

## Is ocean acidification from rising carbon dioxide a grave threat?

'Global warming' is in the news almost daily these days, but rarely do we hear about its 'evil twin' or 'the other carbon dioxide (CO<sub>2</sub>) problem', viz. ocean acidification. Global warming, caused mainly by anthropogenic CO<sub>2</sub> emissions, is apparently accompanied by ocean acidification, which is another major growing global problem with continued increase in atmospheric CO<sub>2</sub> levels. While there is large uncertainty in the detection and attribution of climate warming because of the large natural variability in surface temperatures, ocean acidification is relatively a certain and straight forward consequence of rising atmospheric CO<sub>2</sub>.

Is ocean acidification a serious threat to marine life? Why is so little attention paid to this other CO<sub>2</sub> problem? What is the present level of understanding of this problem? Has ocean acidification already manifested at least in some parts of the global oceans? What are its likely consequences? Is life on this planet headed toward extinction because of ocean acidification? What can we do to prevent ocean acidification?

Before answering the above questions, it is important to appreciate the role of the ocean in regulating the temperature of the earth and atmospheric CO<sub>2</sub>. The thermal heat capacity of the ocean is about 1000 times that of our atmosphere, which implies that most of the heat gained by the planet due to global warming would end up in the ocean. The 2013 IPCC (Intergovernmental Panel on Climate Change) assessment confirms this: 93% of the time-integrated infrared radiative energy trapped by greenhouse gases in the recent decades can be found in the ocean. Thus, the ocean is soaking up a lot of heat and moderating the planetary temperature rise.

The ocean is not only regulating the temperature rise, but is also moderating the atmospheric CO<sub>2</sub> increase. Of the 40 billion tonnes of CO<sub>2</sub> (or ~10 billion tonnes of carbon) that is emitted each year in the recent decades by human activities such as fossil fuel burning and deforestation, only about 45% accumulates in the atmosphere (Le Quéré, C. *et al.*, *Earth Syst. Sci. Data*, 2016, **8**, 605–649). Nearly a quarter is taken up by the land biosphere and 30% by the ocean. Without CO<sub>2</sub> uptake by the land and ocean, all the emitted fossil CO<sub>2</sub> would have accumulated in the atmosphere and CO<sub>2</sub> rise in the industrial period could be ~250 ppm instead of the observed 120 ppm.

Ocean stores not only heat but also a lot of CO<sub>2</sub> (or carbon). The total amount in today's oceans is estimated at ~39,000 billion tonnes of carbon (Archer, D., *Global Warming: Understanding the Forecast*, John Wiley & Sons, 2012, p. 203). This is ~50 times of that in the atmosphere (~800 billion tonnes) at present. Which process is responsible for the storage of such vast quantities of carbon in the ocean? Many of us consider it to be either the solubility of CO<sub>2</sub> (a physical process) or marine life (biology). Actually, it is neither. It is the sea-water carbon chemistry that is responsible for most of the carbon stored in the ocean. Solubility accounts for less than 1% of carbon stored in sea water, and biology for about 2%. As an afterthought, it is probably unphysical to attribute carbon storage to physical, chemical and biological processes separately as they are all inextricably intertwined.

How does the sea water carbon chemistry work? Stated simply, the dissolved CO<sub>2</sub> in sea water (H<sub>2</sub>O) forms carbonic acid (H<sub>2</sub>CO<sub>3</sub>), a weak acid, which in turn dissociates to form bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>) and hydrogen (H<sup>+</sup>) ions. The total amount of carbon in dissolved CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> is collectively called the dissolved inorganic carbon (DIC). Sea-water CO<sub>2</sub> was in equilibrium with atmospheric CO<sub>2</sub> in the pre-industrial period when atmospheric CO<sub>2</sub> was nearly stable and the corresponding pH of sea water was around 8.2. In that equilibrium state and also today, nearly 90% of DIC is in bicarbonate form and 9% in carbonate ions, and only 1% in carbonic acid. When more CO<sub>2</sub> is added to sea water, the equilibrium shifts towards more of dissolved CO<sub>2</sub> and less of CO<sub>3</sub><sup>2-</sup>, with a reduction in pH (Zeebe, R. and Wolf-Gladrow, D., *CO<sub>2</sub> in Seawater: Equilibrium, Kinetic, Isotopes*, Elsevier Oceanography Series, 2001, p. 360). For example, the ocean would be highly acidic with 100% carbon in dissolved CO<sub>2</sub> form for pH less than 3, and alkaline with 100% carbon in CO<sub>3</sub><sup>2-</sup> for pH more than 11.

The atmospheric CO<sub>2</sub> increase in the industrial era has disturbed the pre-industrial equilibrium and anthropogenic CO<sub>2</sub> has invaded the ocean, where it is converted to HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup>. The increase in hydrogen ion concentration translates to a decrease in pH and causes ocean acidification. Since the pre-industrial times, pH of the global surface ocean has decreased by approximately 0.1. One may immediately ask if we should really be concerned about such a small change. Recall that pH is a log

scale: a small change of 0.1 corresponds to a 30% increase in  $H^+$  ions. Such small and slow changes highlight the need for careful long-term observations of pH in the Indian Ocean to understand the impact on marine life in our part of the world.

If the ocean and land are sinks of carbon, why is  $CO_2$  accumulating in the atmosphere now? The answer lies in the slow timescale on which the natural carbon cycle operates: it takes about one million years to completely remove a pulse of emitted  $CO_2$  from the atmosphere–ocean–land system and deposit it as carbonates (e.g.  $CaCO_3$ ) on the ocean floor (Lenton, T. and Britton, C., *Global Biogeochem. Cycles*, 2006, **20**, GB3009, doi:10.1029/2005GB002678). The land biosphere takes up  $CO_2$  (via photosynthesis) on a 100-year timescale, which is primarily dictated by the time it takes for trees to mature; but  $CO_2$  is released back into the atmosphere when the plants die. Moreover, land biosphere has very little capacity to store carbon. The result is limited carbon uptake by land plants. The invasion of  $CO_2$  into the ocean and the consequent ocean acidification is slow because of the sluggishness in the vertical exchange between the surface and deep ocean, and the timescale involved is a few 1000 years. Nearly 35% of  $CO_2$  emissions is likely to remain in the atmosphere even after 1000 years, highlighting the long timescale of the  $CO_2$  problem (global warming and ocean acidification) (Ciais, P. *et al.*, In *Climate Change 2013: The Physical Science Basis*, Cambridge University Press, 2013, pp. 465–570). Chemical weathering of carbonate and silicate rocks would eventually flush the anthropogenic  $CO_2$  out of the atmosphere–land–ocean system on 100,000–1,000,000 year timescales.

How does ocean acidification affect life in the ocean? As discussed earlier, as  $CO_2$  invades the ocean on millennial timescale, pH declines and carbonate ion concentration decreases. The resultant reduction in carbonate saturation levels in the marine environment could be detrimental to coral reefs and other calcifying organisms such as calcareous planktons (calcifying phytoplanktons), foraminifera, echinoderms, crustaceans and molluscs, as they produce carbonate ( $CaCO_3$ ) shells and skeletons from calcium and carbonate ions. Other consequences are depressed metabolic rates, growth, reproduction and immune responses in some organisms. Thus, physiological processes such as photosynthesis, carbonate production and consequently marine food chain could be threatened. In some sense, excess  $CO_2$  is like an acid and it dissolves  $CaCO_3$  in shells and skeletons of marine organisms. The take home message is ocean acidification could undermine the functioning of the marine ecosystem and disrupt the provision of goods and services associated with the ocean.

The pH of global surface ocean has already decreased from 8.2 to 8.1 in the industrial era. Current generation of earth system models project that the pH could drop by another 0.4 to 7.7 by 2100 for the business-as-usual  $CO_2$  emission scenario of RCP8.5 (Ciais, P. *et al.*, In *Climate Change 2013: The Physical Science Basis*, Cambridge University Press, 2013, pp. 465–570). The dilution of sea water by melting glaciers would have negligible offsetting effect as the projected addition of freshwater by 2100

is at most a metre into a water column of about 4000 m. Because cold water can hold more dissolved  $CO_2$ , the first signs of acidification are expected to emerge in the polar regions. On future ocean acidification, the IPCC assessment is that the surface waters could become seasonally corrosive to  $CaCO_3$  in parts of the Arctic and in some coastal upwelling systems within a decade, and parts of the Southern Ocean within 1–3 decades in most scenarios (Ciais, P. *et al.*, In *Climate Change 2013: The Physical Science Basis*, Cambridge University Press, 2013, pp. 465–570). Carbonate undersaturation could become widespread in these regions at atmospheric  $CO_2$  levels of 500–600 ppm. For the high emission RCP8.5-scenario, the projected carbonate saturation level is around 2 by 2100 in the tropical and subtropical regions, where the present-day values are well above 3. The implication is that the marine productivity, corals and fishery in tropical areas could be severely affected by 2100, if global  $CO_2$  emissions track the business-as-usual scenario.

Is the current ocean acidification unprecedented? The current rate of ocean acidification is often compared with the Paleocene–Eocene thermal maximum (PETM; about 55 million years ago), when surface ocean temperatures rose by 5–6 degrees and marine organisms in the deep ocean experienced major extinction. The End-Permian extinction (~250 million years ago) when nearly 90% of life on earth became extinct was also preceded by soaring temperatures and ocean acidification. Palaeoclimate proxies indicate that the catastrophic warming and ocean acidification in these two events took 10,000–100,000 years to develop. Clearly, the current rate of acidification is faster than any time in the last 300 million years and is likely ten times the rate that preceded the PETM.

It is evident that ocean acidification, once initiated, would persist for millennia. Because of this long timescale, the InterAcademy Panel (IAP) made this warning in June 2009: ‘Ocean acidification is irreversible during our lifetimes and those of many generations to come. Marine ecosystems could face grave harm as  $CO_2$  concentrations reach 450 ppm and above’. This threshold of 450 ppm for  $CO_2$  is also consistent with the 2°C warming limit mutually agreed to by the global community at the Paris Climate Summit in 2015. The IAP calls world leaders to ‘recognise that reducing the build-up of  $CO_2$  in the atmosphere is the only practicable solution to mitigating ocean acidification, and implement action to reduce global  $CO_2$  emissions by at least 50% of 1990 levels by 2050 and continue to reduce them thereafter’. Recall the global  $CO_2$  emissions are now 65% above the 1990 levels and we can only hope that the Paris Agreement would help us stay below the 450 ppm threshold, so that irreversible damage to the marine ecosystem could be averted from ‘the evil twin of global warming’ – ocean acidification – in this century.

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