2 Ocean Acidification: Not Yet a Catastrophe for the Great Barrier Reef

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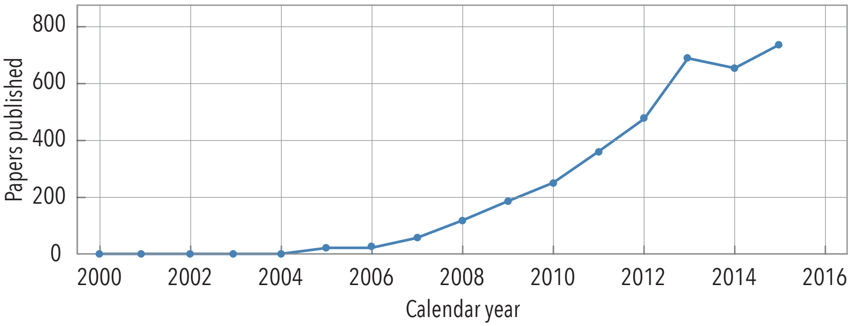
There has been an exponential increase in research on the topic of ocean acidification, which broadly concerns chemical changes in the ocean in response to increased concentrations of atmospheric carbon dioxide (CO_2). Uptake of CO_2 by the oceans from the atmosphere can potentially alter the balance of inorganic chemicals present, in turn affecting biological processes – including photosynthesis and calcification rates at coral reefs (Gattuso & Hansson 2011; Raisman & Murphy 2013). Coral reefs are a major focus of ocean acidification research. There is concern that increased atmospheric CO_2 will significantly reduce calcification and so negatively impact the overall health of these iconic ecosystems – held together by calcium carbonate that is secreted by corals.

In this chapter, we provide some background into the physical and chemical processes associated with ocean acidification, before considering the research into the effects of ocean acidification on biological organisms, with a particular focus on Australia's Great Barrier Reef.

Ocean acidification has been described as an impending 'ocean calamity', and the 'evil twin of global warming'. Public interest has fed the explosion of research on ocean acidification, considered unprecedented in the marine sciences (Browman 2016). Indeed, as shown in Figure 2.1, there were nearly 4000 articles published on ocean acidification between

Figure 2.1 Number of peer-reviewed papers published on ocean acidification



Source: Web of Science, which is an online subscription-based scientific citation indexing service, maintained by Thomson Reuters.

2000 and 2015. Most of the articles describe the effects of changes of pH on biological organisms; many of the claims are based exclusively on laboratory experiments (Riebesell & Gattuso 2015). However, a problem with laboratory experiments is that they cannot capture the complexities of the real world, not even the tremendous natural variability in ocean pH – which is a measure of ocean acidification.

Some basic chemistry

CO_2 occurs naturally in the Earth's atmosphere in very low concentrations, presently at about 400 ppm (parts per million).[1] Accurate measurements of atmospheric CO_2 concentration have been carried out at an observatory in Hawaii since 1959, when the concentration was 312 ppm. Pre-industrial levels are estimated to be about 280 ppm.

There is a natural exchange of gases between the atmosphere and dissolution in the ocean, with flows in both directions. CO_2 dissolves in water with its solubility depending on the temperature: the lower

1 Atmospheric Carbon Dioxide Record from Mauna Loa, https://climate.nasa.gov/vital-signs/carbon-dioxide/

the water temperature, the higher the solubility of a gas such as CO_2. An equilibrium may eventually be established when the flows in each direction are in balance. In turn, the strength of the flow in each direction is directly proportional to the concentration. If the concentration of atmospheric CO_2 increases, this increases the rate of CO_2 flow into the ocean, and eventually a new equilibrium establishes.

After dissolving in the uppermost layer of the ocean, CO_2 generates a number of changes to the chemical composition of the seawater. The chemistry of inorganic carbon in seawater is relatively complex, and can be understood in terms of a set of inter-related equilibrium processes. Dissolved inorganic carbon is mainly present in three chemical forms:

- aqueous (CO_2)
- carbonate ions (CO_3^{2-})
- bicarbonate ions (HCO_3-).

There is also a minor amount present as carbonic acid (H_2CO_3).

So, carbon entering the ocean as CO_2 can be transformed into these other inorganic ions and molecules. When these reactions occur, hydrogen ions (H^+) are liberated into the seawater, and this in turn affects the pH of the seawater (pH is a measurement of the acidity of an aqueous solution, defined as the negative logarithm of the hydrogen ion concentration in the solution).

The term 'ocean acidification' refers to the decrease in pH that occurs when the concentration of CO_2 in the atmosphere increases through a chain of reactions that can cause the ocean pH to drop. A neutral solution (neither acidic nor alkaline) has a pH of 7.0. Acidic solutions have a pH less than 7.0, while alkaline solutions have a pH greater than 7.0. Typically, present-day seawater varies widely in its pH, but generally it is alkaline, having an average pH in the range of 8.2 to 8.4.

Ocean acidification does not imply a scenario where the oceans become acidic (that is, the pH of the ocean falls below 7.0). The whole process could also be referred to, in perhaps less emotive terms, as 'neutralisation', or alternatively 'carbonation' (Gattuso & Hansson 2011) because there is an increase in the concentration of dissolved inorganic carbon.

Another very important component of the inorganic system in seawater is calcium, which can exist as ions in solution (Ca^{2+}) and as solid calcium carbonate ($CaCO_3$). Calcification is controlled by the concentrations of calcium and carbonate ions in the seawater at a particular location. How much the seawater is saturated by these is known as the calcium carbonate saturation state, and it is described by the Greek term Ω (omega). The value of Ω depends on the particular natural form of calcium carbonate considered, commonly either aragonite or calcite. When Ω falls below 1, solid calcium carbonate dissolves.

Some concerns relate to the possibility of the saturation state decreasing as the pH falls. The key issue is, that as the concentration of carbonate ions declines, thereby reducing the value of Ω, it will affect the ability of organisms to undertake calcification, which could potentially have a very detrimental impact on shells and coral reefs.

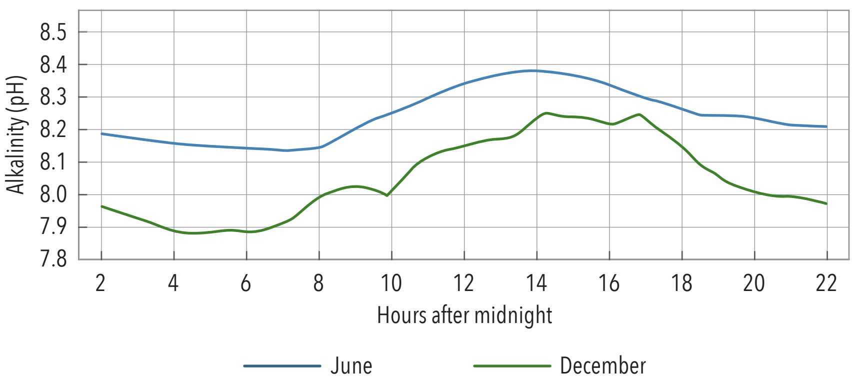
Different processes, operating on very different timescales, become important in determining the fate of CO_2 in the atmosphere. Once released, it takes about a year for CO_2 to mix throughout the atmosphere. The ocean consists, broadly, of three layers: the uppermost, or boundary layer; the mixed layer, affected by waves and turbulence caused from wind stress on the sea surface; and the deep-ocean layer. The very uppermost boundary layer of the ocean almost instantaneously equilibrates with the overlying atmosphere. Below that, is the mixed layer, which then absorbs the CO_2 through the action of wind, waves and resulting turbulence. Once in the mixed layer, CO_2 can be transported to the deep ocean, through processes that occur on millennial timescales.

Variation in pH

Popular articles written for non-scientists often claim that an increase in atmospheric concentrations of CO_2 have already caused a decrease in oceanic pH of 0.1. These same articles claim that the Earth's oceans have a pH of 8.2 and that it will fall to pH 7.8 by 2100.

However, these are average numbers, which fail to provide any indication of the extent of natural variability. For example, early review articles of ocean chemistry, which predate current concerns with acidification, report pH levels of 9.4 in isolated coral reef pools during the warmth of the day, falling to 7.5 at night (Revelle & Fairbridge 1957). At night, organisms continue to respire CO_2, while there is no uptake of it through the mechanism of photosynthesis, which occurs during the day, hence the lower pH level. A recent study at Heron Island on the Great Barrier Reef suggested that pH generally falls below 8.0 soon after midnight in summer, while climbing to about 8.4 in the afternoon in winter, as shown in Figure 2.2 (Kline et al. 2015). Indeed, the night-time pH minima on the reef flat fringing Heron Island are already lower than the pH values predicted for the open ocean by 2100.

Figure 2.2 Variation in daily pH

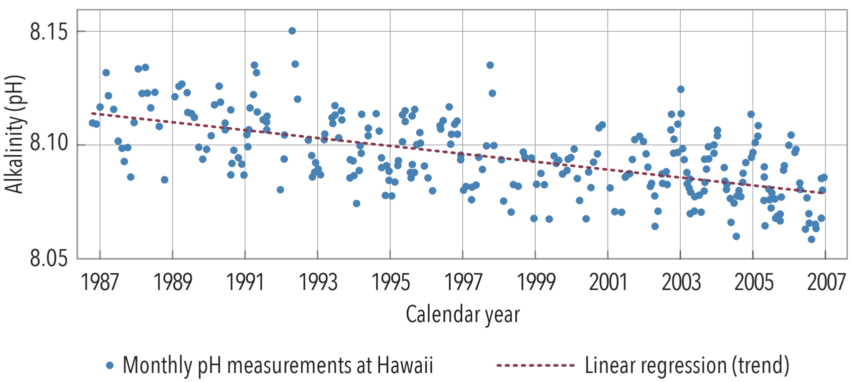


Source: Adapted with permission from Kline, DI et al., 'Six month *in situ* high-resolution carbonate chemistry and temperature study on a coral reef flat reveals asynchronous pH and temperature anomalies,' *PLoS ONE*, vol. 10, no. 6, e0127648, copyright 2015.

Direct continuous measurements of oceanic pH at the same location extend back only a few decades. For example, monthly data from the Hawaii Ocean Time-Series (HOT) programme only commenced in 1988. When values from this programme are averaged, the data indicates a downward trend in pH. This is in accordance with ocean acidification theory, as shown in Figure 2.3. But longer series based on proxy measurements suggest that this type of trend may simply be part of a natural cycle of rising and falling oceanic pH.

In order to understand changes over hundreds of years, approximate pH values have been estimated using boron isotopes in coral; these are known as proxy measurements. Data from such a study of proxies at Flinders Reef on the Great Barrier Reef shows that there have been periods of rising and also falling pH in the range pH 7.9 to 8.2 during the last three centuries – as shown in Figure 2.4 (Pelejero et al. 2005).

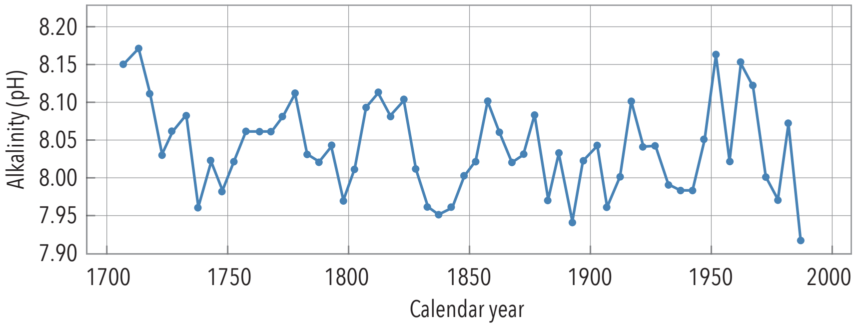
Figure 2.3 Monthly pH measurements



Measurements of pH for surface layers down to 30 m.

Source: Adapted by permission from PNAS – Dore, JE et al., 'Physical and biogeochemical modulation of ocean acidification in the central North Pacific', *PNAS*, vol. 106, no. 30, pp. 12235-12240, copyright 2009.

Figure 2.4 Changes in pH over decadal time scales



Variations in pH at Flinders Reef reconstructed from boron isotopes in coral.

Source: Adapted by permission from The American Association for the Advancement of Science – Pelejero, C et al., 'Preindustrial to modern interdecadal variability in coral reef pH', Science, vol. 309, no. 5744, pp. 2204-2207, copyright 2005.

These values correspond to the range of 7.9 to 8.3, which was reported from a similar study in the South China Sea with specimens that date back 7000 years (Liu et al. 2009).

These relatively long series indicate that comparatively rapid changes in pH have occurred on a decadal time scale before the recent increase in atmospheric concentrations of CO_2. For example, in Figure 2.4, consider the periods 1710 to 1750, 1815 to 1845, and 1950 to 1990. It is evident that the rate of decline in pH was approximately 0.05 pH units per decade in each case. This is more than the rate of decline recorded over recent decades at Hawaii of 0.033 pH units per decade, as shown in Figure 2.3.

It would therefore seem reasonable to conclude that there is nothing particularly unusual about the rate of pH decline over recent decades, because similar rates of change on a decadal scale occurred in the pre-industrial era.

Assessing claims of imminent catastrophe

The Great Barrier Reef is in the Coral Sea, off the coast of Queensland. It is the world's largest coral reef ecosystem comprising more than 2900 individual reefs and 900 islands stretching for 2300 km. The Great Barrier Reef is best known for its diversity of corals, but this ecosystem is also home to seagrass beds, which support significant populations of dugongs.

Review articles in popular scientific journals with titles like 'Ocean acidification hits Great Barrier Reef' have stated that coral growth has been sluggish since 1990 due to an increase in both sea temperatures and 'acidity' as a result of human-caused global warming (Biello 2009). Such claims are based on studies that in turn claim, unequivocally, that the recent decline in coral growth rates is unprecedented (De'ath et al. 2009). During the 2016 federal election campaign in Australia, university researchers quoted such studies as evidence that if there was not an immediate increase in funding the reef was doomed.

But there is reason to doubt the veracity of these claims.

Indeed, concerns about the lack of evidence underpinning many of the claims of imminent catastrophe due to ocean acidification have resulted in calls for 'organised scepticism' from within this same community (Browman 2016). The *Journal of Marine Science* recently published a special issue on the topic of ocean acidification with an introductory article by Dr Howard Browman from the Institute of Marine Research, in Norway. His article documents a long list of issues that need to be addressed if we are to have a reasonable level of confidence in the conclusions from ocean acidification studies.

Key issues that need to be considered when assessing claims of imminent catastrophe can be summarised under the following six headings:

1. Publication bias

Most published scientific studies on ocean acidification report negative effects of CO_2 on organisms, concluding that ocean acidification will be detrimental to marine ecosystems. Some of these studies, particularly those published in 'high impact' journals and featured in the mainstream media, predict an acidification-generated calamity in our oceans. As is true across all of science, however, studies that report no effect of ocean acidification are typically much more difficult to get published and, if published at all, seem to appear in lower-ranking journals. These are subsequently ignored by the mainstream media.

Studies in other related areas of science, for example in fisheries research, have shown that even when original studies have been proven incorrect, they often continue to be quoted in the media (Banobi et al. 2011).

2. Relevant timescales and exposure levels

Many early studies on ocean acidification exposed organisms to water chemistry that greatly exceeded even worst-case climate change scenarios. Not only have pH exposure levels been unrealistic, but studies continue to be undertaken over very short time periods, with inferences subsequently made about effects over decades or centuries. Such studies neglect the potential for acclimation, adaptation, or evolution.

Detailed studies on an important unicellular marine algae that produces calcite scales, *Emiliania huxleyi*, found that the immediate negative physiological response to ocean acidification could be partially compensated by evolutionary adaptation (Lohbeck et al. 2012; Lohbeck et al. 2014).

3. From single organisms to ecosystems

Most ocean acidification research is focused on a single species with investigations into their short-term physiological response. Understanding a whole-of-ecosystem response, however, often requires some understanding of the relative impacts on different species, including through competitive and trophic (feeding) interactions. Even if species are not directly affected by changing water chemistry, they may nonetheless experience changes in abundance or distribution because their prey, predators, or competitors are affected. Although a study of shifts in the composition of corals in response to elevated CO_2 indicated that it was the individual tolerance of different species, rather than competition between species, that determined composition (Brien et al. 2016).

4. The need to consider variability in CO_2 and pH

It is well established that CO_2 and pH vary on a daily, seasonal, and inter-annual basis, including with fluctuations in temperatures, across bodies of ocean, and also with different depths (Hofmann et al. 2011; Waldbusser & Salisbury 2014). Yet experiments on biological systems have generally failed to incorporate this variability into the design of experiments, or into the interpretations of results (Eriander et al. 2016). Some researchers have pointed out that organisms exposed to large ranges in CO_2 and pH during their daily lives, life cycles and distributional ranges, should be more tolerant of ocean acidification (Lewis et al. 2013).

The importance of a naturally fluctuating ocean pH is beginning to be recognised; for example, experiments on barnacles living in an environment with a fluctuating pH indicate environmentally and evolutionarily important responses (Eriander et al. 2016). However, very few studies have reported experimental investigations into the effects of simulated diurnal fluctuations in pH on organisms. Many of the studies on ocean acidification test the response of organisms to different fixed levels of CO_2 above the water in which the experiment is undertaken. The concentration levels of CO_2 are typically assigned:

- ambient (400 – 450 ppm)
- moderate (550 – 600 ppm)
- high (900 – 1200 ppm).

5. Extrapolating from the laboratory

The Free-Ocean CO_2 Enrichment (FOCE) experimental approach has been developed to attempt to address some of the limitations of experiments undertaken in laboratories, by conducting ocean acidification experiments *in situ* – and by enabling the precise control of CO2 enrichment in partially open, experimental enclosures (Gattuso et al. 2014). The first FOCE systems were developed at the Monterey Bay Aquarium Research Institute, but others have since been deployed or are being planned around the world. Although straightforward in concept, the engineering and logistical aspects of FOCE technology are very challenging to implement. The key elements of FOCE experimental units include:

- partially open enclosures that allow for control of seawater conditions, but retain through-flow of ambient seawater
- a CO_2 mixing system
- sensors to monitor pH, as well as other critical environmental parameters
- a control loop to regulate the addition of gases or liquids to each experimental enclosure.

Such experiments on *Porites* corals from Heron Island reef flats show that this important species exerts strong physiological controls on the pH of their calcifying fluid (Georgiou et al. 2015). Over a six-month period, from mid-winter to early summer, the corals maintained their calcifying fluid pH at near-constant elevated levels, independent of the highly variable temperatures and FOCE-controlled carbonate chemistries to which they were exposed. This is an important finding because it implies that corals may have a high degree of tolerance to ocean acidification.

6. Methodological issues

Major methodological issues have been identified not just for some but for the vast majority of ocean acidification studies (Cornwall &

Hurd 2016). Problems included interdependent or non-randomly interspersed treatment replicates, and insufficient methodological detail.

The perception that calcification rates of corals at the Great Barrier Reef are in terminal decline due to ocean acidification is based on a study of 328 colonies of *Porites* corals from 69 reefs (De'ath et al. 2009). This study appears comprehensive and has been extensively reported in the mainstream media. However, after critical examination, the study has been shown to include basic flaws – including a systematic data bias in the last growth band of each core. As a consequence, the study erroneously concluded a recent drop in calcification rates (Ridd et al. 2013).

The potential impact will depend on the organism

Initial concerns about ocean acidification focused on organisms that construct their shells or skeletons from calcium carbonate. Such organisms are referred to as marine calcifiers and include not only corals, but also crabs, clams and conchs (sea snails).

Theoretically, and according to popular science magazines, all corals are already severely and negatively affected by ocean acidification. But this is not evident from methodologically sound studies undertaken at the Great Barrier Reef. A review of the growth rates of six, hard coral species at Lord Howe Island (Anderson et al. 2015) found marked variation in the growth rates of branching coral, while growth rates of the massive *Porites* coral were unchanged. The researchers suggested that a decline in the growth rates of the branching species could be attributable to a reduction in the calcium carbonate saturation state as a consequence of higher summer temperatures. A study measuring calcification rates for 41 long-lived *Porites* corals from seven reefs from the central Great Barrier Reef (D'Olivio et al. 2009), showed good recovery from the major 1998 bleaching event, with no significant trend in calcification rates for the inner reefs. Corals from the mid-shelf central Great Barrier Reef, however, did show a decline of 3.3%.

While most ocean acidification research has been focused on physiological processes, in particular calcification, there have also been studies on three common hard corals to look at their fertilisation, embryonic development, larval survivorship, and metamorphosis (Chua et al. 2013a; Chua et al. 2013b). These studies have found the early life-history stages were unaffected by reduced pH; there was no consistent effect of elevated CO_2 alone, nor in combination with temperature.

Studies of the effect of very high CO_2 levels (up to 2,850 ppm) on molluscs – including oysters, clams, scallops and conchs – have shown that these species will generally build their shells more slowly as CO_2 levels increase (Ries et al. 2009). This same study showed that crabs and lobsters respond quite differently to the same elevated CO_2 levels, showing a general increase in calcification rates.

The varied responses among different organisms reflect their differing abilities to regulate pH at the site of calcification, and:

- the extent to which their outer shell layer is protected by an organic covering
- the solubility of their shell, or skeletal mineral
- the extent to which they use photosynthesis (Ries et al. 2009).

Of course, many marine organisms are not calcifiers, and some of these organisms have also been tested for a response to ocean acidification.

When seagrasses collected from three locations in the Great Barrier Reef region – Cockle Bay, Magnetic Island, and Green Island – were exposed to four different CO_2 concentration levels for two weeks – with water temperature and salinity in the experimental tanks near-constant throughout – all three seagrass species exhibited enhanced photosynthetic responses (Ow et al. 2015). That is growth rates, observed after two weeks of exposure to an enriched CO_2 environment in an indoor aquarium, were higher. This suggests that ocean acidification could mean more seagrass, which would be good for large marine mammals like dugongs (dugongs are vulnerable to extinction because of issues unrelated to changing ocean chemistry).

Also, contrary to expectations, laboratory investigations into the effects of three different CO_2 treatments on anemonefish (commonly known as the clownfish) found that higher CO_2 levels stimulated breeding activity (Miller et al. 2013). The breeding pairs from the fringing reefs of Orpheus Island on the Great Barrier Reef, where they are exposed to the highest CO_2 levels, produced double the number of clutches per breeding pair, and 67% more eggs per clutch than the control. However, young anemonefish that were bred in high CO_2 levels and high temperatures showed decreases in their length, weight, condition, and survival (Miller et al. 2012). Though these effects were absent or reversed when their parents also experienced the higher concentrations (Miller et al. 2013).

Acidification in context

The concept of ocean acidification, and human-caused global warming more generally, has been described as containing a grain of truth embedded in a mountain of nonsense (Lawson 2008; Carter 2010). Indeed, the projected large increase in atmospheric CO_2 will at most cause a small reduction in pH – it will not turn the ocean acidic. Yet this is what is implied by the term ocean acidification. True acidification would require average pH to be reduced below 7.0, at which point shells would indeed begin to dissolve. This is an impossible scenario, however, because of the ocean's effectively limitless buffering capacity

This review focused on (what have been termed) ocean acidification studies on biological organisms, with particular reference to the Great Barrier Reef. It has highlighted the limitations of the current research and the difficulties associated with making generalisations. Most studies have been on single species in contrived laboratory conditions. They have been of short duration, and they have not considered the potential for adaptation. In the few instances where adaptation has been considered, it has been shown to significantly modify the impact of varying pH as a consequence of elevated levels of CO_2.

All of this needs to be assessed against the reality that along the length and breadth of the Great Barrier Reef there are naturally occurring large daily fluctuations in pH, and that it is unclear as to what extent the current trends of apparent pH decline are part of existing natural cycles.