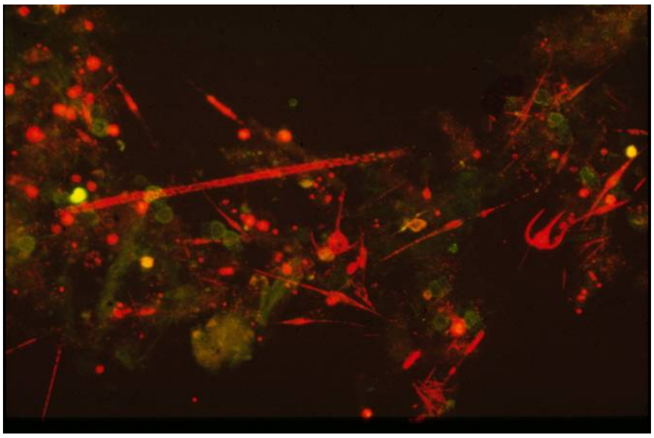

Figure 8. *Epifluorescent photomicrograph of a macroaggregate from the surface waters in the NE Atlantic, showing a range of red autofluorescing (excitation at 450-490 nm) phytoplankton cells containing chlorophyll. Scale bar = 200 μm. From Turley (2000).*

The limited number of global models that have assessed the potential importance of $CaCO_3$ in the 'ballasting' (density-dependent sinking) of aggregates with organic matter, suggest that reduced $CaCO_3$ ballasting could cut the ca. 6–18 PgC direct impact of acidification-driven changes in calcification on fossil fuel CO_2 uptake by 80% (Heinze, 2004). It is possible that the sign of the net CO_2 impact could be reversed, resulting in more fossil fuel CO_2 overall residing in the atmosphere (Barker *et al.,* 2003). However, the importance of mineral ballasting in the transport of organic matter to depth is currently uncertain, partly because of the technical and logistical difficulties of observing and experimenting on the aggregation (and dis-aggregation) processes in the ocean interior.

Aside from potential changes in the efficiency of recycling of organic matter and its associated nutrients, higher ambient concentrations of dissolved CO_2 and acidification have been observed in the laboratory to result in a greater production of organic matter per cell in phytoplankton (Zondervan *et al*., 2002; Bellerby *et al*.; 2007; Riebesell *et al*. 2007). Increased photosynthetic fixation of carbon and subsequent removal from surface waters as sinking particulate organic matter would decrease the concentration of dissolved CO_2 at the ocean surface and thus accelerate the uptake of fossil fuel CO_2 from the atmosphere. However, for this phenomenon (i.e., increased photosynthetic fixation of CO_2 and organic matter export) to be effective there must be sufficient nutrients. A commensurate decrease in the amount of nitrogen and phosphorus required per unit quantity of carbon fixed would facilitate this, an effect which the results of mesocosm experiments support (Bellerby *et al*., 2007; Riebesell *et al*., 2007). The uncertainties of acidification impacts on cellular organic matter composition are large and no global models yet routinely incorporate this effect in predicting future atmospheric CO_2 concentrations. Additional feedbacks as nutrient-to-carbon ratios change may also become important and limit productivity (Thingstad *et al*., 2008).

Whether the supply of organic matter to the deep ocean decreases due to decreased carbonate ballast production, and/or increases due to physiological impacts of higher CO_2, there may be important impacts on the organisms and communities living at the ocean floor because organic matter derived from the surface waters their the main food resource (Turley, 2000). Changes in the supply of organic matter to the deep ocean however it occurs will have implications for the degree of oxygenation of the deep ocean as the bacterial metabolism of this material consumes O_2 throughout most of the modern ocean and surface sediments of the deep sea.

4.3. Impacts of ocean acidification on climate (other than via CO_2)

Blooms of coccolithophores (Figure 5) can modify the surface optical properties of the ocean because the coccolith platelets that are shed in the water column are efficient at scattering sunlight. Any reduction in the number, mass, or shape of coccoliths as a result of ocean acidification (Figure 5) could thus potentially alter the surface energy budget in regions of the ocean where coccolithophorid blooms are common. However, estimates of the total contribution of coccolithophorid blooms to the surface energy budget suggest that even the complete loss of all coccolith production globally would have a radiative forcing (warming) impact of just 0.22 Wm^{-2} (Tyrrell *et al*., 1999), equivalent to no more than 10% of that due to the historical increase in CO_2 alone (IPCC, 2007).

Coccolithophores are also major producers of dimethyl sulphide (DMS) which may have a role in climate regulation via the production of cloud condensation nuclei (Charlson *et al*., 1987). A reduction in the occurrence of coccolithophore blooms that occur in large areas of the global oceans, often of 100 000s km^2 (Figure 5) could lead to a reduced flux of DMS from the oceans to the atmosphere and hence to further increases in global temperatures via cloud changes. Mesocosm experiments have shown changes in DMS production at CO_2 concentrations different to current concentrations (e.g. Vogt *et al*., 2008). However, the existence of global climate impacts via acidification and DMS production should be considered highly uncertain at present.

5. SOCIO-ECONOMIC EFFECTS OF OCEAN ACIDIFICATION

The UK's coastal and shelf sea environments and the biodiversity within them provide a wide range of goods and services that are essential for the maintenance of social and economic well being (Beaumont *et al*., 2008). These goods and services can be defined as provisioning, regulating, cultural and supporting services (MEA, 2003), providing benefits at several levels (local, regional and global) and to different groups (individuals and public bodies).

5.1. Provisioning services (food provision, raw materials)

Globally over 1 billion people rely on fish as their main animal protein source, especially in developing nations (Pauly *et al*., 2005). The UK population traditionally enjoys fish and although its own national industry has declined over recent decades it is still an important industry. In 2006, the UK fishing industry had 6,372 fishing vessels utilising a mixture of gears and techniques to catch a broad variety of fish, such as mackerel, cod, scallops and mussels (Figure 9). Landings into the UK amounted to 614,000 tonnes of sea fish with a total value of £610 million (James, 2007). Shellfish (nephrops, crabs, mussels etc) comprised 40% of total harvest. The fleet comprised 12, 934 fishers with 80% of these being full time fishers.

Mounting evidence indicates that ocean acidification will likely impair calcification in animals with calcium carbonate shells and skeletons (e.g. Section 3, and reviews by Kleypas *et al.,* 2006; Gazeau *et al.,* 2007; Fabry *et al*., 2008; Hoegh-Guldberg *et al*., 2008). This includes commercially valuable molluscs, crustaceans and echinoderms. Further, most other commercially harvested species, such as finfish, prey on shellfish, echinoderms, crustaceans or their predators. Ocean acidification could therefore lead to degradation of marine resources which would result in a reduction in fish harvest and protein provision, and loss of revenue and jobs. For instance, using the Defra Sea Fisheries Statistics 2006 (James, 2007), and assuming a 10-25%

reduction in growth/calcification (with a doubling in atmospheric CO_2, see section 3) results in 10-25% loss of shellfish landings that is equivalent to £24.4 - 61 million per year loss in value and around 1000-3000 potential job losses.

***Figure 9**. Image of aquaculture/fishing activity around UK. © Crown copyright 2009 Reproduced by permission of Cefas, Lowestoft*

Two significant raw materials extracted from the UK marine environment are fishmeal and fish oil, and seaweed. Fishmeal and fish oil are key constituents of pelleted diets for the intensive production of carnivorous fish species. In 2004, 192,000 tonnes of fishmeal were consumed in the UK of which 50,000 were produced locally with the remainder imported. The total value of the UK fishmeal market in 2004 was £81 million (European Parliament Report, 2004). Reduction in availability of these raw materials could therefore impact the extent and/or market cost of UK finfish aquaculture. In 2004, England, Scotland and Wales had 613 fish and shellfish farming businesses operating on 1329 sites, employing 3,412 people. The main finfish species farmed are salmon (139 000 tonnes mainly in Scotland) and rainbow trout (16 - 17,000 tonnes) (Defra, 2008). There is also a limited production of other species, such as carp and brown trout, and relatively new species to aquaculture such as turbot, halibut, cod and Arctic char have produced encouraging results. Thus should acidification have significant impact on the production of these raw materials there could be socio-economic consequences on industries dependent on them.

Globally, warm water coral reefs are valuable marine ecosystems. They are important for nature and represent a very high value for humankind, supporting millions of people through provision of food and income. Cesar *et al*. (2003) estimate that coral reefs provide nearly US$ 30 billion each year in net benefits in goods and services to world economies, including tourism, fisheries and coastal protection. Increased stress on food production systems such as coral reefs, driven by climate change or ocean acidification, could thus have significant repercussion on food provision and/or security; particularly in developing countries where fish provide the major protein source (Pauly *et al*., 2005).

Pearls are created naturally by shellfish through the secretion of aragonite but can also be cultured artificially in oysters. Currently, the global pearl farming industry is worth $1.5 billion each year and is expected to grow into a $3 billion per year industry by 2010 (International Pearl Convention, 2007). A reduction in aragonite saturation may impact the rate of production and quality of both natural and cultured pearls and therefore the future pearl market. Less expensive "Mother of Pearl" used frequently in costume jewellery, button making and the arts and craft industry may also be impacted.

5.2. Regulating services (e.g. gas and climate regulation)

In addition to physical processes such as ocean mixing, tides, current and air-sea exchange, the chemical composition of the atmosphere and ocean is maintained through a series of biogeochemical processes regulated by marine organisms. Their ability to fix CO_2 through photosynthesis and transfer a proportion of this to the deep sea via this biological pump is a key part of the global carbon cycle - essentially the oceans are buffering the effects of climate change through the removal of a large proportion of the anthropogenic CO_2 (see sections 2 and 5). A recent study to value the role of marine biodiversity in gas and climate regulation found that the Isles of Scilly marine environment was fixing 136,495 tC y^{-1} with a mean net present value of £47 million (Davis *et al*., 2008), implying that on a UK scale the value would be £ billions. Any stressor reducing ocean productivity and the biological pump would have substantial environmental and economical impacts. The economic cost of replacing these natural processes with industrial processes would be exorbitant.

Sediments play a crucial role in a number of key ecosystem processes, in particular the microbial cycling of carbon and nitrogen (section 3, Figure 4). In addition, the behavioural characteristics of species that live in or/and on the sediment are important determinants of sediment biogeochemistry and element cycling, as their activities result in a release of dissolved and particulate nutrients from the sediment to the water column where they support primary productivity. Changes to this coupling, of sediment and pelagic biogeochemistry, through ocean acidification could have worrying knock-on consequences to shelf sea productivity and the food webs it supports, but this is highly uncertain.

5.3. Cultural services (e.g. leisure and recreation)

A significant component of leisure and recreation in the UK depends upon coastal marine biodiversity (e.g. bird watching, sea angling, rock pooling and diving) which in turn supports employment and small businesses. The rapid growth of sea angling based on sustainable practices is recognized as significant opportunity for UK economy. If UK marine biodiversity declines as a result of ocean acidification and other drivers, the value of this sector will decrease, with a potential loss of revenue. In addition, the occurrence of harmful or unpleasant algal bloom can reduce the aesthetics of beach recreation, as has been experienced in the Adriatic over the last decade.

The enormous biodiversity supported by coral reefs underpins substantial tourist industries for many tropical countries, including UK entities, and often provide their main revenue. Countries with coral reefs attract millions of SCUBA divers every year, yielding significant economic benefits to the host country. Globally, tourism is estimated to provide US$ 9.6 billion in annual net benefits (Cesar *et al*., 2003) and a multiple of this amount in tourism spending. Coral reef biodiversity also has a high research and conservation value, as well as a non-use value, estimated together at US$ 5.5 billion annually (Cesar *et al.,* 2003). Loss of coral reefs and their diversity would impact global tourism to these areas and their enjoyment by tourists, including those from the UK.

5.4. Supporting services (e.g. biologically mediated habitat)

Maerl beds, mussel patches and cold-water corals are among the most important biologically mediated habitats in UK waters supporting a large number of species. This includes the provision of refuge and food for juvenile life stages of commercially important shellfish such as the queen scallop, Atlantic cod, saithe and pollack (Hall-Spencer *et al*., 2003). Cold water corals grow in deep, CO_2 rich waters and may be even more vulnerable to ocean acidification through shoaling of the ASH than their tropical coral reefs (Guinotte *et al*., 2006; Roberts *et al*., 2006; Turley *et al*., 2007). Around 70% of known locations of these old, slow growing corals may be in undersaturated, corrosive waters by the end of this century, with some affected even earlier, thereby impacting economically valuable species that take refuge and feed there (Guinotte *et al*., 2006; Roberts *et al*., 2006).

Globally, coral reefs and mangroves play an important role in shore protection and enhance local productivity and biodiversity. It is estimated that tropical coral reef calcification rates will decrease with decreasing $CaCO_3$ saturation so that reef erosion will be greater than reef accretion in the next few decades depending on the location of the reef (Kleypas *et al*., 2006). This protective function of reefs was valued at US$ 9.0 billion per year by Cesar *et al*. (2003) so any decline in this function will have a socio-economic impact either through loss of low lying land habitat and infra structure or through a need for investment in shore protection.

In addition to these quantified values, reefs have drawn a mass of medical and pharmaceutical research interest in the pursuit of finding cures for human diseases. Any loss in these roles will have significant socio-economic impacts on the people that depend on these services.

6. KEY LINKAGES:

CO_2 flux into ocean [very high confidence] causes oceanic pH and carbonate ion concentration to decrease [very high confidence] this links to impacts on organisms through changes in physiology [medium confidence], calcification/dissolution [medium confidence] and changes in nutrient chemistry and speciation [low confidence]. All marine organisms face the potential risk of physiological impacts [medium confidence] and early-life stages are particularly vulnerable [medium confidence]. Short-term acidification events cause benthic shell-forming organisms such as shellfish to have reduced growth [medium confidence] and reduced survival [medium confidence] while important planktonic organisms (e.g. coccolithophores) have reduced growth [low confidence]. These impacts may harm economical valuable species [low confidence], with potential impacts [low confidence] on the provision of ecosystem goods and services, and human wellbeing. Any changes in plankton will alter the carbon and nutrient cycles [medium confidence] and impact up the food web [low confidence]. 55.5 million years ago an ocean acidification event could have been the cause of the mass extinction of benthic calcifiers [low confidence] while the pelagic calcifiers survived because there was time for them to adapt and/or track their habitat [medium confidence]. However, the rate and potential extent of today's change is much greater, implying that there could be substantial extinctions in both benthic and planktonic realms [medium confidence]. Ocean acidification is intimately linked to a dramatic reduction in the oceans buffer capacity [very high confidence] reducing future ocean CO_2 uptake and increasing the fraction of emitted CO_2 retained in the atmosphere and as such is linked to climate. Under a Business As Usual CO_2 emissions scenario, ocean acidification will cause the additional uptake of no more than a few 10s of PgC by year 2100 due to reduced calcification [medium confidence], but because of reduced mineral ballasting of organic matter aggregates the net CO_2 change could be negligible (a few PgC) [low confidence]. Physiological changes resulting in greater carbon fixation will have an important impact on drawing down CO_2 [low confidence]. The flux of organic matter to deep ocean ecosystems will tend to be increased due to physiological changes [medium confidence], but decreased due to reduced aggregate ballasting [low confidence], either way impacting dissolved oxygen concentrations [high confidence]. Only a relatively minor (< 0.22 W m^{-2}) increase in absorbed sunlight will occur as a result of decreased coccolith reflectivity [low confidence] and less DMS-induced cloud cover [low confidence].

7. KEY LINKS TO OTHER ECOSYSTEM LINKAGES REPORT CARD REVIEWS

Arctic sea ice: Wintertime sea-ice cover acts as a lid preventing CO_2 taken up during summer blooms from returning to the atmosphere. The formation of sea-ice also produces brines which promote the sinking of surface water to depth, carrying absorbed fossil fuel CO_2 with it. However, associated changes in biological productivity and ecosystem composition and nutrient cycling makes the net CO_2 impact uncertain. Sea ice provides important habitat for marine organisms such as ice algae, which are primary producers of the Arctic food web. Loss of these may well impact on the amount of food available which may be confounded by stress from ocean acidification. Reduced or undersaturated waters with respect to aragonite and calcite will be an additional stressor to Arctic ecosystems, especially those with an important role for calcifiers.

A view from above: changing seas, seabirds and other food sources (to include fish): Loss of organisms through acidification will impact the food web right through to seabirds. If there is a change in the availability of food or nutritional quality of the food then the seabirds will also suffer as a result.

Non-natives: invaders from another place: Depending on the type of invaders this could additionally impact changes in the ecosystem or it could alleviate them. Some non-natives may benefit from space becoming available and may fill an important ecosystem function; however others undoubtedly will also be impacted by OA. One acidification event, 55.5 millions years ago, was associated with a massive dinoflagellate bloom indicating that some species are more capable of adapting to the environmental changes than others. In addition alien species tended to do well in natural CO_2 vent areas with lower pH than the native species.

Coastal economies and people – the consequences of change: There could be loss of mariculture, depleted biodiversity and food availability through food web changes, migration of species, impacting on fish stocks, fisheries, jobs, tourism and coastal protection. Changes in land use could impact ocean acidification through changing export of DIC. Acidification of coastal waters near industrial sites may be higher through atmospheric deposition of sulphur and nitrogen. Ocean acidification and climate change are added stressors to poorly managed fisheries.

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