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Impacts of ocean acidification

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EXECUTIVE SUMMARY

Ocean acidification is closely linked with climate change, sharing the same driver - increasing atmospheric CO_2. However, it is a separate process from the physical environmental perturbations arising from energy flux changes in the Earth system. Ocean uptake of CO_2 has reduced the extent of anthropogenic greenhouse warming; it has also increased surface ocean hydrogen ion concentration by ~30% to date, and decreased surface carbonate ion concentration by ~16%. These effects – ocean acidification – are expected to greatly intensify in the next 100 years unless strong and urgent mitigation measures are taken at the global scale.

Evidence from experiments and observations indicate that future ocean acidification will affect many marine organisms, with implications for ecosystems and ecosystem services. Attention to date has mostly focused on species-specific responses, revealing high taxonomic variability. Research is now addressing the more complex issues of marine community responses to ocean acidification, together with additional stressors, over longer timescales. There remain many uncertainties relating to the scale and direction of socio-economic impacts, primarily operating through commercially-important species, biogeochemically-driven feedbacks to the climate system and global element cycles. Ecologically-important cold- and warm-water corals seem to be at particular risk, with the latter also having high economic importance for several UK Overseas Territories and many other tropical nations.

Ocean acidification is a global scale threat but impacts will be felt at the local and regional level. It is highly likely that UK coastal waters, ecosystems and habitats will be significantly impacted this century if global CO_2 emissions continue to rise. The most effective way of reducing the impact of ocean acidification is the rapid and substantial reduction of CO_2 emissions.

1. WHAT IS ALREADY HAPPENING?

1.1.1 Already-occurring changes in ocean chemistry

Direct effects of increased atmospheric CO_2 on ocean carbonate chemistry

The ocean has a major role in the global storage and cycling of carbon: it contains ~55 times more carbon than the atmosphere and ~30 times more than the terrestrial biosphere, and it has absorbed ~25% of all anthropogenic CO_2 emissions, thereby slowing the increase in atmospheric concentration of this greenhouse gas (Le Quéré *et al.*, 2009). Dissolved CO_2 reacts with seawater to form carbonic acid (H_2CO_3), with other chemical consequences affecting the balance of ions: in particular, the concentrations of bicarbonate (HCO_3^-) and hydrogen ions (H^+) increase, the latter reducing pH, while the concentration of carbonate ions (CO_3^{2-}) decreases (Figure 1).

These chemical changes are estimated to have already reduced mean surface ocean pH by ~0.1 units (corresponding to a ~30% increase in H^+ concentration), from the pre-industrial global mean value of around 8.2 (Royal Society, 2005). CO_2-induced changes in the chemistry of deeper waters occur more slowly, with rates of change being a function of large-scale ocean circulation and mixing processes (Orr, 2011). Measurements at ocean time series stations and transect-based observations confirm these changes, indicating an anthropogenically-induced surface pH decrease of ~0.002 units per year since 1990 (Doney *et al.*, 2009; Orr, 2011; Bates *et al.*, 2012). In the North Atlantic, there has been marked spatial variability in the pH decrease over that period, with

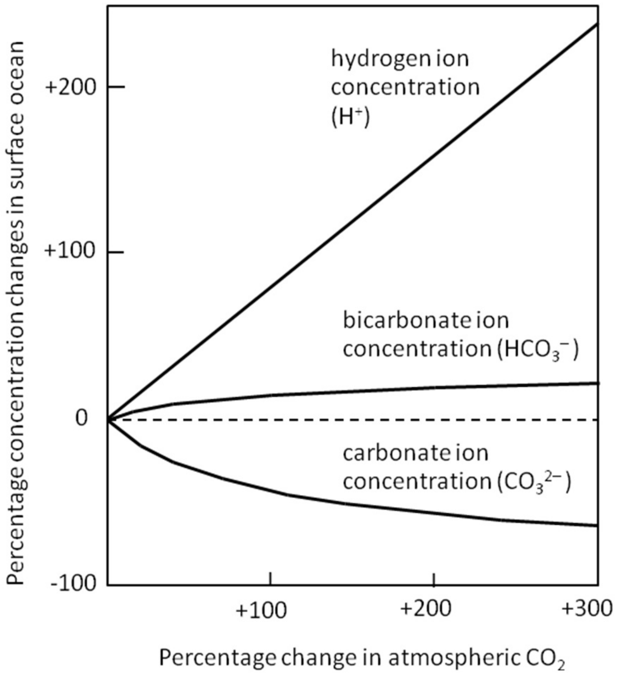

Figure 1: Percentage changes in average global surface ocean ion concentrations resulting from up to a four-fold change (300% increase) in atmospheric carbon dioxide, compared to pre-industrial values and at an assumed uniform and constant upper ocean temperature of 18°C. Values for atmospheric CO_2 change from 280 ppm to 1120 ppm; bicarbonate ions from 1770 to 2120 μmol kg-1; carbonate ions from 225 to 81 μmol kg-1; and for pH from 8.18 to 7.65 (where pH is defined as the negative decimal logarithm of the hydrogen ion activity, and a linear relationship is assumed between activity and concentration). Re-presented from Williamson and Turley (2012); data from Royal Society (2005).

ocean acidification apparently occurring more rapidly in the European region (on-shelf and off-shelf) than either in the Caribbean or central Atlantic (Schuster *et al*., 2009).

Although high resolution, decadal scale time series data are currently lacking for UK waters, a spatially-comprehensive observation programme for pH-related parameters, including benthic measurements, is now in place, involving the Centre for Environment, Fisheries and Aquaculture Science (Cefas), Marine Scotland and other partners, with part support through the UK Ocean Acidification (UKOA) research programme. Recent surveys (Figure 2) have been supplemented by data from UKOA research cruises in 2011 and 2012. The UK is strongly involved in the development of a global network for ocean acidification observations, started in 2012 by a range of international and national bodies, and is also contributing to a regional coordination initiative, led jointly by OSPAR (Oslo and Paris Conventions for the protection of the environment of the North East Atlantic) and ICES (International Council for the Exploration of the Sea).

Changes to calcium carbonate saturation

The saturation state (Ω) of calcium carbonate ($CaCO_3$) minerals determines their rate of inorganic formation or dissolution in seawater. If seawater is undersaturated (Ω< 1), exposed carbonates dissolve. Saturation state is a function of the concentration of CO_3^{2-} as well as temperature, salinity and pressure. Values are also structurally-specific, with the three main forms of $CaCO_3$ produced by organisms being (in order of increasing solubility) calcite, aragonite and high magnesium-calcite.

The vast majority of the surface ocean remains supersaturated (Ω> 1) with respect to the three main forms of $CaCO_3$ facilitating the biotic production of carbonate-based shells, skeletons and liths. However, since increasing ocean acidification is lowering the carbonate ion concentration (Figure 1), calcite, aragonite and Mg-calcite saturation states are all decreasing – with potential biological consequences (see Sections 1.1.2 and 1.2.2 below). Differences in species' physiology are important in determining their vulnerability to decreasing saturation state, including their ability to cover $CaCO_3$ with organic material (e.g. the periostracum of many molluscs).

$CaCO_3$ saturation decreases with water depth, as a result of remineralisation of organic matter (by biological respiration/decomposition, with release of CO_2) and pressure-dependent effects on solubility. Whilst the aragonite saturation horizon (ASH; below which aragonite dissolves) is always shallower than the calcite saturation horizon (CSH), the depths of these horizons vary between ocean basins as a result of other differences in water chemistry. For example, the ASH is mostly <600m in the North Pacific but >2000m in most of the North Atlantic (Guinotte *et al*., 2006). As anthropogenic CO_2 invades the ocean interior and carbonate ion concentrations are reduced, the saturation horizons are rising, currently at around 4 m per year (at a depth of ~1700m) in the Iceland Sea (Olafsson *et al*., 2009).

Upwelling of CO_2-rich waters

Wind-driven upwelling of water from below the ASH (i.e. with Ω< 1) occurs at many locations on the western edge of continents. Off the western coast of North America, undersaturated and low pH (~7.6) water can occupy the shelf from February to September and anthropogenically-driven reductions of ocean pH are implicated in extensions of the severity and duration of such conditions (Feely *et al*., 2008). Other upwelling regions that do not currently experience undersaturated conditions at any time of year can be expected to start to do so seasonally. Such effects would occur much before annual mean surface undersaturation (the property most often calculated in ocean models).

Temporal and spatial variability

Superimposed on these relatively consistent large-scale and long-term trends, many marine systems – particularly those in economically-important coastal and shelf seas – show high temporal and spatial variability in carbonate chemistry (Hofmann *et al*., 2011). In UK/European shelf seas, both observations and modelling show that CO_2 levels in near-surface seawater can currently vary between 200-450 ppm, contributing to a pH change of as much as 1.0 (typically 0.3-0.4) over an annual cycle (Blackford and Gilbert, 2007; Artioli *et al*., 2012) (Figure 3). This variability is due to three main processes:

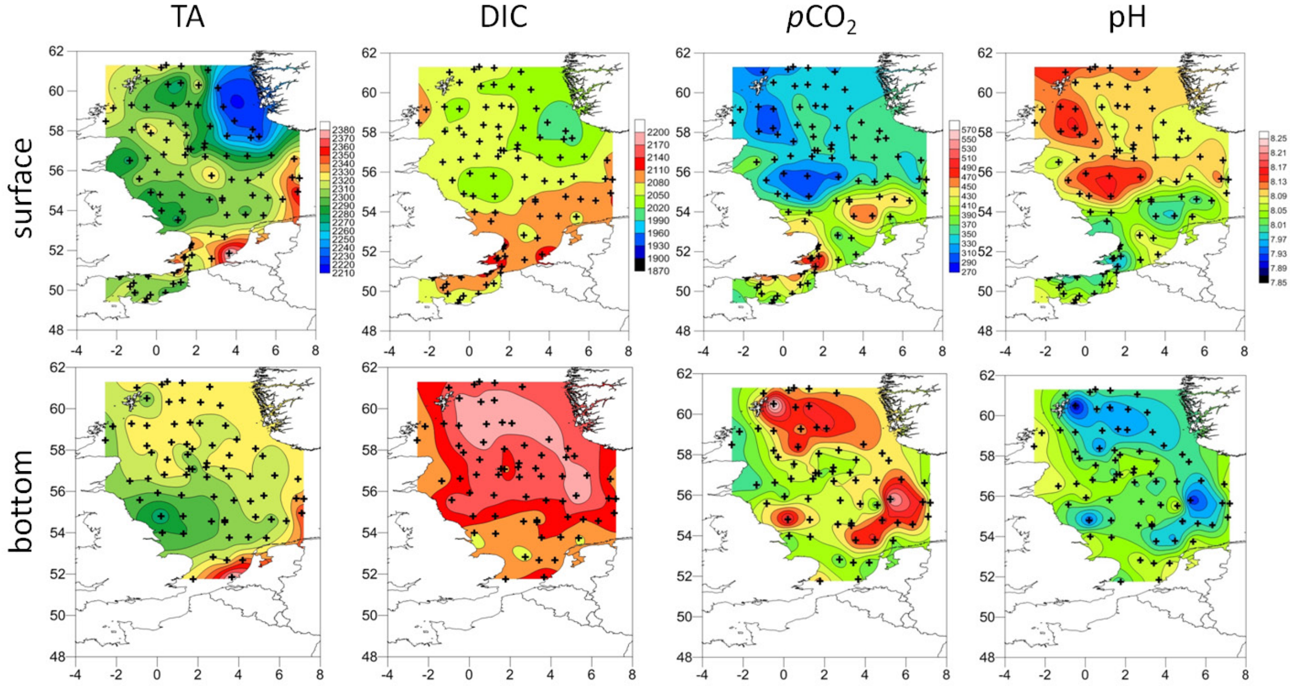

Figure 2: Preliminary surface and bottom data for observed total alkalinity (TA) and dissolved inorganic carbon (DIC), and calculated pCO2 and pH for the North Sea in July-August 2011, showing marked vertical and horizontal variability. Image from N. Greenwood and D. Pearce, Cefas; unpublished.

• Water temperature is more spatially and temporally variable in shallow shelf seas than the open ocean. Temperature affects CO_2 solubility, hence pH.

• The biological processes of photosynthesis and respiration/decomposition take up and release CO_2 respectively. Such processes vary seasonally, over day-night cycles and locally (e.g. due to frontal systems and the inherent patchiness of biological activity)

• Land-based boundary conditions, particularly river inputs with their unique carbon signatures, derived from geology and land use. Riverine nutrient inputs, mostly anthropogenic, also serve to enhance biological production (and subsequent respiration/decomposition), as above.

The combined effects of the above not only result in strong seasonal variability (e.g. Melzner *et al*., 2012) but also diurnal variability in pH and related ocean carbonate chemistry, that may be of similar magnitude (Litt *et al*., 2010; Hydes and Hartman, 2011; Hofmann *et al*., 2012). Such dynamic 'background' conditions could mean that organisms from coastal waters and shelf seas are less susceptible to future changes in pH than those from the open ocean, as the former may have a greater ability and potential for adaptation. But it could also mean that coastal/shelf sea organisms might be exposed to harmful pH thresholds more quickly. In either case, annual mean pH values are likely to be poor predictors of impacts; instead minimum pH levels and/or the temporal extent of low pH (together with other stress conditions) could be more important.

A further spatial variability in pH relevant to biota occurs at the micro-scale, since there can be rapid changes in carbonate chemistry across the boundary layer surrounding individual planktonic organisms (Flynn *et al*., 2012). In considering such effects, linear concentrations of H^+ may be more relevant to physiological and biogeochemical processes than the logarithmic pH scale.

1.1.2 Already-occurring impacts on marine organisms

Two important and closely-related biological processes – acid-base regulation and calcification – are fundamentally linked to carbonate chemistry in the immediate external environment of marine organisms. It is therefore likely that the ocean acidification that has already occurred in the past few hundred years (albeit superimposed on high natural variability) has already had physiological and ecological consequences, both negative and positive. Such impacts are, however, difficult to show conclusively, due to: taxonomic variability (discussed in greater detail with regard to future effects, in Section 1.2.1); the lack of long time-series of high-quality chemical data with which biological observations can be compared; and the interacting impacts with other changes in environmental conditions, climatic and non-climatic (such as temperature, nutrients, pollutants, food-web structure and local/regional circulation changes).

The occurrence of other forcing factors, that may interact synergistically or antagonistically with ocean acidification, or over-ride its effects, means that great care must be taken in interpreting data that are only based on correlations, not necessarily causal. For example, change in temperature change, rather than pH, would seem to be the primary driver of observed changes in abundance of calcifying plankton in the North East Atlantic over the period 1960-2009 (McQuatters-Gollop *et al*., 2010; Beaugrand *et al*., 2012).

Reduced bio-calcification has been shown in most, but not all, experimental studies of ocean acidification impacts

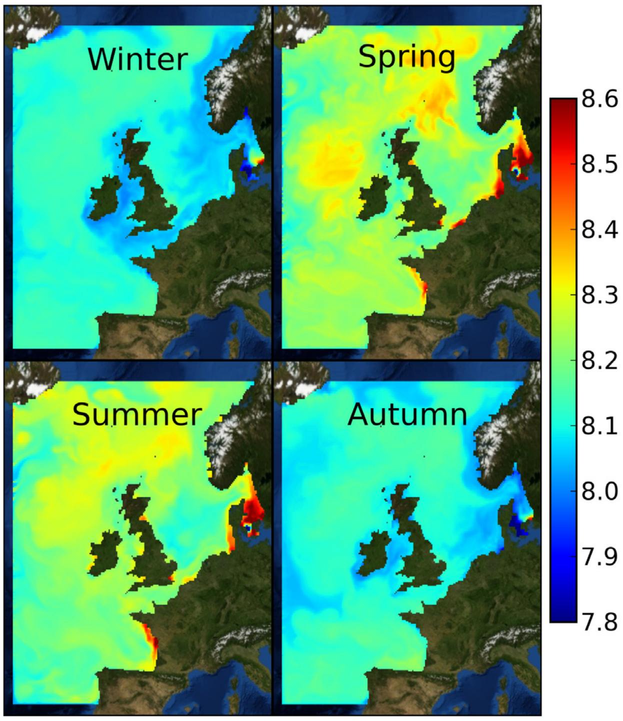

Figure 3: Model simulation of seasonal changes in surface pH under current conditions in the North West European shelf, accounting for riverine inputs and biological processes (Artioli et al.*, 2012).*

(Andersson *et al.*, 2011; Riebesell and Tortell, 2011; also see Section 1.2.2 and Table 1) and such effects may already be occurring in the field. In the Southern Ocean, shell-thinning has been reported for the planktonic foraminifera *Globigerina bulloides* (Moy *et al.*, 2009), with enhanced shell erosion of the pteropod *Limacina helicina antarctica* occurring in low saturation regions, consistent with experimental data (Bednaršek *et al.*, 2012). There is also increasing evidence that calcification by natural populations of warm water corals[1] is not only sensitive to pH variability but may also have been adversely impacted by recent trends.

For example:

• At CO_2 seep sites in Papua New Guinea (where pH is reduced to ~7.8), coral diversity and calcification rates are much decreased (Fabricius *et al.*, 2011).

• Coral reefs in the tropical Pacific off central America produce <2% inter-skeletal pore cement increasing their susceptibility to erosion (Manzello *et al.*, 2008). In contrast, reefs in the tropical Atlantic off the Bahamas (where pH is higher) have ~60% inter-skeletal pore cement.

• In the Red Sea, coral calcification rates seem closely linked to natural fluctuations in saturation state and temperature (Silverman *et al.*, 2007).

• Decreases in net calcification of 14-21%, and in growth of 13-30% have been reported over the past ~25 years for corals in the Great Barrier Reef (De'ath *et al.*, 2009, 2012). Sea surface temperature is uncorrelated to this decline.

Nevertheless, opposite effects on calcification have been observed in some field data for calcareous phytoplankton: heavily or over-calcified strains of the coccolithophore *Emiliana huxleyi* may dominate in lower pH waters, with lower carbonate availability (Beaufort *et al.*, 2011; Smith *et al.*, 2012).

For commercially-important shellfish, deleterious impacts of ocean acidification would be first expected in regions where coastal waters are strongly influenced by upwelling of high CO_2/low pH water. Data from oyster hatcheries in north-west North America indicate that such effects are now occurring (Barton *et al.*, 2012).

2. WHAT COULD HAPPEN?

1.2.1 Potential future impacts on ocean chemistry

Global and regional changes in carbonate chemistry

For all IPCC climate change scenarios (as used in the 4th Assessment Report and those developed for AR5), global ocean models unanimously project reduced future surface pH and decreased calcium carbonate saturation throughout all oceans, with the severity of such effects matching the projected increases in atmospheric CO_2 (Joos *et al.*, 2011). Undersaturation with respect to aragonite is expected to occur within decades for polar and sub-polar surface waters, initially in the Arctic (Steinacher *et al.*, 2009) associated with decline in depth of saturation horizons (Orr *et al.*, 2005).

Modelled estimates of future seawater pH around UK coastal and shelf waters are generally consistent with global projections. However, variability and uncertainties are greater due to riverine inputs, biotically-driven processes (and their own variability) and geochemical interactions between the water column and underlying sediments (Blackford and Gilbert, 2007; Artioli *et al.*, 2012). Preliminary modelling data by UKOA researchers indicate that much of the North Sea seafloor is likely to become seasonally undersaturated (during late winter/early spring) with regard to aragonite by 2100 under high CO_2 emission scenarios (Artioli *et al.*, 2013).

Climatic feedbacks

The most important direct climatic feedback of future ocean acidification is the increase in the Revelle buffer factor, decreasing the rate of further CO_2 uptake by the 'solubility pump' (Gehlen *et al.*, 2011). Climate change doubly aggravates the chemical change of decreasing buffer capacity, due to the inverse relationship between temperature and CO_2 solubility, and also because of increased stratification (slowing

[1]The UK has direct interests in warm-water corals through its responsibility for biodiversity in its Overseas Territories, including Anguilla, Virgin Islands and the British Indian Ocean Territory (BIOT/Chagos). The BIOT/Chagos Marine Protected Area, declared in 2010, includes ~4,000 km^2 of coral reef habitat, around half the "good quality" total for the Indian Ocean. Indirect interests relate to the global role of healthy coral reefs in reducing coastal erosion, supporting fisheries and alleviating poverty, e.g. via tourism.

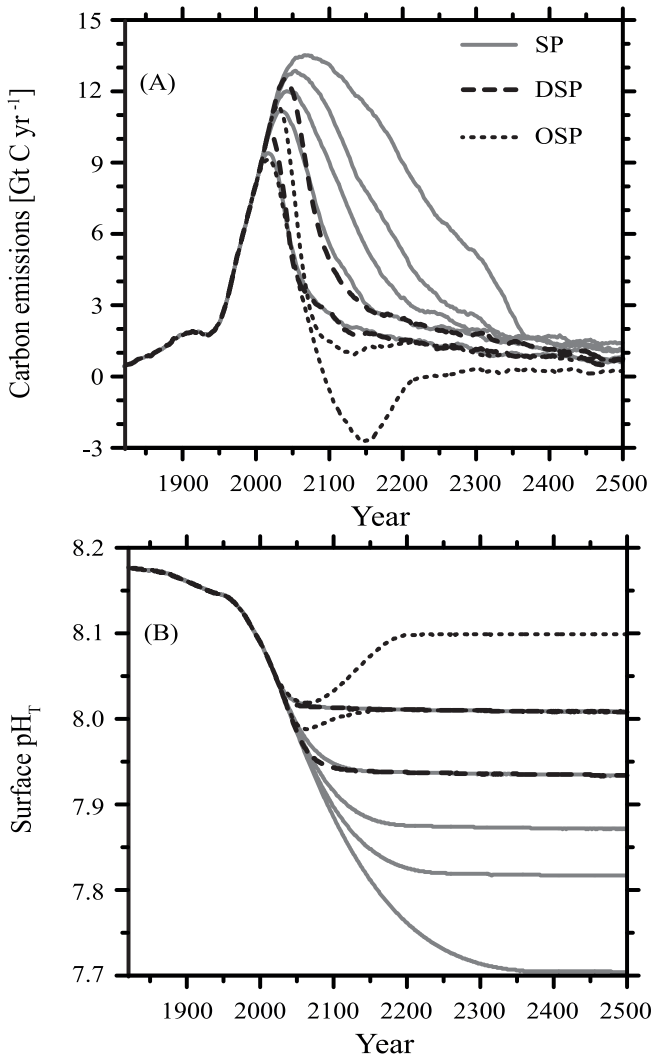

Figure 4: The relationship between changes in global annual carbon emissions over the period 1800-2500 (panel A) and global mean surface pH (B). Dotted lines labelled OSP (Overshoot Stabilization Profile) show pathways requiring negative emissions (i.e. CO_2 removal from the atmosphere) to stabilize atmospheric CO_2 at 350 and 450 ppm; dashed lines labelled DSP (Delayed Stabilization Profile) show delayed approach to emissions reductions to achieve stabilization at 450 and 550 ppm. From Joos et al. *(2011), modified by Williamson and Turley (2012) with permission of authors and Oxford University Press.*

the surface-to-deep exchange of carbon). Combined effects are estimated to decrease future CO_2 uptake by ~30% by 2100 under business-as-usual emission scenarios (Sarmiento *et al.*, 1998). Indirect climatic feedbacks, operating through changes in biological processes, are considered in Section 1.2.2 below.

Indirect consequences for ocean chemistry

Ocean acidification has the potential to change the chemical speciation and solubility of a range of elements. A noteworthy speciation effect is the pH-dependence of boron ions, with implications for the isotopic composition of boron included in biominerals (Hemming and Hönisch, 2007). This effect offers opportunities for palaeo-pH reconstructions, although the interpretation of the observed changes is not straightforward.

Other potential effects of future ocean acidification on seawater chemistry include changes in metal toxicity (Roberts *et al.*, 2013), also on nitrogen cycling and nutrient availability. Some of these impacts may be mediated through microbial processes (Section 1.2.2; Table 2).

Ocean acidification in relation to climate change mitigation and remediation options

As indicated above, future changes to ocean chemistry are closely linked to future anthropogenic CO_2 emissions and atmospheric levels. Thus emission pathways that stabilize atmospheric CO_2 at 450, 550, 650, 750 or 1000 ppm are expected to stabilize mean surface ocean pH, at around 8.01, 7.94, 7.87, 7.82 and 7.71 respectively (Figure 4; Joos *et al.*, 2011). To prevent the mean surface pH from falling below 8.0, strong and rapidly-implemented global mitigation is required: thus it is estimated that global CO_2 emissions would need to peak by 2016, and reduce by ~5% per year after then (Bernie *et al.*, 2010).

Socio-economic inertia, including existing and planned investment in fossil fuels, would seem to make this mitigation response unrealistic. A range of climate remediation (geoengineering) approaches have been proposed to constrain the global temperature increase that would otherwise occur under current CO_2 emission trajectories (Royal Society, 2009). Many, but not all, of these proposed techniques could also reduce ocean acidification to some degree, directly or indirectly (Williamson and Turley, 2012); however, there are major geopolitical and governance issues associated with such approaches.

The long-term legacy of CO_2 emissions on ocean chemistry

Modelling studies (and geological precedents; Hönisch *et al.*, 2012) indicate that full recovery from the current anthropogenic perturbation to the global carbon cycle is likely to take 50,000-100,000 years, involving equilibration with carbonate minerals and the carbonate-silicate cycle (Archer and Brovkin, 2008). Within the next 1,000 years, marine $CaCO_3$ sediment dissolution is estimated to 'neutralize' 60-70% of anthropogenic CO_2 emissions, whilst 20-30% remains in the ocean water column and the remaining ~10% is accounted for by terrestrial weathering of silicate carbonates (Archer *et al.*, 2009).

1.2.2 Potential future impacts on marine organisms, ecosystems and biogeochemical processes

Physiological and species-specific responses

A wide range of laboratory-based studies (mostly short-term, on single species) have shown that many marine organisms are potentially affected, in many ways, by the levels of surface ocean pH projected for 2100 under business-as-usual scenarios for future CO_2 emissions. Most of such impacts are deleterious; however, some species could benefit, whilst others seem unlikely to be affected. A summary of the responses of different taxonomic groups to ocean acidification is provided in Table 1, based on Williamson

Table 1: Summary of likely main effects of future ocean acidification on different groups of marine organisms, mostly based on laboratory experiments. See Williamson and Turley (2012) for ~50 references relating to this table.

Group	Main acidification impacts
Warm water corals	A relatively well-studied group. The great majority of experiments show that increasing seawater CO_2 decreases adult coral calcification and growth, and suppresses larval metabolism and metamorphosis. Although most warm water coral reefs will remain in saturated waters by 2100, saturation levels are predicted to decline rapidly and substantially; thus coral calcification may be unable to keep up with natural bioerosion. Interactions with other climatic and anthropogenic pressures give additional cause for concern.
Cold water corals	Cold water corals The long-lived nature of cold-water corals, and their proximity to aragonite saturation horizons, makes them vulnerable to future reduced depth of the ASH. Around 70% of known cold water coral locations are estimated to be in undersaturated waters by the end of this century. Experiments found the effect of pH change on calcification was stronger for fast growing, young polyps.
Molluscs	Significant effects on growth, immune response and larval survival of some bivalves. However, there is high inter-specific variability and negative impacts may be mitigated if food availability is high. Pteropods seem particularly sensitive and are a key component of high latitude food webs. Molluscs are important in aquaculture, and provide a small yet significant protein contribution to the human diet.
Echinoderms	Juvenile life stages, egg fertilization and early development can be highly vulnerable, resulting in much reduced survival. Adult echinoderms may increase growth and calcification; such responses are, however, highly species specific.
Crustaceans	The relative insensitivity of crustaceans to ocean acidification has been ascribed to well-developed ion transport regulation and high protein content of their exoskeletons. Nevertheless, multiple stress effects may be important; e.g. spider crabs narrow their thermal tolerance range by ~2˚C under high CO_2 conditions.
Foraminifera	Shell weight sensitive to CO_3^{2-} decrease in the laboratory with field evidence for recent shell-thinning.
Fish	Adult marine fish are generally tolerant of high CO_2 conditions. Responses by juveniles and larvae include diminished olfactory and auditory ability, affecting predator detection and homing ability in coral reef fish; also reduced aerobic scope and enhanced otolith growth in sea bass.
Coralline algae	Meta-analysis showed significant reductions in photosynthesis and growth due to ocean acidification treatments. Elevated temperatures (+3°C) may greatly increase negative impacts. Field data at natural CO_2 vents show sensitivity of epibiont coralline algae.
Non-calcified macroalgae; sea grasses	Both groups show capability for increased growth. At a natural CO_2 enrichment site, sea grass production was highest at mean pH of 7.6.
Coccolithophorres	Most studies have shown reduced calcification in higher CO_2 seawater; however, the opposite effect has also been reported. Ocean acidification impacts on coccolithophore photosynthesis and growth are equivocal, even within the same species. This variability may be due to the use of different strains, experimental conditions and species-specific sensitivities to carbonate chemistry.
Bacteria	Most cyanobacteria (including *Trichodesmium*, a nitrogen-fixer) show enhanced photosynthesis and growth under increased CO_2 and decreased pH conditions. Heterotrophic bacteria investigated to-date show many responses with potential biogeochemical significance, including decreased nitrification and increased production of transparent exopolymer particles (affecting aggregation of other biogenic material and its sinking rate). Adaptation to a high CO_2 world is likely to be more rapid by bacteria and other short-generation microbes than by multicellular organisms.

and Turley (2012). For other broad-based, recent reviews see Andersson *et al*. (2011), Riebesell and Tortell (2011), Widdicombe *et al*. (2011), Pörtner *et al*. (2011), Whiteley (2011) and Wicks and Roberts (2012). Data meta-analyses have been carried out by Hendricks *et al*. (2010) and Kroeker *et al*. (2010; 2013) for a wide range of organisms, and by Liu *et al*. (2010) for microbes.

This paper is unable to cover all aspects of biological responses to projected ocean acidification. However, the following general features are noteworthy:

• Calcification is likely to be the process most sensitive to future changes in carbonate chemistry. Negative effects predominate; nevertheless, increased calcification under reduced pH can also occur, although at metabolic cost

(Wood *et al*., 2008). Intra-specific variability in responses has been documented for several species and examined in most detail for the photosynthetic coccolithophorid *Emiliana huxleyi*, reviewed by Riebesell and Tortell (2011). For this species – and potentially others – strain turnover, acclimatization and adaptation may all result in long-term calcification responses being markedly different from short-term experimental outcomes (Lohbeck *et al*., 2012; Kelly and Hofmann, 2012). In short-term studies, different strains of *E. huxleyi* respond differently to low pH conditions (Langer *et al*., 2009). Such factors greatly complicate the application of laboratory results to the field.

• Sensitivity differences between taxa may reflect species-specific responses to different carbonate chemistry variables, as well as differences in the ability of species and groups to regulate internal pH. Enzyme function, protein phosphorylation, and the carrying capacity of haemoglobin for O_2 are all pH-sensitive, and there is a metabolic cost in regulating pH to maintain these processes (Pörtner *et al*., 2011).

• For all organisms, prolonged exposure to pH values lower (or higher) than the conditions under which they evolved will require more energy for internal pH regulation, reducing the energy available for growth, maintenance or reproduction. Organisms with an active high-metabolic lifestyle, such as teleost fish and cephalopods (producing relatively high, but variable, levels of CO_2 internally through tissue respiration), may be better able to cope with future ocean acidification than those with low-metabolic life styles, such as bivalves and echinoderms (Melzner *et al*., 2009).

• For more sedentary species, even small changes in physiology or behaviour can produce major changes in population success under competitive environmental conditions. Indirect ecological implications may, however, not be apparent in relatively short-term laboratory experiments where food and nutrients are usually abundant, and competitors and predators absent.

Ecosystem responses in 'the real world'

In the seas around the UK (and elsewhere), biotic responses to future ocean acidification will occur on decadal timescales in the context of other environmental pressures, genetic variability/selection, and a very wide range of ecological interactions. Six main research approaches are now being used to investigate such factors:

i) inclusion of other stressors (primarily temperature) as well as pH/carbonate chemistry changes in experimental treatments;

ii) extending the duration of ocean acidification experiments to cover seasonal physiological cycles, likely to be temperature-linked, and (preferably) multi-generational responses;

iii) increased focus on reproductive processes and early life-cycle stages, potentially critical for population success;

iv) use of field mesocosms and other manipulations to investigate community-wide ecosystem responses to raised CO_2;

v) studies at CO_2 seeps and vents, where there has been the opportunity for natural adaption; and

vi) syntheses of information through ecosystem models that include trophic dynamics and pelagic-benthic interactions.

Around 20 published studies have now included the additional effect of increased temperature. As discussed by Wicks and Roberts (2012) and Hale *et al*., (2011), both synergistic and antagonistic effects can occur. Whilst understanding of that interaction is far from complete, CO_2 effects on thermal tolerance are closely linked to energy metabolism (Pörtner *et al*., 2011); furthermore, they, may vary across species' ranges, and are likely to be subject to adaptive evolution (Kelly and Hofmann, 2012).

Studies using naturally-high CO_2 environments [approach (v) above] have included those by Hall-Spencer (2008), Cigliano *et al*. (2010), Fabricius *et al*., (2011), Rodolfo-Metalpa (2011) and Johnson *et al*. (2012). Additional ecosystem-based insights are emerging, arising from the EU EPOCA and MedSeA projects (the former now completed), the German BIOACID programme and the UK Ocean Acidification research programme.

Biogeochemical responses to future ocean acidification

There is potential for many biogeochemical effects of ocean acidification, mostly mediated through biological processes. Table 2 (based on Gehlen *et al*., 2011) provides a summary of current understanding for 12 such processes, primarily open ocean, that may have significant climatic feedback. These are evenly divided – five each – between those that are likely to exert positive feedback (increasing atmospheric CO_2, and worsening climate change) and those that may have negative feedback; for two processes the direction is not known.

Greatest certainty, and largest long-term effect, is associated with the two chemical processes – changes in the CO_2 buffer factor and increased carbonate dissolution,. These have positive and negative feedback respectively. For all the biologically-mediated processes, the magnitude of effect is assessed as either medium or low; however, for most of these, the level of understanding is also rated as low, with a mixture of positive and negative climatic feedbacks.

For further discussion, see Gehlen *et al*. (2011), also companion papers by Weinbauer *et al*. (2011), Riebesell and Tortell (2011), Andersson *et al*. (2011), Widdicombe *et al*. (2011) and Hopkins *et al*. (2011).

Palaeo-precedents that may inform the future

The current rate of decrease in surface ocean pH due to rising atmospheric CO_2 is considered to be the most rapid global change in marine chemistry for at least 55 million years – and probably 300 million years (Zeebe and Ridgwell, 2011; Hönisch *et al*., 2012). Because of the different timescales of previous changes in atmospheric and ocean chemistry, caution is needed in using such events as analogues to current or future changes; nevertheless, the geological record does potentially provide insights into ecosystem impacts, scope for adaptation and rates of recovery.

The last time that atmospheric CO_2 has been as high as it is now (~390 ppm) was during the Pliocene, three million years ago (Seki *et al*., 2010). The higher CO_2 led globally to a ~3°C warming, with regional increases that were twice as high. The climate change led to latitudinal migration of organisms (as also occurred during the more recent glacial-interglacial cycles, although associated with CO_2 reductions rather than increases). However, because the change occurred over several millennia, without additional anthropogenic pressures, it did not cause large scale marine extinctions. The slower timescale also allowed for some $CaCO_3$ buffering to occur: ocean pH remained above 8.0, and no calcification response has been found (Zeebe and Ridgwell, 2011).

The late Cretaceous (97-66 million years ago) was another period with high CO_2, However, the Cretaceous ocean then had a two-fold higher Ca concentration, allowing low pH and low carbonate ion concentrations to co-exist with supersaturation of the surface ocean. Furthermore, the gradual increase of CO_2 and decrease in pH over millions of years would have allowed genetic adaptation to high CO_2 conditions.

The Palaeocene-Eocene Thermal Maximum (PETM) ~55 million years ago is considered to provide the best analogue for current/future ocean acidification. Sediments deposited in this period show a high degree of dissolution of carbonates with a geochemical signature indicating a massive carbon input and a transient temperature rise (Dickens *et al*., 1995; Speijer *et al*., 1997).

Biotic responses to the PETM were very different in planktonic and deep sea benthic ecosystems (Sluijs *et al*., 2007). Whilst the former showed major compositional changes, benthic organisms in the deep sea (mainly foraminifera) suffered ~40% extinction. Those that survived were either non-calcifiers, or were small and thin-walled suggesting low saturation conditions (Thomas, 2007; Ridgwell and Schmidt, 2010). A detailed analysis of marine ecosystem responses to PETM events is currently being carried out, with comparisons to present-day conditions (Gibbs *et al*., 2013; Figure 5).

3. KNOWLEDGE GAPS

The top priority knowledge gaps that need to be addressed in the short term to provide better advice to policy makers are:

a. A sustained, quality-controlled and global scale observational database to provide information on baseline

*Table 2: Summary of likely main effects of future ocean acidification (OA) on global-scale biogeochemical processes and feedbacks to the climate system via atmospheric CO_2 (+ve feedback,increasing CO_2; -ve, decreasing) based on Table 12.1 of Gehlen et al. (2011) and the ~70 references cited in that paper. Note that: this table focuses on water column effects in the open ocean; all processes except (1) and (5) involve indirect effects, mediated by marine biota (mostly phytoplankton, and bacteria); and information for processes (7) and (8) is based on Hopkins et al. (2011). Level of understanding: H, high; M, medium; L, low. * + ve feedback on global warming*

Process	Effect of future OA	Feedback	Magnitude	Level of understanding
1. CO_2 buffer factor	Decreased ocean uptake capacity	+ ve	Large	H
2. Photo-synthesis	Enhanced biological production and organic export from upper ocean	– ve	Medium	M
3. C:N ratio of biomass	Increased C;N ratio, affecting food quality and carbon export	– ve	Small to medium	L
4. Calcification	Overall decrease in biocalcification (but not all species/strains?)	– ve	Small to medium	L/M
5. Carbonate dissolution	Increased $CaCO_3$ dissolution in particles and sediments, increasing ocean alkalinity	– ve	Small in short-term; large in long-term	M
6. Ballast effect (sinking particles)	Decreased $CaCO_3$ production will reduce organic matter export	+ ve	Small to medium	L
7. Dimethyl suphide (DMS)	Reduced DMS production	[+ ve]*	Small?	L
8. Organo-halogens	Contradictory evidence: both enhancement and reduction may occur	?	Small?	L
9. Nitrogen fixation	Enhanced N_2 fixation – with enhanced biologicalproduction	– ve	Medium	M
10. Oxygenation	Shallower remineralization increases O_2 demand; expansion of low O_2 regions	+ ve	Medium	L
11. Nitrification	Reduced nitrification	?	Small	L
12. Nitrous oxide production	Decreased O_2 levels wil increase N_2O production	+ ve	Medium	L

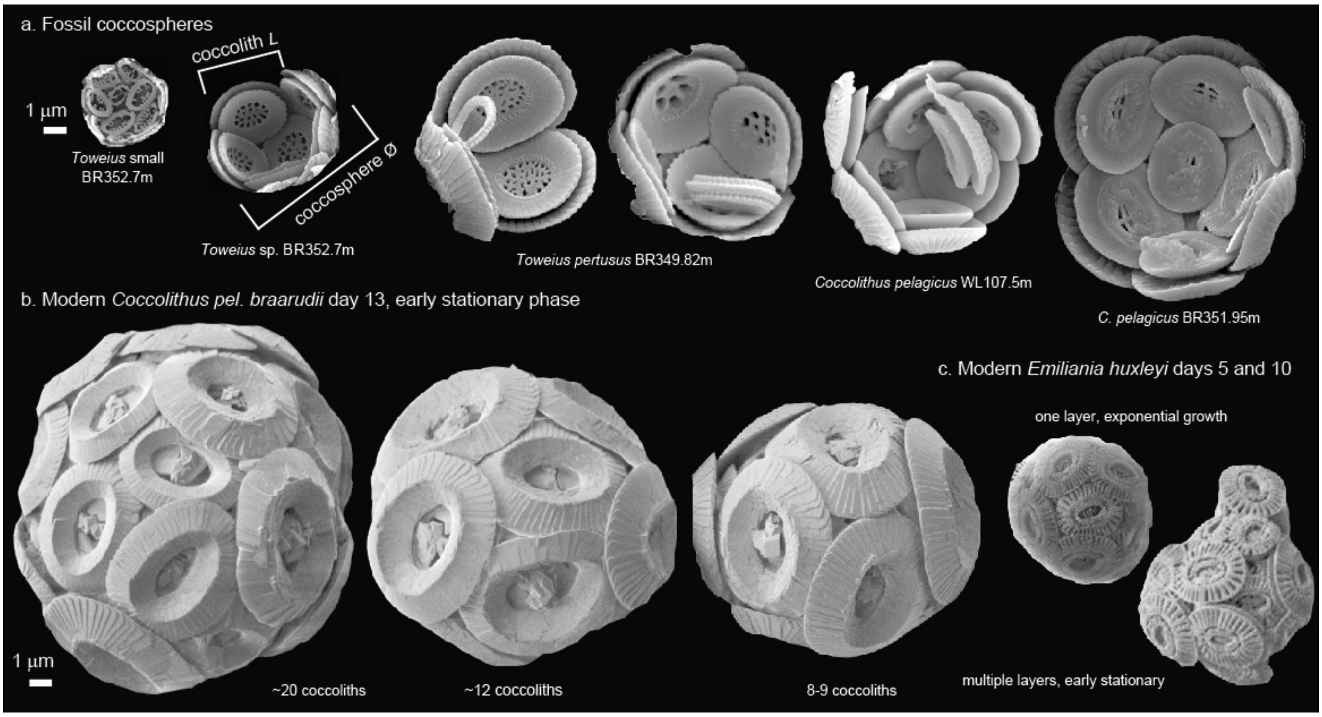

Figure 5: Past ocean acidification events are being studied to provide insights into potential future changes. The image shows fossil (above) and modern (below) coccospheres used for an analysis of environmental factors affecting growth rates of calcified marine micro-plankton, with fossil material from the Palaeocene-Eocene Thermal Maximum ~55 million years ago (Gibbs et al., 2013; figure re-use by permission from Macmillan Publishers Ltd..

conditions, variability and trends in the carbonate chemistry system in coastal waters, shelf seas and the open ocean.

b. Improved understanding of the impact of future ocean acidification on ecologically- and economically-important marine organisms, taking into account the full life cycle and physiology of individuals, environmental variability in seawater chemistry, potential adaptation, other stressors and ecological interactions.

c. Improved understanding of the impact of future ocean acidification on biogeochemical processes and their potential feedback to CO_2 and climate, considered over the full range of ecologically-important scales. Hence, with (2) above, improved understanding of the impact of changing ocean chemistry on the goods and services provided by the marine environment.

4. SOCIO-ECONOMIC IMPACTS

The 2010-2011 MCCIP review of ocean acidification (Turley *et al*., 2010) provided a relatively detailed review of how ocean acidification might affect marine goods and services of socio-economic value. Such information has been updated by Turley and Boot (2010, 2011), Pinnegar *et al*., (2012) and Hilmi *et al*., (2013). As shown in Figure 6, the linkage between direct effects and socio-economic consequences is not straightforward. The goods and services potentially affected can be grouped as provisioning, regulating, cultural and supporting (Beaumont *et al*., 2008; UK National Ecosystem Assessment, 2011), providing benefits at several levels (local, national, European and global) and to different societal groups and institutions (individuals, private sector and public bodies).

As discussed in Section 1.2.2 above, ocean acidification is likely to impair calcification in marine organisms with calcium carbonate structures, e.g. the shells of most molluscs, the carapaces of crustaceans and echinoderms, and the skeletal framework of corals. These groups (particularly molluscs and crustaceans) include many commercially-valuable species: ocean acidification could therefore lead to a reduction in their harvest, with associated loss of revenue and jobs.

Thus, if the future effect of ocean acidification were to be a 10-25% reduction in growth/calcification of shellfish that could in turn result in an overall 10-25% loss of shellfish harvest, both from free-living populations and from aquaculture – with total UK economic losses estimated at £100 - 500 million per year by 2080, depending on CO_2 emission scenarios (Pinnegar *et al*., 2012; 2013). However, such an extrapolation may be over-simplistic, since there is a wide range in species' vulnerability. Thus some species may be unaffected, at least directly, whilst the most sensitive ones may experience near-total recruitment failure (Barton *et al*., 2012). There may also be indirect effects mediated through food-webs (Le Quesne and Pinnegar, 2012), together with interactions with other stressors, likely to have increasing future importance (Melzner *et al*., 2012; Turley *et al*., 2012) and with combined effects that could be additive, synergistic or antagonistic. More optimistically, there might also be inter-generational adaptation to high CO_2 conditions, by at least some groups (Kelly and Hofmann, 2012).

Adult teleost fish are generally considered tolerant of high CO_2 conditions (Melzner *et al*., 2009). Nevertheless, that does not mean that finfish fishery yields will be unaffected by ocean acidification, since:

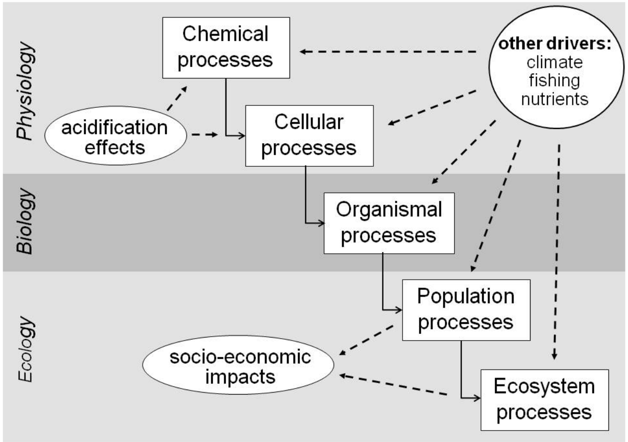

Figure 6: The relationship between acidification effects, biological complexity, other drivers and socio-economic impacts. Redrawn from Le Quesne and Pinnegar (2012).

Figure 7: The sensitivity of herring larvae to the combined and separate effects of high CO_2 and temperature are being investigated. Image: R Shields, Swansea.

• Most, if not all, commercially-important species are trophically connected to calcifying groups, at least at some stage in their life cycles e.g. importance of crustaceans and pteropods in diet of salmonids (although with scope for diet changes by some groups; Le Quesne and Pinnegar, 2012)

• Ocean acidification may affect sensory perception and larval behaviour of some fish, with implications for population success (Munday *et al*., 2009, 2010; Simpson *et al*., 2011).

•Larval stages are more sensitive; for cod, developmental effects of high CO_2 have been shown (Frommel *et al*., 2012), although at levels that are much higher (1,800 ppm) than those expected to be widely encountered in coastal habitats.

The physiological effects of changes in carbonate chemistry and interactions with temperature are currently being investigated for the larvae of a range of commercially-important species, including *Nephrops*, herring (Figure 7), sea bass and flatfish, as part of the UK Ocean Acidification research programme and by Cefas Weymouth.

Warm and cold-water corals represent further components of the marine environment delivering high value goods and services that are threatened by ocean acidification. (Hoegh-Goldberg *et al*., 2008; Veron *et al*., 2009; Maier *et al*., 2012). Through their direct provision of food and income, and indirect benefits for tourism and limiting coastal erosion, the total economic value of warm-water coral reefs has been estimated at around US$ 30 billion pa (Cesar *et al*., 2003). The combined effects of different stressors is of particular concern with regard to the structural integrity of coral reefs, and the habitat they provide for other marine organisms: covering less than 1% of the Earth's surface, coral reefs are nevertheless home to ~25% of all fish species.

The role of ocean biogeochemistry in the global carbon cycle and climate regulation is hard (but not impossible) to quantify in economic terms (Mangi *et al*., 2011). Whilst the overall direction of effects of future ocean acidification is currently uncertain, as discussed above (e.g. Table 2) the risk of significant adverse impacts, via positive feedbacks, cannot be ruled out and continues to give cause for concern. At the UK/European scale, CO_2-related changes to coupled sediment and pelagic biogeochemical processes are potentially the most important, closely linked to other environmental changes.

5. CONFIDENCE ASSESSMENTS

The literature on ocean acidification is growing very rapidly (Gattuso and Hansson, 2011). Since the previous MCCIP review of this topic (Turley *et al*., 2010), it has increased by more than 300 papers per year, nearly doubling the total (EPOCA database; summary graph in Laffoley and Baxter, 2012). Under such circumstances, one might expect scientific confidence to have risen, and that is true for many aspects, Nevertheless, key uncertainties in several areas have still to be satisfactorily resolved, and some may have increased, due to the increased awareness of: i) spatial and temporal variability in physico-chemical conditions (at local levels and short timescales, rather than global and annual/decadal); ii) the inter- and intra-specific spectrum of biological responses, and iii) the importance of multiple stressors, the potential for adaptation and the role of competitive interactions in determining population- and ecosystem-level responses.

Such complexity makes it hard to reduce the totality of information on ocean acidification and its effects to a handful of summary statements, with semi-quantitative estimates of their current confidence. Nevertheless, recent attention has been given to synthesis activities, including: the book Ocean Acidification (eds. Gattuso and Hansson; 2011); input to the 5th Assesment Report of the Intergovernmental Panel on Climate Change (IPCC), currently in preparation; and an expert survey on the scientific confidence relating to current understanding of ocean acidification and its impacts (Gattuso *et al*., 2013).

Table 3 summarises information from Gattuso *et al*. (2013), providing data on experts' certainty, expressed as percentages, of 22 statements. For all but one of those statements, the median confidence value is >67%, hence can be considered 'high' on a low-medium-high scale covering the range 0-100%. However, the confidence in statements relating

Table 3: Summary of information on confidence in statements on ocean acidification and its impacts by experts (n = 53); data from Gattuso et al. (2012) with sequence of statements re-arranged in order of median confidence estimates. Colour coding relates to topic area; see key below. The assistance of Dawn Ashby in re-presenting these data is gratefully acknowledged.

to chemical topics was generally higher than for biological topics, in turn higher than for socio-economic topics. The confidence assessments given here (below) draw strongly on that data, combining some of the statements and focusing on aspects of particular interest to MCCIP.

What is already happening?

Anthropogenic ocean acidification is caused by CO_2 emissions to the atmosphere; it is occurring with measurable chemical consequences, at a faster rate than any equivalent natural change in the past 55 million years.

Level of agreement / consensus	Amount of evidence	Overall confidence
High	High	High

Marine organisms vary in their vulnerability to ocean acidification; some of those that are sensitive may have already been impacted where pH is naturally low, e.g. coastal upwelling.

Level of agreement / consensus	Amount of evidence	Overall confidence
High	Medium	Medium

If a single confidence assessment is required for "what is already happening", the most appropriate level is considered to be 'high' (i.e. not changing since 2010), although covering a wide range of aspects with different component uncertainties, as indicated above and in previous text.

What could happen?

The magnitude of future ocean acidification depends on anthropogenic CO_2 emissions: without rapid and strong mitigation, polar regions will become undersaturated for calcium carbonate within decades, with global average pH in the upper ocean being in the range 7.7 -8.0 by 2100. Subsequent recovery would take thousands of years.

Level of agreement / consensus	Amount of evidence	Overall confidence
High	High	High

Future ocean acidification under current trends would have serious impacts on marine biodiversity, ecosystem functions, and biogeochemical processes in UK seas and globally, with potentially significant climatic feedbacks.

Level of agreement / consensus	Amount of evidence	Overall confidence
High	Medium	Medium

Future ocean acidification under current trends would also have substantive impacts on a range of ecosystem services; however, complex processes and interactions are involved, and the scale of socio-economic impacts is currently uncertain.

Level of agreement / consensus	Amount of evidence	Overall confidence
Medium	Low	Low

If a single confidence assessment is required for "what could happen", the most appropriate level is considered to be 'medium' (i.e. not changing since 2010), although covering a wide range of aspects with different component uncertainties, as indicated above and in previous text.

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