

## CHAPTER 8

### Reviewing the Impact of Increased Atmospheric CO<sub>2</sub> on Oceanic pH and the Marine Ecosystem

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**ABSTRACT:** The world's oceans contain an enormous reservoir of carbon, greater than either the terrestrial or atmospheric systems. The fluxes between these reservoirs are relatively rapid such that the oceans have taken up around 50% of the total carbon dioxide (CO<sub>2</sub>) released to the atmosphere via fossil fuel emissions and other human activities in the last 200 years. Whilst this has slowed the progress of climate change, CO<sub>2</sub> ultimately results in acidification of the marine environment. Ocean pH has already fallen and will continue to do so with certainty as the oceans take up more anthropogenic CO<sub>2</sub>. Acidification has only recently emerged as a serious issue and it has the potential to affect a wide range of marine biogeochemical and ecological processes. Based on theory and an emerging body of research, many of these effects may be non-linear and some potentially complex. Both positive and negative feedback mechanisms exist, making prediction of the consequences of changing CO<sub>2</sub> levels difficult. Integrating the net effect of acidification on marine processes at regional and basin scales is an outstanding challenge that must be addressed via integrated programs of experimentation and modelling. Ocean acidification is another argument, alongside that of climate change, for the mitigation of anthropogenic CO<sub>2</sub> emissions.

#### 8.1 Introduction

The 1999 EU Energy Outlook to 2020 suggests that, despite anticipated increases in energy generation from renewable sources, up to 80% will still be accounted for by fossil fuels. On current trends, CO<sub>2</sub> emissions could easily be 50% higher by 2030. Already about 50% of anthropogenic CO<sub>2</sub> has been taken up by the oceans [1] and thus the oceans have been acting as a buffer, limiting atmospheric CO<sub>2</sub> concentrations. CO<sub>2</sub> in the atmosphere is relatively inert but when dissolved in seawater it becomes highly reactive and takes part in a range of chemical, physical, biological and geological reactions, some of which are predictable while some are more complex. Warming of the oceans will only have a small direct impact on the rate of oceanic uptake via changes in the solubility of CO<sub>2</sub>. However, the oceans' capacity to absorb more CO<sub>2</sub> decreases as they take up CO<sub>2</sub>.

Of all the predicted impacts attributed to this inevitable rise in atmospheric CO<sub>2</sub> and the associated rise in temperature (e.g. large-scale melting of ice sheets, destabilisation of methane hydrates, sea level rise, slowdown in the North Atlantic thermohaline circulation) one of the most pressing is the acidification of surface waters through the absorption of atmospheric CO<sub>2</sub> and its reaction with seawater to form carbonic acid [2, 3].

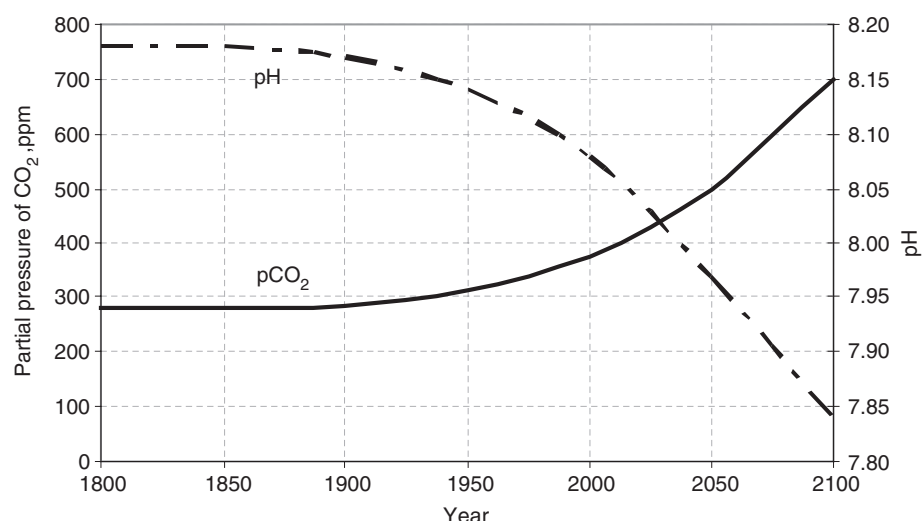
Predictions of atmospheric CO<sub>2</sub> concentrations, due to the unrestricted release of fossil fuel CO<sub>2</sub>, by 2100 are 700 ppm [4] and by 2300 are 1900 ppm [3, 5] (based on median scenarios). This would equate to a decrease in surface ocean pH of 0.3 and 0.8 pH units from pre-industrial

levels respectively [2, 3]. The top-end prediction of 1000 ppm CO<sub>2</sub> by 2100 would equate to a pH decrease of 0.5 units which is equivalent to a threefold increase in the concentration of hydrogen ions [5]. While climate change has uncertainty, these geochemical changes are highly predictable. Only the timescale and thus mixing scale length are really under debate. Such dramatic changes in ocean pH have probably not been seen for millions of years of the Earth's history [6, Figure 8.1].

#### 8.2 Global Air-Sea Fluxes of Carbon Dioxide

There has been an increase in atmospheric carbon dioxide from 280 ppm in AD1800 to 380 ppm at the present day. This increase is due to a supply of anthropogenic CO<sub>2</sub> to the atmosphere which is currently estimated at 7 GtC yr<sup>-1</sup> [4]. The observed annual increase in atmospheric CO<sub>2</sub> represents 3.2 GtC yr<sup>-1</sup>, the balance being removed from the atmosphere and taken up by the oceans and land. There is now generally good agreement that the ocean absorbs  $1.7 \pm 0.5$  GtC yr<sup>-1</sup> [4]. Note that the rate-limiting step in the long-term oceanic uptake of anthropogenic CO<sub>2</sub> is not air-sea gas exchange, but the mixing of the surface waters with the deep ocean [7]. Whilst the ocean can theoretically absorb 70–80% of the projected production of anthropogenic CO<sub>2</sub>, it would take many centuries to do so [8].

There is also a large natural annual flux of CO<sub>2</sub> between the ocean and the atmosphere of almost 90 GtC yr<sup>-1</sup> that, pre-1800, was believed to be almost in balance. This



**Figure 8.1** The past and projected change in atmospheric CO<sub>2</sub> and seawater pH assuming anthropogenic emissions are maintained at current predictions (redrawn from Zeebe and Wolf-Gladrow 2001).

huge influx and efflux is due to a combination of marine productivity and particle sinking (the biological pump) and ocean circulation and mixing (the solubility pump). Phytoplankton growth consumes dissolved inorganic carbon (DIC) in the surface seawater causing an undersaturation of dissolved CO<sub>2</sub> and uptake from the atmosphere. The re-equilibration time for CO<sub>2</sub> is slow (typically several months) due to the dissociation of CO<sub>2</sub> in seawater (see below). Ocean circulation also results in air-sea exchange of CO<sub>2</sub> as the solubility of CO<sub>2</sub> is temperature dependent. Warming decreases the solubility of CO<sub>2</sub> and promotes a net transfer of CO<sub>2</sub> to the atmosphere, whereas cooling results in a flux from the atmosphere to the ocean. Anthropogenic CO<sub>2</sub> modifies the flux from the solubility pump as CO<sub>2</sub> availability does not normally limit biological productivity in the world's oceans.

However, the observation that the net oceanic uptake of anthropogenic CO<sub>2</sub> is only about 2% of the total CO<sub>2</sub> cycled annually across the air-sea interface ought to be of major concern. The significant perturbations arising from this small change in flux imply that the system is extremely sensitive. Any resulting changes in the biogeochemistry of the mixed layer could have a major impact on the magnitude (or even sign) of the total CO<sub>2</sub> flux and hence on the Earth's climate [9].

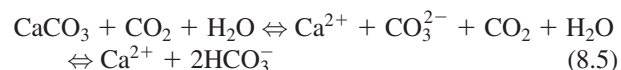
### 8.3 The Carbonate System

The chemistry of carbon dioxide in seawater has been the subject of considerable research and has been summarized by Zeebe and Wolf-Gladrow [2]. Dissolved inorganic carbon can be present in any of 4 forms, dissolved carbon dioxide (CO<sub>2</sub>), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) and carbonate ions (CO<sub>3</sub><sup>2-</sup>). Addition of CO<sub>2</sub> to seawater, by air-sea gas exchange due to increasing CO<sub>2</sub>

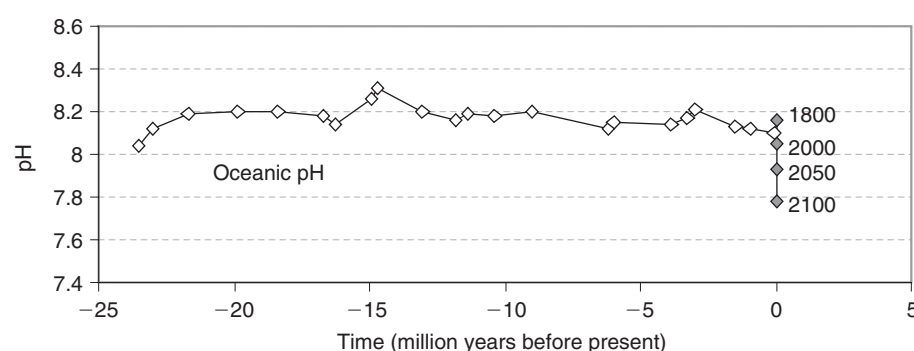
in the atmosphere, leads initially to an increase in dissolved CO<sub>2</sub> (equation 8.1). This dissolved carbon dioxide reacts with seawater to form carbonic acid (equation 8.2). Carbonic acid is not particularly stable in seawater and rapidly dissociates to form bicarbonate ions (equation 8.3), which can themselves further dissociate to form carbonate ions (equation 8.4). At a typical seawater pH of 8.1 and salinity of 35, the dominant DIC species is HCO<sub>3</sub><sup>-</sup> with only 1% in the form of dissolved CO<sub>2</sub>. It is the relative proportions of the DIC species that control the pH of seawater on short to medium timescales.



It is also important to consider the interaction of calcium carbonate with the inorganic carbon system. Calcium carbonate (CaCO<sub>3</sub>) is usually found in the environment either as calcite or less commonly aragonite. Calcium carbonate dissolves in seawater forming carbonate ions (CO<sub>3</sub><sup>2-</sup>) which react with carbon dioxide as follows:



This reaction represents a useful summary of what happens when anthropogenic carbon dioxide dissolves in seawater. The net effect is removal of carbonate ions and production of bicarbonate ions and a lowering in pH. This in turn will encourage the dissolution of more calcium carbonate. Indeed, the long-term sink for anthropogenic CO<sub>2</sub> is dilution in the oceans and reaction with carbonate sediments.



**Figure 8.2** Past (white diamonds, data from Pearson and Palmer, 2000) and contemporary variability of marine pH (grey diamonds with dates). Future predictions are model derived values based on IPCC mean scenarios.

As can clearly be seen above, formation of calcite (the reverse of equation 8.5) actually produces CO<sub>2</sub>.

Seawater at current pH levels is highly buffered with respect to carbon dioxide and has a great capacity to absorb carbon dioxide, as most of the CO<sub>2</sub> added will rapidly be converted to bicarbonate ions. It can be shown that if the atmospheric CO<sub>2</sub> levels doubled, dissolved CO<sub>2</sub> would only rise by 10%, with most of the remaining 90% being converted to bicarbonate ions. However, if bicarbonate ions increase, then the equilibrium of reaction 3 will be forced forwards and hence the pH of the seawater will be reduced. This is of great importance both for seawater chemistry and for the buffering capacity of seawater as it reduces the ability of seawater to buffer further CO<sub>2</sub> increases [2]: i.e. as the partial pressure of carbon dioxide increases the buffering capacity of seawater decreases.

The mean pH of seawater has probably changed by less than 0.1 units over the last several million years [6, Figure 8.2]. Since the start of the Industrial Revolution (circa 1800), the release of anthropogenic CO<sub>2</sub> to the atmosphere and subsequent flux into the surface oceans has already led to a decrease in the pH of oceanic surface waters of 0.1 unit [10, 5]. The same calculations show that the current rate of increase in atmospheric CO<sub>2</sub> concentration (15 ppm/decade) will cause a decrease in pH of 0.015 units/decade [11]. Globally, oceanic surface water pH varies over a range of 0.3 pH units, due to changes in temperature and seasonal CO<sub>2</sub> uptake and release by biota. However, the current surface ocean pH range is nearly distinct from that assumed for the inter-glacial period and the predicted pH for 2050 is nearly distinct from that of the pre-industrial period (Figure 8. 2). In some sense therefore the marine system is accelerating its entry into uncharted territory. Whilst species shifts and adaptation of physiology and community structure might maintain the system's gross functionality over longer timescales, the current rates of environmental change are far more rapid than previously experienced. We do not know if marine organisms and ecosystems will be able to adapt at these timescales.

## 8.4 Ecosystem Impacts

Although studies looking at ecosystem response are in their infancy, reduced pH is a potent mechanism by which high CO<sub>2</sub> could affect marine biogeochemistry [5, 12, 13]. The changes to the carbonate chemistry of the system [14, 15] may affect plankton species composition and their spatial or geographical distribution [16], principally by inhibiting calcifying organisms such as coccolithophores, pteropods, gastropods, foraminifera and corals in waters with high CO<sub>2</sub> [5]. Reduced calcification in cultures of two species of coccolithophores has been observed when grown at 750 ppm CO<sub>2</sub> [17]. Other non-calcifying organisms may grow in their place and impact the structure and processes occurring in the whole ecosystem. The main calcifiers in the ocean are the planktonic microalgae, coccolithophores [18], which secrete calcite platelets called liths. These organisms can form massive blooms, often of 100,000s km<sup>2</sup>. They play an important role in the global carbon cycle through the transport of calcium carbonate to the marine sediments. Coccolithophores are also a major producer of dimethyl sulphide (DMS) which may have a role in climate regulation via the production of cloud condensation nuclei [19]. A reduction in the occurrence of the coccolithophore blooms that occur in large areas of the global oceans could lead to a reduced flux of DMS from the oceans to the atmosphere and hence further increases in global temperatures via cloud changes. International efforts to examine the impacts of high CO<sub>2</sub> in more natural enclosed seawater systems (mesocosms) with blooms of coccolithophores shows that calcification, growth rates and exudation can be affected by high CO<sub>2</sub> and this has implications on biogeochemical cycling, carbon export and food web dynamics [20, 21]. Over long timescales calcium carbonate is the major form in which carbon is buried in marine sediments, hence species composition is intimately linked to the strength of the biological pump and carbon burial in sediments [22, 23].

The effect of high CO<sub>2</sub> on tropical coral reefs has received particular attention [24, 25, 26] because calcification

rates in corals (which secrete a more thermodynamically stable form of CaCO<sub>3</sub>, aragonite) decline under elevated CO<sub>2</sub> conditions. Predictions are that coral calcification rates may decrease by 21–40% over the period 1880–2065 in response to changes in atmospheric CO<sub>2</sub> concentrations [27, 28, 29]. Reduction in coral calcification can result in declining coral cover and loss of the reef environments [25]. Coral reefs are essentially oases of high productivity such that they produce 10–12% of the fish caught in the tropics and 20–25% of the fish caught by developing nations [30]. The sea contributes about 90% of the animal protein consumed by many Pacific Island countries.

Calcification rates respond not only to carbonate saturation state, but also to temperature, nutrients, and light. It has been argued that increasing temperature, at least in corals, may invoke a biological response that leads to higher calcification rates in the short term. This might offset the impact of declining carbonate ion concentrations [31]. Although there is concern over these studies [5, 25] they do show the importance of looking at the impacts synergistically.

Extensive cold water corals have been discovered in the last decade in many of the world's oceans that may equal or even exceed the coverage of the tropical coral reefs [32]. A decrease in the depth below which aragonite dissolves, due to reduced carbonate ion concentrations, may make these ecosystems particularly vulnerable [33]. This effect will be greatest in the higher latitudes and impact calcifying organisms that live there [5]. For instance, pteropods are the dominant calcifiers in the Southern Ocean and are an important part of the Antarctic food web and ecosystem.

The availability of marine nutrients, necessary for primary production, is affected by pH. The form of both phosphorus and nitrogen, the key macro nutrients, are pH sensitive; acidification provoking a reduction in the available form of phosphate (PO<sub>4</sub><sup>3-</sup>) and a decrease in ammonia (NH<sub>3</sub>) with respect to ammonium (NH<sub>4</sub><sup>+</sup>), changing the energetics of cellular acquisition. A second consequence of low pH may be the inhibition of microbial nitrification [34] with a resulting decrease in the oxidised forms of nitrogen (e.g. NO<sub>3</sub><sup>-</sup>). As a result we may see a decrease in the NO<sub>3</sub><sup>-</sup> dependant denitrification process which removes nitrogen from the marine system in the form of nitrogen gas. The resulting build-up of marine nitrogen (mainly as NH<sub>4</sub><sup>+</sup>) may trigger eutrophication effects.

The solubility (and availability) of iron, an important micro-nutrient, is likely to increase with acidification, perhaps increasing productivity in some remote ocean basins that are currently iron limited. The net effect of these processes is likely to change the nutrient availability to phytoplankton, impacting species composition and distribution and consequently the rate of carbon cycling in the marine system. Changes to the phytoplankton community structure are likely to affect the organisms that prey on phytoplankton, including economically important species [35, 36, 37].

If the environmental CO<sub>2</sub> concentration is high (equivalent to three-fold increases in atmospheric CO<sub>2</sub> relative to pre-industrial), fish and other complex animals are likely to have difficulty reducing internal CO<sub>2</sub> concentrations, resulting in accumulation of CO<sub>2</sub> and acidification of body tissues and fluids (hypercapnia) [38]. The effects of lower level, long term increases in CO<sub>2</sub> on reproduction and development of marine animals is unknown and of concern. High sensitivity to CO<sub>2</sub> is shown by squid (Cephalopods), because of their high energy and oxygen demand for jet propulsion, with a relatively small decrease in pH of 0.25 having drastic effects (reduction of c. 50%) on their oxygen carrying capacity [39].

Experiments, using CO<sub>2</sub> concentration beyond that expected to be seen in the next few hundred years, have shown that decreased motility, inhibition of feeding, reduced growth, reduced recruitment, respiratory distress, decrease in population size, increased susceptibility to infection, shell dissolution, destruction of chemosensory systems and mortality can occur in high CO<sub>2</sub>/low pH waters in the small range of higher organisms tested to date, many of which are shellfish [5]. However, further experiments are required to investigate the impacts of the CO<sub>2</sub> and pH levels relevant to ocean uptake of anthropogenic CO<sub>2</sub>.

Juvenile forms of shellfish may be less tolerant to changes in pH than adults. Indeed, greater than 98% of the mortality of settling marine bivalves occurs within the first few days or weeks after settling. This is thought to be in part due to their sensitivity to the carbonate saturation state at the sediment-water interface [40]. The higher seawater CO<sub>2</sub> concentrations that will occur in the future may therefore enhance shell dissolution and impact recruitment success and juvenile survival.

The average carbonate saturation state of benthic sediment pore waters could decline significantly, inducing dissolution of carbonate phases within the pore-water-sediment system [14]. Further, the benthic sediment chemistry of shallow coastal seas exhibits a delicate balance between aerobic and anaerobic activity which may be sensitive to varying pelagic CO<sub>2</sub> loads. In short, marine productivity, biodiversity and biogeochemistry may change considerably as oceanic pH is reduced through oceanic uptake of anthropogenic CO<sub>2</sub>.

Changes that may occur in the same time frame as increased seawater CO<sub>2</sub> and reduced pH, include increased seawater temperature, changes in the supply of nutrients to the euphotic zone through stronger water column stratification, changes in salinity, and sea-level rise. There are likely to be synergistic impacts on marine organisms and ecosystems. There is surprisingly little research on the potential impact of a high CO<sub>2</sub> ocean on marine organisms and ecosystems let alone the impact this might have when combined with other climate-induced changes. This needs to be redressed. Whilst about 28 million people are employed in fishing and aquaculture with a global fish trade of US\$53,000 million [30], the marine environment provides other valuable services [41] and its existence and



diversity is treasured. As the oceans play a key role in the Earth's life support system, it would seem that a better understanding of the impacts of high CO<sub>2</sub> on the marine environment and consideration of mitigation and stabilization choices is worthy of substantial investment.

### 8.5 International Recognition

The global scientific community is increasingly concerned about the impacts of a high CO<sub>2</sub> ocean. This community includes the International Global Biosphere Programme (IGBP), the Scientific Committee on Oceanic Research (SCOR), the Commission on Atmospheric Chemistry and Global Pollution (CACGP) and the International Council for Science (ICSU). A SCOR and IOC-funded International Science Symposium held at UNESCO, Paris on 10–12 May 2004, *Symposium on the Ocean in a High-CO<sub>2</sub> World*, brought together scientists working in this area for the first time. The scientific consensus has been summarised in the report *Priorities for Research on the Ocean in a High-CO<sub>2</sub> World* [42] and the overwhelming conclusion was that there is an urgent need for more research in this area. The Royal Society formed an international working group to report on ocean acidification and published on 30 June 2005 [5]. Commissions and conventions that are policy instruments for the protection of our seas (such as the OSPAR (Oslo–Paris) Commission and the London Convention) have held workshops on the environmental impact of placement of CO<sub>2</sub> in geological structures in the maritime area and recognise the significance of ocean acidification caused by uptake of anthropogenic CO<sub>2</sub> as a strong argument, along with climate change, for global mitigation of CO<sub>2</sub> emission. A report to Defra, summarising the current knowledge of the potential impact of ocean acidification (by direct uptake or by release from sub-seabed geological sequestration) concluded that there was a need for urgent research to help inform government of the potential impact of both ocean uptake of anthropogenic CO<sub>2</sub> and its release from maritime sea bed geological structures [43].

### 8.6 Conclusions

This paper outlines only a few of the potential effects that higher CO<sub>2</sub> may have on the marine system. Many other processes are pH sensitive: for example, changes in pH also have the potential to disrupt metal ion uptake causing symptoms of toxicity, and intra-cellular enzymatic reactions are also pH sensitive [5]. Given continued CO<sub>2</sub> emissions, further marine acidification is inevitable and effects on the marine ecosystem are likely to be measurable. Whilst many of the effects are nominally negative, some could be considered positive. How these may balance out is unknown. The scientific community is far from being

able to predict accurately the impact of acidification on the oceans and whether an appreciable decline in resource base may occur. We also need to address the key question of whether marine organisms and ecosystems have the ability to adapt to the predicted changes in CO<sub>2</sub> and pH. Ocean acidification will occur within the same time scales as other global changes associated with climate impacts. These also have much potential to alter marine biogeochemical cycling.

Modelling techniques provide an important mechanism for resolving whole system impact. Indeed, several researchers cite the need for integrated modelling studies [e.g. 35]. The problem is multi-disciplinary. We need to integrate atmosphere, hydrodynamic and ecosystem modellers, to build on experimental knowledge, and require significantly more system measurements in order to validate models. UK and international momentum is building towards this challenge and many of the required collaborations are being forged. However, the provision of manpower, computer, experimental and observational resources still needs to be addressed. Mitigation of CO<sub>2</sub> emissions will decrease the rate and extent of ocean acidification [5]. This is another powerful argument to add to that of climate change for reduction of global anthropogenic CO<sub>2</sub> emissions.

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