5 Acidification and its effect on the ecosystems of the ICES Area

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5.1 Introduction

This section focuses on the impacts of ocean acidification (OA) on ecosystems and higher trophic levels in the ICES Area. One of ICES distinguishing features is its access to scientists across the entire marine field; this section is based on the Report of the Workshop on the Significance of Changes in Surface CO_2 and Ocean pH in ICES Shelf Sea Ecosystems (WKCpH; ICES, 2007c), updated to include recent research, using inputs from the chairs of ICES working groups.

A number of collections of papers have been published recently in peer-reviewed journals, notably "The ocean in a high-CO_2 world II" (Gattuso et al., 2008; available online at: http://www.biogeosciences.net/special_issue44.html), and these are referred to in the text whenever relevant to impacts on ecosystems.

More general background on the chemical and physical effects of OA can be found in the freely available reports of scientific bodies or governmental institutions, such as the Intergovernmental Panel on Climate Change (IPCC, 2005), the National Oceanic and Atmospheric Administration/National Science Foundation/US Geological Survey (NOAA/NSF/USGS; Kleypas et al., 2006), and the German Advisory Council on Climate Change (WBGU, 2006), as well as in recent journal articles about the historical context (e.g. Pelejero et al., 2010), and in papers in the five 2011 special issues of the online journal *Biogeosciences* (available at: http://www.biogeosciences. net/volumes_and_issues.html.

Oceanic uptake of atmospheric CO_2 has led to a perturbation of the chemical environment, primarily in ocean surface waters, which is associated with an increase in dissolved inorganic carbon (DIC). The increase in atmospheric CO_2 from ca. 280 ppmv (parts per million by volume) 200 years ago to 390 ppmv today (2011) has most probably been caused by an average reduction across the surface of the oceans of ca. 0.08 pH units (Caldeira and Wickett, 2003) and a decrease in the carbonate ion (CO_3^{2-}) of ca. 20 μmol kg^{-1} (Keshgi, 1995; Figure 5.1). It has been estimated that the level could drop by a further 0.3–0.4 pH units by the year 2100 if CO_2 emissions are not regulated (Caldeira and Wickett, 2003; Raven et al., 2005). A study of potential changes in most of the North Sea (Blackford and Gilbert, 2007) suggests that pH change this century may exceed its natural annual variability. Impacts of acidity-induced change are likely, but their exact nature remains largely unknown, and they may occur across the whole range of ecosystem processes. Most work has concentrated on open-ocean systems, and little research has been applied to the complex systems found in shelf-sea environments.

5.2 Evidence for pH change in the water column

A small number of long-term (>10 years) observatories have recorded atmospheric carbon dioxide (pCO_2) in both the atmosphere and the water column (Figure 5.2a). A strong seasonal cycle is observed in pCO_2, caused by variations in temperature and biological drawdown resulting from photosynthesis and respiration; therefore, a minimum record of 10 years is required to estimate a meaningful average and deduce any trend. These stations are relatively rare, with limited geographic coverage. The principal stations are the Hawaii Ocean Time-series (HOT, Figure 5.2 lower graph),

the Bermuda Atlantic Time-series Study (BATS), and the European Station for Time Series in the Ocean (ESTOC), situated off the Canaries. All of these time-series demonstrate high natural variability, but all confirm that pH is decreasing. Owing to instrument limitation, many of the historical measurements of pH are of limited accuracy, and those prior to the 1970s are suspect and generally not reliable. Consequently, care must be taken when using pre-1970s datasets, because potential sampling bias and geographic variation can lead to erroneous interpretation of results. In the deep ocean, the natural pH range and likely future change is a function of depth, with the greatest variation at the surface. In contrast, in shelf seas, which are well mixed in winter, even benthic organisms are exposed to a full range of pH variation and will soon experience the effects of increased levels of atmospheric CO_2.
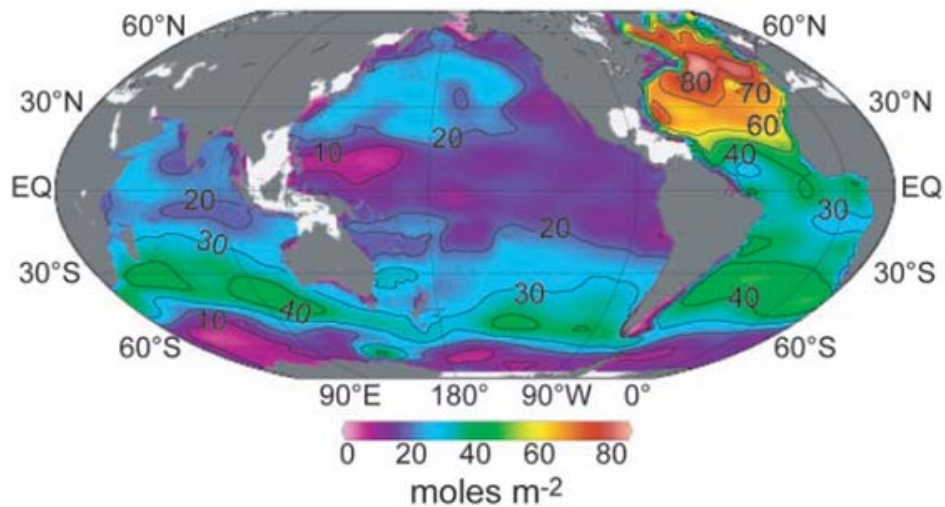

Figure 5.1. Worldwide distribution of Oceanic uptake of anthropogenic CO_2 (mol m^{-2}). This increase is greatest in the ICES region. (Source: Sabine *et al.*, 2004. Courtesy of *Science*.)

5.3 The historical context to changes in oceanic pH

Boron isotopes in fossil foraminifera from seabed sediment cores can be used to reconstruct past records of pH. The record (Figure 5.3) from the eastern equatorial Atlantic demonstrates the change in pH over the past 650 000 years, revealing a cyclical pattern that is associated with alternating glacial/interglacial periods. Present-day measurements of pH are comparable with the lowest values estimated in the past, with a transition from low to high pH states at intervals of ~50 000 years. From an historical perspective, the present levels of pCO_2 are already high, and anthropogenic emissions are further increasing the natural concentration. Natural cycles in seawater pH could enhance or mitigate the vulnerability of marine organisms to future OA. Catastrophic events in the past, associated with the Palaeocene−Eocene Thermal Maximum (PETM), suggest that the saturation state was important, and the record also suggests that, once established, high pCO_2 levels persist for thousands of years (Pelejero and Calvo, 2007).

5.4 Model predictions

The saturation depth (or horizon) is the depth at which a shell or bone made of calcite or aragonite would dissolve if there were no biological activity. Figure 5.4 shows a modelled estimate of the aragonite saturation horizon produced by Orr *et al.* (2005). The map shows that, in the Southern Ocean, aragonite in shells will dissolve at all depths. In the North Atlantic, bottom-dwelling organisms will be affected, and only those in relatively shallow areas will remain viable. The calcite/aragonite ratio is

species-dependent; thus the difference between these two saturation conditions gives rise to species-dependent responses to future conditions. In waters below the saturation horizon, shell formation will be at a substantial metabolic cost.

In future, in upwelling areas, it is likely that intermediate waters from below the depth of the aragonite-saturation horizon, which are rich in CO_2, will be upwelled onto the shelf, as is now occurring off the Oregon coast (Chan *et al.*, 2008). In some cases, such as the Baltic, low saturation states are already occurring because the low-alkalinity waters in this brackish sea afford little buffering (Figure 5.5).
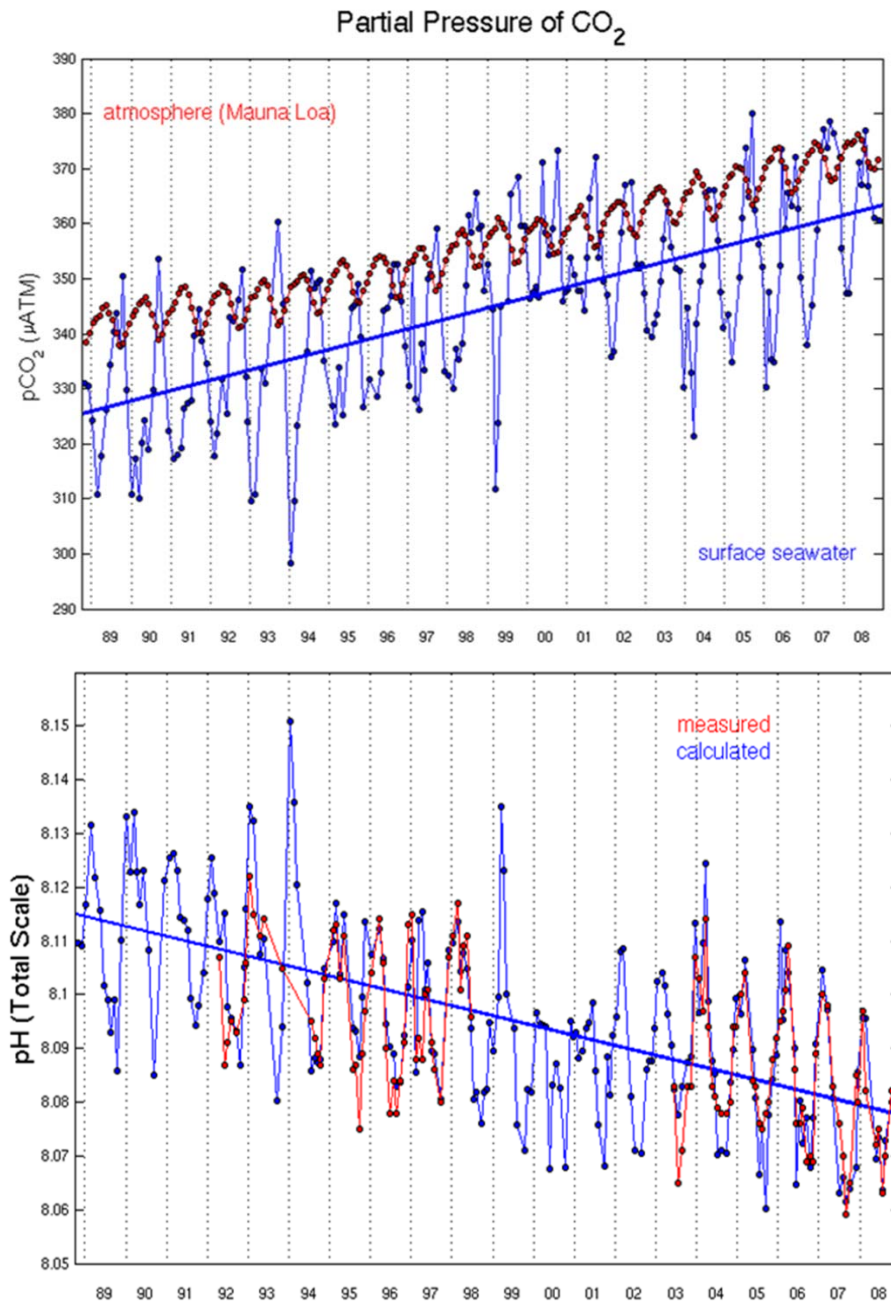

Figure 5.2. (upper graph) Time-series (1989–2008) of the change in pCO₂ (atmosphere and seawater). (lower graph) The pH change in seawater as recorded at the Hawaii Ocean Time-series (HOT) site, showing a decline in pH over 20 years of 0.03 units, which is approximately half the annual variability. (Figures supplied by HOT.)
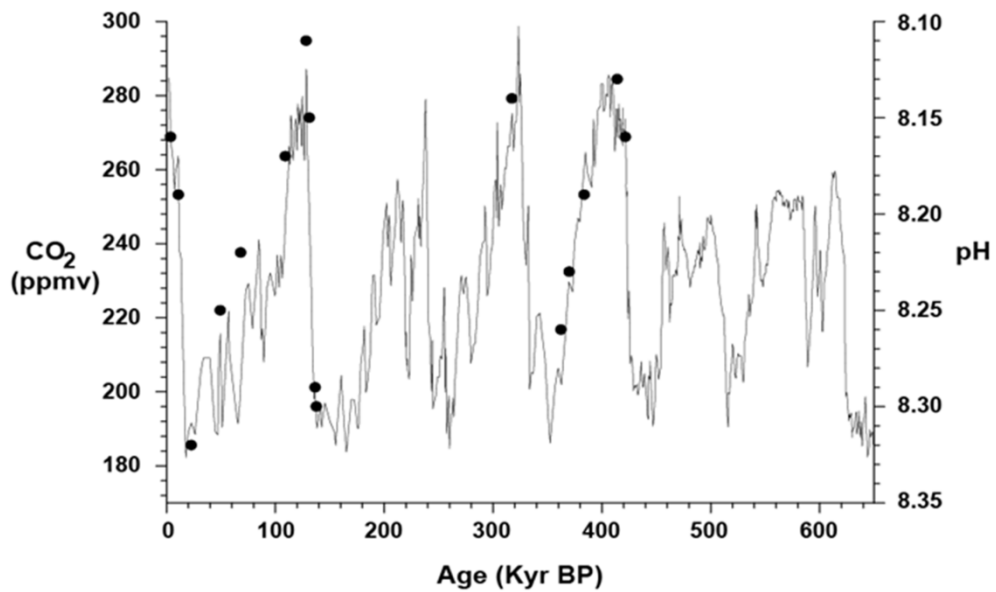
Figure 5.3. Estimated sea surface pH (solid circles) reconstructed using boron isotopes in planktonic foraminifera from a sediment core (ODP668B) retrieved in the eastern equatorial Atlantic (Hönisch and Hemming, 2005), superimposed on the record of atmospheric CO₂ (Petit *et al.*, 1999; Siegenthaler *et al.*, 2005). Redrawn from Pelejero and Calvo (2007).
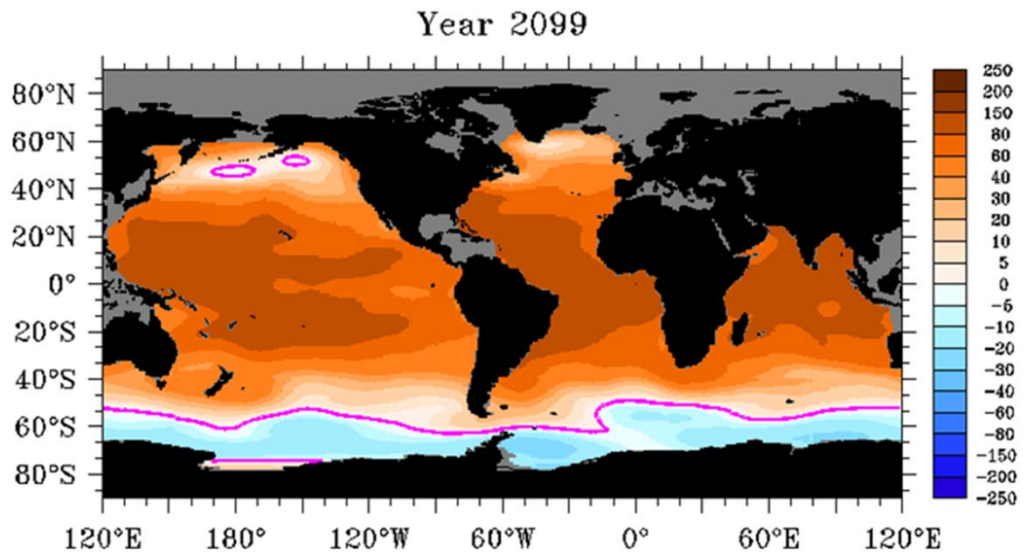

Figure 5.4. Global model predictions for 2099 of the depth (m) of aragonite saturation, i.e. the depth at which dissolution of aragonite occurs. (Source: Orr *et al.*, 2005; courtesy of *Nature*.)

5.5 Effect of pH (and temperature) changes on metals and contaminants

In addition to the chemical changes within the carbonate system of the oceans, other potential impacts on chemical speciation (e.g. metal and contaminant availability) must also be considered. Many metals and organic contaminants in the marine environment are bound, either by adsorption onto particles (of inorganic sediment, or of suspended or dissolved organic matter) or by complexing agents, such as metal-binding ligands. They may even be adsorbed onto plastic particles, which are commonly found in sediments and the water column. Their availability to biota or other chemical reactions depends on their binding coefficients (i.e. their adsorption–desorption behaviour). Temperature and pH are the key parameters in the regulation of binding processes. The predicted decrease in pH and increase in temperature may

not be significant in regulating the availability of many organic contaminants in the short-to-medium term, but in some circumstances, such as metal complexation, the changes could lead to increased bioavailability of previously bound metals. In certain circumstances, some metals that are essential trace nutrients (e.g. iron) may be limiting to phytoplankton growth or toxic (e.g. free copper or organotins).

Organic metal complexes are known to play a significant role in the geochemical cycle of reactive trace metals (Hirose, 2002), and changes in the equilibrium between bound and free-metal ions result from an increase in hydrogen ion concentration. Importantly, marine microalgae process and excrete metal-binding ligands that allow them to obtain competitive advantages over other species in sequestering metals (Vasconcelos *et al.*, 2002); consequently, they can have an important influence on heavy-metal concentrations in seawater (González-Dávila, 1995). It is, therefore, likely that future changes in pH will influence metal complexation, which in turn may have a substantial impact on biota, either toxicologically or via ecosystem processes, such as microalgal bloom dynamics.

The potential for increased concentrations of CO_2 to alter the fate and transport of trace metals in sediment and seawater has recently been investigated in controlled experiments by Ardelan *et al.* (2009). Toxicological effects of changes in contaminant availability and fate caused by climate change have been described by Noyes *et al.* (2009), and the specific case of a climate impact on contaminants in the Arctic was the subject of a paper by Donald *et al.* (2005). It can be concluded that there are still many uncertainties regarding the exact influence of acidification on ocean chemistry with respect to metals and contaminants, but that the topic is worthy of consideration when trying to evaluate potential impacts of climate change and acidification on marine ecosystems.
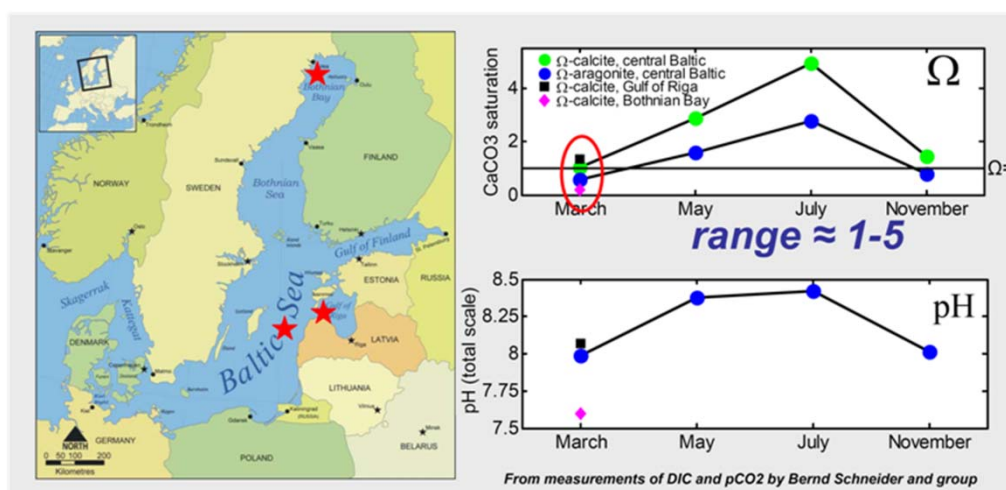

Figure 5.5. Low saturation state (Ω) in the Baltic. Note: aragonite saturation is below 1, although pH is not very low, because of low total alkalinity. (Source: Tyrell *et al.*, 2008.)

5.6 Impacts on calcifying organisms in the water column

Research into water-column processes has focused primarily on those organisms that calcify. This group includes the coccolithophores, pteropods, and foraminifera, of which the first two are important in the carbon cycle but do not constitute a major food source.

5.6.1   Coccolithophores

Emiliania huxleyi is numerically the most abundant coccolithophore in the ocean and became prominent during glacial periods of enhanced ocean productivity. The species, which is ubiquitous in the ICES Area (De Bodt *et al.*, 2010), forms a major sink of carbon and is responsible for one-third of the production of marine calcium carbonate (Iglesias-Rodríguez *et al.*, 2008). Coccolithophores are important because they both fix carbon and photosynthesize (Figure 5.6).
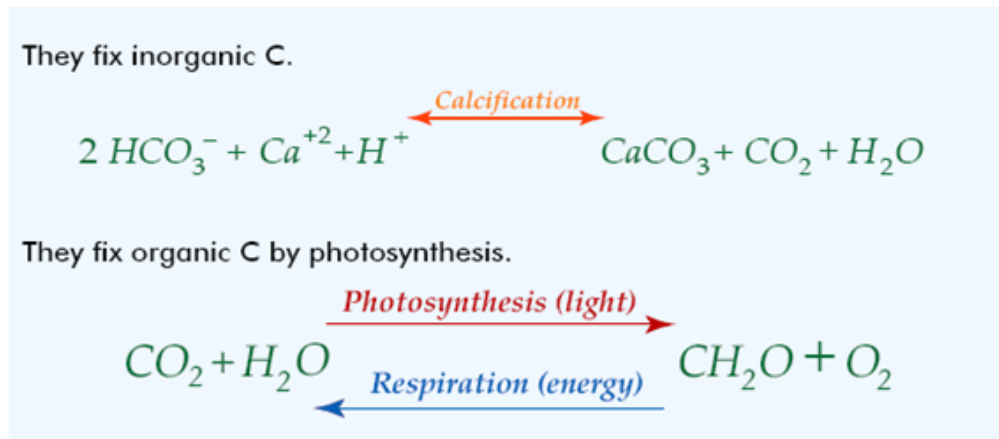
They fix inorganic C.

$$2\ HCO_3^- + Ca^{+2} + H^+ \xleftrightarrow{\ Calcification\ } CaCO_3 + CO_2 + H_2O$$

They fix organic C by photosynthesis.

$$CO_2 + H_2O \underset{Respiration\ (energy)}{\overset{Photosynthesis\ (light)}{\rightleftarrows}} CH_2O + O_2$$

Figure 5.6. The function of coccolithophores in the fixing of carbon from the oceans and the drawdown of CO_2.

The majority of experiments (Riebesell *et al.*, 2000; Suggett *et al.*, 2007; also Figure 5.7) demonstrate the dissolution of liths when exposed to increased concentrations of CO_2. Others demonstrate reduced calcification rates (De Bodt *et al.*, 2010) corresponding to a reduction in the availability of carbonate ions. Other recent work, looking at changes over a longer term, indicates that, despite a decreasing pH, the net primary production is increasing, with a 40% increase in coccolithophore mass over the past 220 years (Iglesias-Rodríguez *et al.*, 2008). This apparently contradictory message may be the result of differences in methodology or in the time-scale associated with the experiments. The sudden changes in pH experienced by organisms in experiments may not be representative of possible adaptation over a longer natural time-scale. However, it should be noted that predicted changes in pH over the next 80 years, as simulated by many experiments, are much greater than those experienced over the past 220 years.

An additional consideration is that the increase in aqueous CO_2 will favour an increase in photosynthesis and thus increase the energy available to a cell. Depending on the species involved, this increase may offset the additional metabolic cost of making liths because of the reduced availability of carbonate ions. Different strains of *E. huxleyi* have responded in different ways (Suggett *et al.*, 2007), so although one strain may suffer from acidification, the species is likely to survive and, more broadly, may be replaced by another with a similar function.
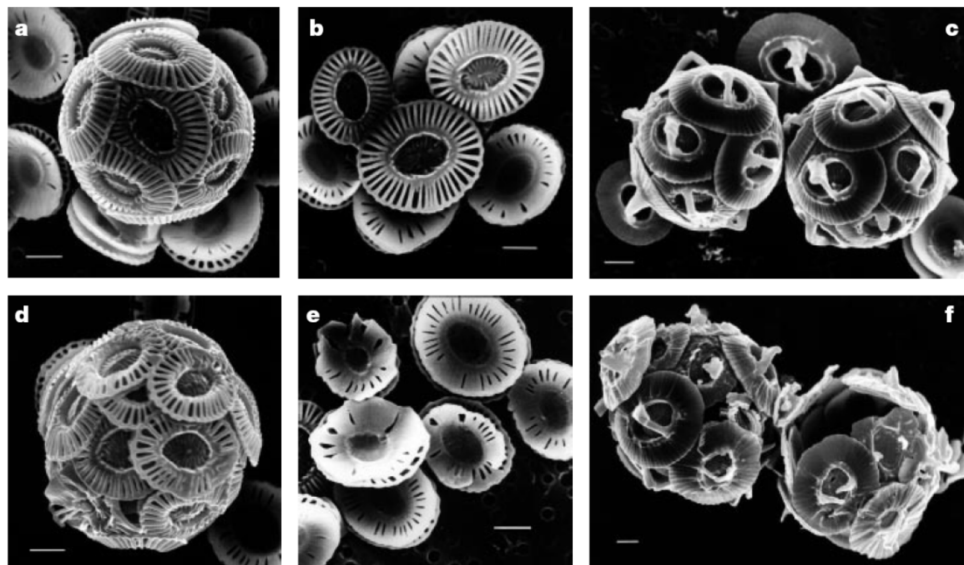
Figure 5.7. Scanning electron microscopy (SEM) photographs of coccolithophorids under different CO_2 concentrations: *Emiliania huxleyi* **(a, b, d, and e) and** *Gephyrocapsa oceanica* **(c and f) collected from cultures incubated at levels corresponding to pCO_2 levels of about 300 ppmv (a, b and c) and 780–850 ppmv (d, e, and f). Scale bars represent 1mm. Note the difference in the coccolith structure (including distinct malformations) and in the degree of calcification of cells grown at normal and elevated CO_2 levels. (Source: Riebesell** *et al.,* **2000; courtesy of** *Nature***).**

5.6.2 Pteropods

In the Barents Sea, pteropods (sea butterflies), which have calcareous shells, are a significant food source for herring (*Clupea harengus*), cod (*Gadus morhua*), and haddock (*Melanogrammus aeglefinus*), whereas, in the Southern Ocean, they are consumed by zooplankton and whales. Herring are an important part of the ecosystem because the adults are commercially valuable and the juveniles are an important food source for fish such as cod, and for marine mammals and seabirds. As the saturation of aragonite, the mineral that constitutes most of the shell, falls below 1, the shell should begin to dissolve (Figure 5.8). Thus, by 2040, there could be notable effects on pteropods in northern waters. When saturation is <1, these organisms are likely to experience an enhanced metabolic (sublethal) cost to maintaining their skeleton. A recent paper (Comeau *et al.*, 2009) has quantified this effect and suggests a 28% reduction in calcification at the pH values predicted to occur by 2100.
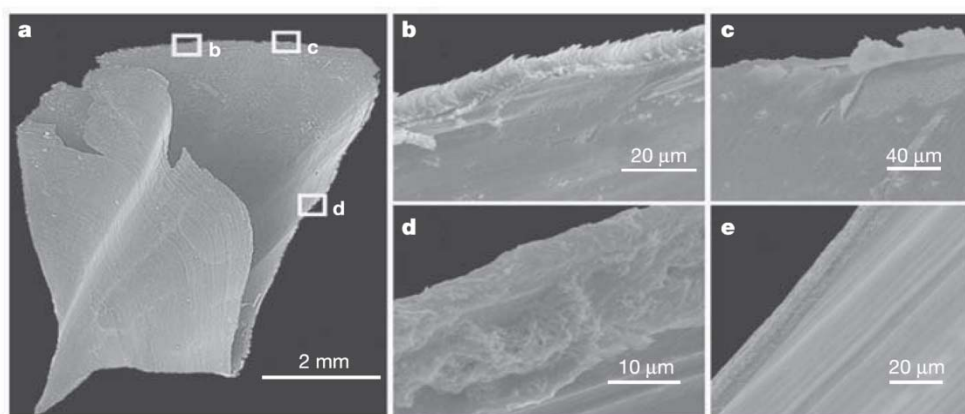

Figure 5.8. The effects of higher pH on the shell formation of pteropods. (Source: Orr *et al.,* **2005; courtesy of** *Nature.)*

Ocean acidification can have multiple impacts on marine phytoplankton, either directly (by affecting their metabolism) or indirectly (by changing the ecosystem around them to make them more or less competitive). Direct effects include the speciation of nutrients that are strongly pH-dependent (e.g. nitrogen, phosphorus, and silicon). As successful growth depends on nutrient affinity, particular groups of phytoplankton can be positively or negatively selected (Turley *et al.*, 2009). The process of photosynthesis is favoured by an increase in CO_2 and may enhance plant growth. Thus, there will be winners and losers (Figure 5.9), depending on which species or groups are affected, in what manner these changes can alter productivity, and on feedback from biogeochemical cycles. Phytoplankton also play an important role in the stabilization of climate by influencing the partitioning (exchange) of climate-relevant gases (e.g. CO_2) between the ocean and atmosphere (Rost *et al.*, 2008). The potential direction (positive or negative) of this exchange is at present unknown.
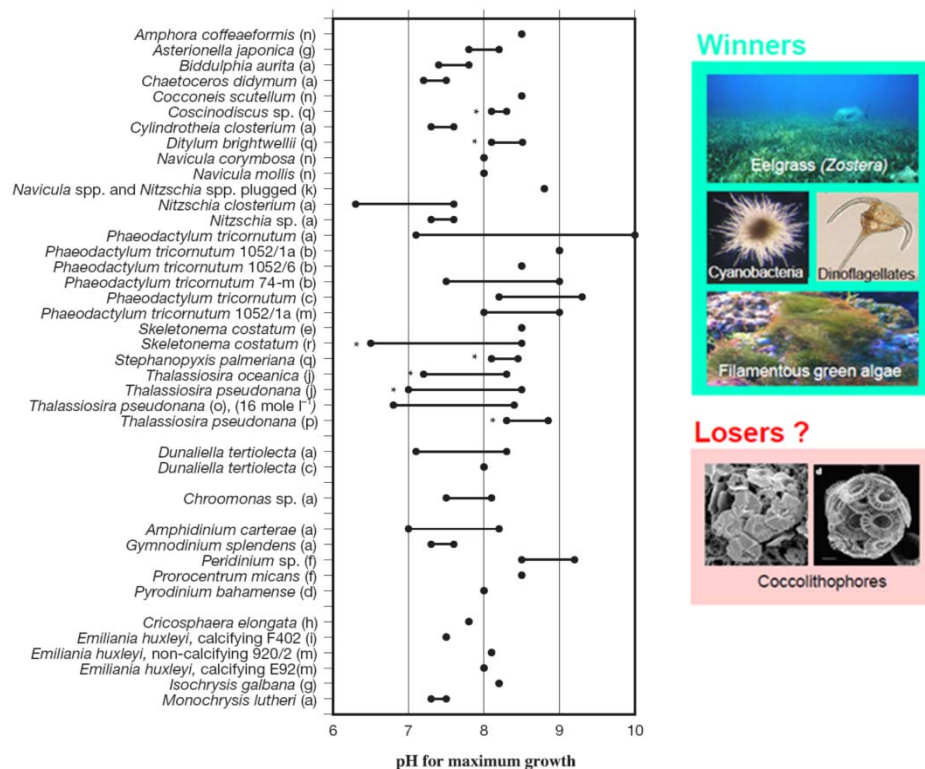

Figure 5.9. There will be winners and losers in a response to future change. Preferred pH range for a number of phytoplankton species/taxa. (Source: Hinga, 2002.)

5.6.3 Diatoms

Experimental studies of diatoms have demonstrated a resilience to changes in CO_2 concentration with respect to the process of silicification (Rost *et al.*, 2008), although shifts in their composition and dominance in phytoplankton communities in the equatorial Pacific and the Southern Ocean have been observed at different levels of CO_2 (Tortell *et al.*, 2002; Tortell and Long, 2009). These studies have demonstrated that elevated CO_2 concentrations lead to an increase in primary production and favour the growth of larger chain-forming diatoms.

5.6.4 Dinoflagellates

Although this group is ecologically and economically important, knowledge of the uptake of inorganic carbon by dinoflagellates is relatively limited (Hansen, P.J., *et al.*, 2007). Dinoflagellates are known to be able to accumulate inorganic carbon by involving the active uptake of either CO_2 or bicarbonate (HCO_3), or both, at up to 70-fold the ambient concentration (Berman-Frank *et al.*, 1998). In communities where other phytoplankton populations decrease in response to low pH, dinoflagellates, with greater resilience to acidification, may prosper. One subgroup of dinoflagellates form calcareous resting cysts (e.g. *Calciodinellum levantium*; Meier *et al.*, 2008). Calcification rates for these dinoflagellates may be affected in future by an expected change in the saturation state of the ocean.

5.6.5 Cyanobacteria

Nitrogen-fixing cyanobacteria provide a biological source of new nitrogen for large parts of the ocean (Barcelos e Ramos *et al.*, 2007) and are involved in photosynthesis, being responsible for up to 60% of primary production in low-productivity areas (Iturriaga and Mitchell, 1986). This group is one of the potential winners under projected climate conditions of high pCO_2. Experiments (Barcelos e Ramos *et al.*, 2007; Hutchins *et al.*, 2007; Levitan *et al.*, 2007) have demonstrated enhanced cell-division rates, increased CO_2 fixation (up to 128%), and increased N_2 fixation (100%) under future scenarios of CO_2 concentration compared with present conditions. Such changes could enhance the productivity of nitrogen-limited oligotrophic oceans and increase biological carbon sequestration.

5.6.6 Bacteria, Archaea, and viruses

The increase in CO_2 in the surface ocean and the concomitant reduction in pH may have many direct and indirect effects on microbes and the ecosystem processes in which they are involved (Hutchins *et al.*, 2009). At the organism level, physiological transformations, such as inorganic carbon fixation (photosynthesis by cyanobacteria, chemosynthesis by nitrifying proteobacteria and Archaea, and dinitrogen fixation by diazotrophs, such as *Trichodesmium* and *Crocosphaera*), depend on the availability of dissolved CO_2. However, physiological enhancement is taxon-specific and may not be evident if the present-day pCO_2 is already saturated by virtue of carbon-concentrating mechanisms. Whether or not these mechanisms might be relaxed to compensate for higher pCO_2 is another, as yet unresolved matter.

At the community level, the effect of raised pCO_2 in perturbation experiments suggests little impact on heterotrophic bacterial diversity (Woolven-Allen, 2008). However, experimental simulation of OA indicates the potential for a weakened biological carbon pump because of increased microbial respiration associated with enhanced degradation of polysaccharides (Piontek *et al.*, 2009). More importantly, it is known that the acid−base balance in seawater affects the availability of nutrients to all microbes, not just those that fix CO_2. In a scenario of future losers and winners, ocean nitrification may become inhibited at lower pH because of a reduction in the availability of ammonia to chemoautotrophs; however, more ammonia may be diverted to other microbes, such as photoautotrophic picocyanobacteria, that are well adapted to assimilate this form of reduced nitrogen. However, most marine microbes are not obligate autotrophs but are heterotrophic or parasitic (viruses); thus, the effect of acidification is via propagation through the microbial loop and the viral shunt. In other words, because they do not get energy from photosynthesis but feed on other organisms, they rely on their hosts.

It appears, therefore, that the impact of OA on microbes cannot be predicted solely from the outcome of isolated cause-and-effect relationships. Exogenous disturbance of microbial foodwebs can lead to counterintuitive changes because of complexity in system constraints, such as elemental stoichiometry (Thingstad *et al.*, 2008). Plausible scenarios may be developed based on knowledge of structure and function in present-day microbial foodwebs, but biological adaptation and evolution may limit the time-domain to which these scenarios apply.

Some definitions

Phototrophs get their energy from sunlight, *lithotroph*s from inorganic compounds, and *organotrophs* from organic compounds. The *viral shunt* is the process that moves material from heterotrophs and photoautotrophs into particulate organic matter (POM) and dissolved organic matter (DOM). The *microbial loop* describes the process by which bacteria consume DOM and thus balance the viral shunt. These systems are important for the control of macronutrients to pico-, nano-, and phytoplankton.

In terms of the secondary effects of microbial processes, ecological interaction becomes an important consideration in assessing the pathway and strength of the acidification signal through the system. It may be presumed that the net outcome of these potentially opposing effects will predict the fate of a virus specific to a given host. However, a contradictory association of lower viral production with higher host abundance has been found under conditions of elevated CO_2, apparently because of altered host–virus interaction (Larsen *et al.*, 2008).

5.7   Impacts of high CO_2 on the physiology of invertebrates and fish

A range of direct physiological impacts of OA have been suggested (Fabry *et al.*, 2008; Figure 5.10); some may be common across many higher taxa, whereas others are specific to individual species or limited groups of species. Although notable work on physiological impacts has been conducted, knowledge is still limited to a few species and often to only short-term experiments. Some studies have reported apparently contradictory results. It is not yet clear whether these contrasts represent methodological differences or reflect true physiological features.
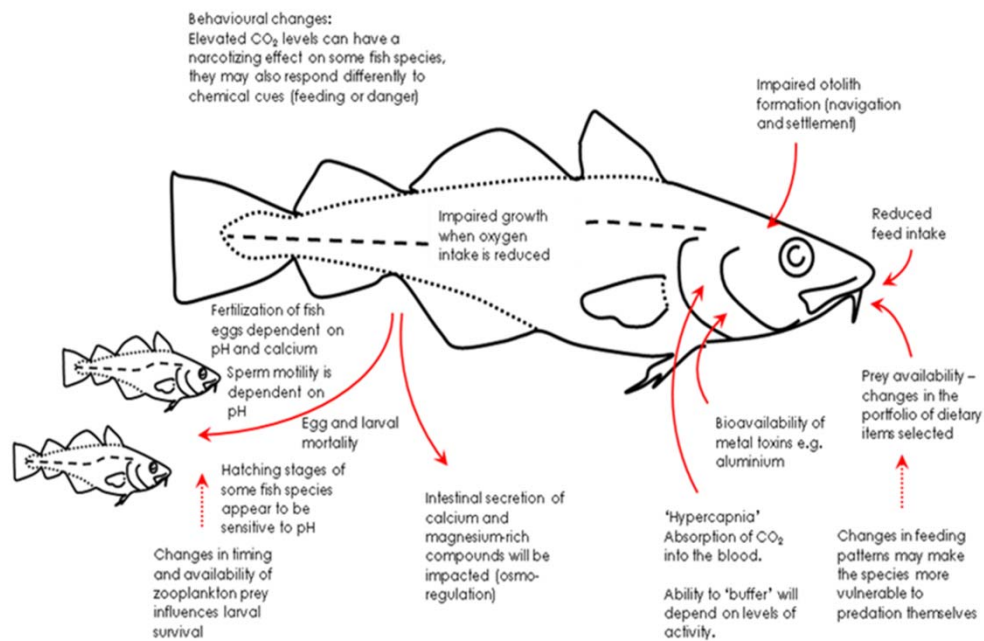
Figure 5.10. The potential mechanisms by which ocean acidification (OA) may affect fish throughout their life cycle. (Courtesy of John Pinneager.)

The physiological impacts of acidification, as reviewed by Fabry *et al.* (2008), are grouped into three categories: (i) impacts on reproduction and early development, (ii) calcification (see Section 5.9), and (iii) broad impacts on physiology caused by changes in the balance of the internal acid−base balance.

5.7.1 Reproduction and early development

Reproduction and early life stages (fish eggs and larvae) are expected to be particularly sensitive to the direct impacts of OA (Ishimastu *et al.*, 2004; Fabry *et al.*, 2008; Melzner *et al.*, 2009b). As the sperm and eggs of broadcast-spawners are directly exposed to changes in seawater chemistry, the more specialized buffering mechanisms found in more fully developed organisms are not found in the early life stages, which are known to be most susceptible to environmental toxicants (McKim, 1977).

Experimental results for reproduction and early development stages so far exhibit a range of sensitivities to OA. Among invertebrates, there is almost a complete spectrum of sensitivities, ranging from brittlestars that die with only minor changes in pH (Dupont *et al.*, 2008), to sea urchins that demonstrate abnormal development under moderate levels of CO_2 enrichment (Kurihara and Shirayama, 2004), and to tunicates that exhibit improved development under CO_2-enriched conditions (Dupont and Thorndyke, 2009). To date, no theories have been put forward to explain the relative sensitivity of different taxa. The onset of OA will proceed alongside global temperature change. A study of fertilization and development of the rock oyster (*Saccostrea glomerata*) under co-varying pH and temperature found that fertilization and development were reduced under elevated CO_2 conditions, and that fertilization and development were more sensitive to CO_2 at temperatures above and below the optimal temperature for fertilization (Parker *et al.*, 2009).

Comparatively little work has been conducted on the effects of environmentally realistic levels of OA on fish reproduction and development. Studies conducted at high levels of CO_2 enrichment, in relation to potential effects of oceanic carbon

sequestration, have demonstrated that fish larvae are sensitive to high levels of CO_2 enrichment and that, under extreme conditions, death can occur (Hayashi *et al.*, 2004; Ishimatsu *et al.*, 2004). However, experiments under highly elevated CO_2 conditions have only limited applicability to realistic scenarios of OA. A study of two species of reef cardinal fish (*Ostorhinchus doderleini* and *O. cyanosoma*) found that there was no impact on egg hatch rate, size at hatching, or developmental time at levels up to 1030 ppmv CO_2 (Munday *et al.*, 2009b). In additional, unpublished preliminary work on cod, it was demonstrated that developing eggs and larvae did not die as a direct response to elevated CO_2 concentrations up to 4000 ppmv (A. Frommel, IFM-GEOMAR, pers. comm.; W. Le Quesne, Cefas, pers. comm.). This suggests that many marine fish larvae may be unlikely to die as a direct result of OA. Sublethal effects require more detailed investigation; a study on white sea bass (*Atractoscion nobilis*) found enhanced otolith growth under elevated CO_2 conditions (Checkley, D. M., *et al.*, 2009).

5.7.2 Internal acid–base balance

An emerging theory of the general sensitivity of species to changes in acid–base balance predicts that active organisms, and species with large amounts of extracellular fluid, such as blood, will be less sensitive to OA (Melzner *et al.*, 2009b). Active animals (e.g. fish, squid, and some crabs) may be pre-adapted to cope with OA because (i) CO_2 builds up in the body during exercise, and (ii) they possess specialized structures to control and maintain internal CO_2 levels. The metabolic costs of regulating acid–base balance have yet to be investigated; if regulation of acid–base balance comes at a notable metabolic cost, this could have implications for individual performance and energy flow through foodwebs.

The onset of OA will occur over a period of decades and will proceed alongside changes in global temperature; therefore, acidification impacts need to be considered in light of a parallel development in climate change. Increasing water temperatures have led to an observed shift in the geographic range of a number of species, including commercially targeted fish (Perry *et al.*, 2005). The upper thermal limit of the spider crab (*Hyas araneus*) decreases by at least 1.5°C under the CO_2 conditions expected by 2100 (Walther, K., *et al.*, 2009). This indicates that OA may reduce the thermal tolerance window within which species can survive (Pörtner and Farrell, 2008) and could exacerbate changes in biogeographic range as a response to warming.

5.8 Impacts on deep-water corals

Within the ICES Area, there are extensive reefs of cold-water corals, especially in Norwegian and Canadian waters, and the full extent of their distribution was only begun to be realized in the past decade (see Section 8.3.3). In the North Atlantic, *Lophelia* (Figure 5.11) is the dominant deep-water colonial coral. It is a true hard coral, formed by a colony of individual coral polyps that produce a calcium carbonate skeleton. It feeds by catching food from the surrounding water. Unlike its tropical relatives, *Lophelia* does not need algae and light for survival, and it is found mainly at depths between 200 and 1000 m. The record for the deepest reef is 3000 m, and the shallowest living *Lophelia* reef is found at 40 m in Trondheim Fjord, Norway.

Figure 5.11. *Lophelia*, **a typical cold-water coral that feeds by extracting food particles from the surrounding water. (Courtesy of Jan Fossa.)**

Lophelia reefs provide habitat for a large number of invertebrate species (e.g. crustaceans, molluscs, starfish, brittlestars, and sea urchins), and a wide variety of animals (e.g. sponges, bryozoans, hydroids, and other coral species) grow on the coral itself (Mortensen and Fosså, 2006; Roberts *et al.*, 2009a). Fish (e.g. redfish (*Sebastes marinus*), saithe (*Pollachius virens*), cod, ling (*Molva molva*), and tusk (*Brosme brosme*)) are also found in the coral habitat (Husebø *et al.*, 2002; Costello *et al.*, 2005). Although experimental fishing with longlines has demonstrated that catches of redfish are greater in coral habitats than in surrounding areas (Husebø *et al.*, 2002), it is still uncertain whether or not this habitat is important for fish or fish stocks (Auster, 2005). Up to the present, the largest threat to *Lophelia* reefs has been bottom-trawling (Fosså *et al.*, 2002; Hall-Spencer *et al.*, 2002; Grehan *et al.*, 2005), but in future, OA may become a serious problem if anthropogenic CO_2 emissions are not markedly reduced or halted in order to stabilize pH in the oceans (Orr *et al.*, 2005; Guinotte *et al.*, 2006).

The largest reef system in Norway, the Røst Reef, grows along the continental break off the Lofoten Islands at ca. 300–350 m depth. Model scenarios (Orr *et al.*, 2005) reveal that undersaturated conditions may be reached at the end of the century. Under these conditions, *Lophelia* will most probably have serious difficulties in producing a skeleton. Severe stress levels may occur even before the seawater becomes undersaturated. Preliminary results indicate that *Lophelia* may reduce its calcification rate with even a small change in pH (Maier *et al.*, 2008). Lowering the pH by 0.15 and 0.3 units reduced coral calcification by 30 and 56%, respectively. Also, the effect of changes in pH (0.3 units lower than in ambient water) on calcification rate was stronger for fast-growing young polyps (59% reduction) than for older polyps (40% reduction). This implies that the young and fast-calcifying corallites exhibit the most negative response to OA (Maier *et al.*, 2008). It has also been demonstrated that the metabolic rate in *Lophelia* increases threefold for a temperature increase of only 3°C (Dodds *et al.*, 2007). *Lophelia* therefore seems to be sensitive to changes in both pH and temperature. Given these concerns, there is an urgent need for further studies on

the potential direct physiological effects on *Lophelia*, particularly growth and calcification under altered pCO_2 and pH in interaction with anticipated changes in temperature (Roberts *et al.*, 2009a). In addition, the potential indirect ecological effects of OA (e.g. changes in primary production, food supply, and benthic–pelagic coupling) may play a role in a future changing environment.

5.9 Impacts on shellfish: calcification

Many marine invertebrates, including commercially important wild-harvest and aquaculture species, form shells hardened by calcium carbonate. The process of calcification is particularly sensitive to OA, because the concentration of available carbonate in seawater decreases as pH decreases, so that the formation of calcium carbonate structures becomes increasingly expensive in terms of energy. Calcium carbonate can be laid down in a number of ways and in varying chemical forms; therefore, different calcifying species may have different sensitivities to lower pH conditions. Ries *et al.* (2009), in a study of 18 calcifying species using 60-day exposures, found a range of responses, including both increases and decreases in the rate of calcification under elevated CO_2 levels. They also found that calcification by mussels (*Mytilus edulis*) was insensitive to CO_2 enrichment over the range tested; this contrasts with the linear decline in calcification by *M. edulis* with increasing CO_2 reported by Gazeau *et al.*, (2007), which was based on a short-term exposure. However, both sets of authors report linear declines in calcification by the oyster (*Crassostrea virginica*) in response to elevated CO_2. In experiments using slightly different techniques, Findlay *et al.* (2009) came to an alternative conclusion. These experiments, which were performed on a number of species, as well as *M. edulis*, displayed no significant change in the ability of mussels to calcify at high levels of CO_2; although the rate of dissolution increased, the net result was a greater shell weight. Other work on mussels (Beesley *et al.*, 2008) has demonstrated that, although growth is not reduced, it does come at an energetic cost, with an associated reduction in health. Mussels are easily able to survive short periods of low pH, but may suffer energetically from long periods of exposure. These results suggest that animals can rapidly adapt by changing their internal biology. In the long term, adaptation may come at the cost of overall growth; however, this will be a function of other factors, such as food availability and other stresses.

Arnold *et al.* (2009) studied the survival of the four larval stages of the European lobster (*Homarus gammarus*) at high CO_2 levels (1200 ppm) and pH 8.1. No effect was observed on carapace length or the duration of the larval stages, although the pH was not especially high.

5.10 Impacts on shellfish aquaculture

The global aquaculture industry continues to expand rapidly, producing more than US$35 billion (€27 billion) of marine aquaculture products in 2008, when molluscs and crustaceans (Figure 5.12) accounted for more than 40% of marine aquaculture production by value.
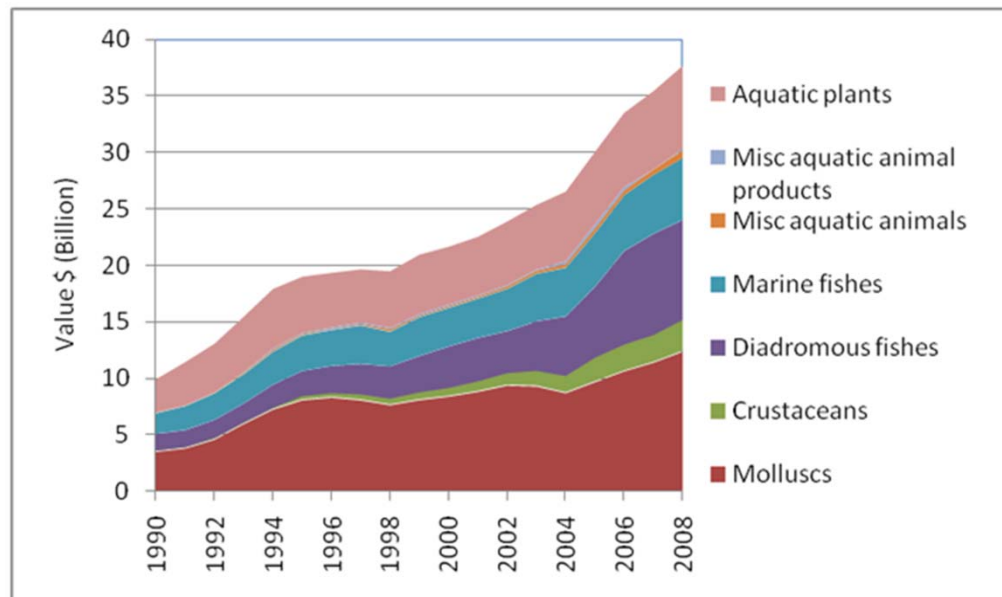
Figure 5.12. Global value of marine aquaculture products; note the increasing proportion of shellfish (molluscs and crustaceans). (Source: FAO.)

As noted above, calcifying organisms may be especially susceptible to the effects of OA. A reduction in growth rate in a farmed species would therefore affect the operations of the industry, although a more detailed, linked bioeconomic assessment would be required to gauge the implications in terms of production and profitability. Assessments of the impacts of acidification on calcifying species consistently find variations in sensitivity and response (Miller *et al.*, 2009). It may be possible, therefore, to replace sensitive aquaculture species that are negatively affected by acidification with alternative, more resilient species. However, there are likely to be transition costs associated with changing to production of a different species.

Commercial oyster hatcheries on the Pacific coast of the US are finding it difficult to keep the larvae of the Pacific oyster (*Crassostrea gigas*) alive in culture, with two of the largest hatcheries reporting production rates down by as much as 80%. Moreover, there has been little or no "natural" recruitment for several years in areas where naturalized populations were previously established. In regions of upwelling along the continental shelf of western North America, Feely *et al.* (2008) have determined that the surface waters have a lower pH and a lower aragonite saturation than expected. At 40–120 m depth in many locations along the coast, but at the surface in the region near the California–Oregon border, pH was reported to be 7.75, with an aragonite saturation of 1.0. Whether or not the recent recruitment and aquaculture failures are linked to changes in carbonate chemistry is unknown.

Most mariculture currently occurs in relatively shallow coastal margins, which have two different and opposing characteristics that are important for future changes. Typically, coastal systems with low salinity will have lower total alkalinity than those with high salinity and, therefore, have less buffering to changes in pH. However, in semi-enclosed areas of high primary productivity (e.g. the Sète Lagoon in France and the Rias Baixas in Spain), pH will be high, often exceeding 8.1.

5.11 Effects on fisheries

The direct biological impacts of OA occur at the cellular level; however, it is the expression of these effects at population and ecosystem levels, and their interaction

with the socio-economic status of fishing communities, that is of concern to society. To date, research on the effects of acidification have concentrated on physiological effects. The productivity of commercially important stocks depends upon both the physiological status of target species and the ecological setting within which they occur. This requires scaling-up from physiological experiments to the prediction of population- and ecosystem-level effects accompanied by consideration of ecology as well as physiology. Determining the resulting impact that this has on fishing businesses and communities will involve further socio-economic assessments of the status of fisheries and the capacity for adaptation, within fisheries and markets, to changes in resource productivity.

From an ecological perspective, two key questions can be asked about the potential impacts of OA on fisheries: (i) will the relative composition of the species making up a marine community be altered, and (ii) will overall system productivity or productivity at a given trophic level be altered? The drivers of these changes fall into two classes: direct and indirect effects. Direct effects are the result of the action of OA on the physiological condition of an organism. Indirect effects may result in changes in ecological interactions, such as reduced prey availability if a prey organism is directly affected.

The above discussion of the impacts of OA on higher trophic-level organisms suggests that many fish will be broadly insensitive to direct impacts of acidification, although some invertebrates, especially calcifiers, may suffer from direct impacts. A study on cod found that juveniles held at ca. 3000 ppmv CO_2 for 12 months did not show any change in swimming performance or resting and active metabolic rates compared with a control group (Melzner *et al.*, 2009a), supporting the contention that developed fish are robust to acidification effects. In contrast, a study of two species of reef cardinal fish (*Ostorhinchus doderleini* and *O. cyanosoma*) found that aerobic scope was reduced by 33 and 47%, respectively, at approximately 1000 ppmv CO_2, and that temperature and CO_2 had a synergistic effect on aerobic scope (Munday *et al.*, 2009a). A reduction in aerobic scope could lead to a smaller window of thermal tolerance and thus a more restricted geographic distribution (Pörtner, 2008). Furthermore, a change in aerobic scope indicates that there could be an underlying change in energy partitioning, possibly the result of the increased costs of maintaining internal ionic balance. Similarly, the work on calcifiers discussed above indicates that calcification under acidified conditions may incur greater energetic costs. The increased costs of maintenance or growth reduce the efficiency by which food is transformed into somatic growth and, likewise, trophic-transfer efficiency. The latter would progressively reduce production at higher trophic levels, with potentially important impacts for fisheries. The impact of acidification on the internal energy budgets of organisms is poorly understood and should be a priority for future research.

Direct effects on the physiology of organisms may lead to changes in behaviour, growth rates, or mortality rates. However, changes in physiological rate do not necessarily translate into an identical linear change at the population level, and any response may vary depending on its condition. This is illustrated and considered in more detail in terms of possible population-level effects of acidification-induced changes on reproduction and early development. Within fishery assessment and modelling, reproduction is normally considered within stock–recruitment (S–R) relationships. Standard S–R theory assumes that the maximum number of recruits that can enter a population each year is limited by the carrying capacity of the system, and that recruitment is limited to this level by competition for food or space (Beverton and Holt, 1957). The other key aspect of most S–R relationships is the

maximum survival rate of developing larvae that is achieved at low population numbers in the absence of competition. Ocean acidification could affect the maximum survival rate if the development success of larvae is reduced. Alternatively, OA could affect the carrying capacity by altering either the availability of planktonic food for larvae or the energetic requirements of developing larvae such that limiting competition sets in at a different level. Similarly, a smaller thermal-tolerance window could reduce the availability of suitable habitat and thus carrying capacity.

So, what are the potential population-level impacts of acidification-induced changes in larval survival or carrying capacity? In the absence of exploitation, or under optimal management conditions, recruitment is likely to be highly density-dependent; thus the population is expected to be insensitive to moderate levels of variation in larval survival, but fishery production would be closely related to changes in carrying capacity (food availability). Conversely, if a population is reduced to low levels, it will be insensitive to changes in carrying capacity but very sensitive to changes in larval survival. A physiologically mediated reduction in larval survival would render a stock more susceptible to overfishing and could hinder the rebuilding of overexploited stocks. Mortality of the early life stages of broadcast-spawning species is typically high and highly variable, owing to natural match–mismatch and density-dependent processes in the planktonic stages (Hjort, 1914; Cushing, 1990; Goodwin *et al.*, 2006). Direct effects of acidification could be swamped by natural variability, and actually observing a reduction in recruitment caused by acidification would require a long time-series of data unless the effect is very large.

Indirect effects are likely to be more relevant than direct effects, but are even harder to quantify. Ocean acidification may influence the structure and productivity of primary and secondary benthic production, which in turn may indirectly affect the productivity of fish communities and higher trophic levels. Changes in food source (e.g. Barents Sea herring feeding on pteropods) may result in shifts in species distributions, lower species abundance, or diet shifts. However, predicting indirect foodweb effects is difficult because many marine organisms have broad and variable diets, and are able to switch diets depending on prey availability (Pinnegar *et al.*, 2003; Trenkel *et al.*, 2005; Pinnegar and Blanchard, 2008). The possible effects of acidification on the timing of appearance, abundance, and quality of larval-fish prey sources, such as phytoplankton and zooplankton, remain unknown (Edwards and Richardson, 2004). The gaps in knowledge that need to be addressed are extensive, but research could focus on key target fishery species, particularly those that depend heavily on calcifying taxa (e.g. pteropods) as prey. A key unknown in assessing the relative importance of acidification for fisheries is how physiological effects will scale-up to population and ecosystem levels. Acidification effects have yet to be observed in shelf seas, so direct effects in the next 50 years are likely to be relatively minor compared with the massive impacts of overexploitation over the past few decades (Jennings, 2004; Dulvy *et al.*, 2005). However, combined temperature and acidification effects could interact with fishing effects, especially if environmentally driven changes leave stocks less resilient to overexploitation (Planque *et al.*, 2010).

5.12 Conclusions

Since the beginning of the industrial age, surface ocean pH, carbonate ion concentrations, and aragonite and calcite saturation states have been decreasing because of the uptake of anthropogenic CO_2 by the oceans.

- By the end of this century, pH could decrease further by as much as 0.3–0.4 units.

- Aragonite and calcite saturation horizons ($\Omega = 1$) are rising at ca. $1-2$ m year^{-1} and could reach the surface as soon as 2020 in the Arctic Ocean.
- Natural processes, such as freshwater input (e.g. Baltic) and coastal upwelling, may accelerate the shoaling of corrosive waters in shallow regions of the oceans.

Although the chemical change of the oceans is unambiguous, predicting the ecological impact of this change is not straightforward. Publications such as Iglesias-Rodriguez *et al.* (2008) and Wood *et al.* (2008) for coccolithophores, and Findlay *et al.* (2008) for mussel growth, have contradicted previous works (e.g. Riebsell *et al.*, 2000; Gazeau *et al.*, 2007). Recent review papers by Hendriks *et al.* (2010) and Kroeker *et al.* (2010), who used meta-analysis to synthesize a number of experiments, were inconclusive, with Kroeker *et al.* (2010) stating that there is evidence of strong negative responses associated with increasing CO_2, whereas Hendriks *et al.* (2010) concluded that the evidence is not clear. However, CO_2-rich, O_2-poor water has already affected shell fisheries off Oregon (Feely *et al.*, 2008).

One of the challenges of the many national and international ongoing programmes on OA (e.g. European Project on OCean Acidification (EPOCA); Biological Impacts of Ocean Acidification (BIOACID)) is to produce results that not only test a positive hypothesis (e.g. what happens at 680 ppmv), but are also robust enough to identify negative results (e.g. what happens at 680 ppmv but over a number of life cycles). Unfortunately, proving a negative usually takes substantially longer than proving a positive. Currently funded programmes, although extensive, are not sufficiently targeted at studying effects at higher trophic levels. Furthermore, at species level, experiments do not include multiple stressors, such as higher temperatures and potential anoxia, in addition to increased CO_2 concentrations.

Although a single-species approach to testing responses of organisms to CO_2 enrichment provides a logical starting place for the assessment of potential ecosystem impacts of acidification, more emphasis needs to be placed on scaling based on observed physiological and biological effects in order to predict population, community, and ecosystem responses. This requires the explicit incorporation of ecology into acidification studies because density-dependent processes and ecological feedbacks may variously buffer or amplify the manifestation of biological effects at the population and community levels, or may even lead to counterintuitive outcomes. Future work should focus on key environmental areas that sustain ecosystems as well as individual species, with cold-water coral reefs as a prime example of potentially affected ecosystems.