



The Acid Ocean – the Other Problem with CO2 Emission

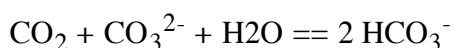
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The Royal Society has just issued a summary report on the effects of CO₂ on the pH chemistry of seawater and aquatic organisms and ecosystems. In addition to its pivotal role in the atmosphere in the regulation of global climate, CO₂ and its sister chemical species, HCO₃⁻ and CO₃²⁻ comprise the carbonate buffer system which regulates the pH of seawater. The new report can be found [here](#). Acidifying the ocean is particularly detrimental to organisms that secrete shell material made of CaCO₃, such as coral reefs and a type of phytoplankton called coccolithophorids [Kleypas et al., 1999]. The ocean pH change will persist for thousands of years. Because the fossil fuel CO₂ rise is faster than natural CO₂ increases in the past, the ocean will be acidified to a much greater extent than has occurred naturally in at least the past 800,000 years [Caldeira and Wicket, 2003].

For those of you who look back on your freshman chemistry days with less than fondness, the acidity or pH of an aqueous solution is a measure of the concentration of H⁺ ions in the solution, with low pH meaning high H⁺ concentration. H⁺ ions are aggressive little guys, and too much H⁺ in water can burn the skin off your hand or make a coral limestone go fizz. The link between CO₂ and H⁺ arises by the combination of CO₂ and water, H₂O, to form carbonic acid, H₂CO₃. An acid is a chemical species that releases H⁺ ions into solution, as does H₂CO₃ to form HCO₃⁻ and CO₃²⁻. Adding CO₂ to water causes the pH to drop.

The pH of seawater is buffered by the chemistry of carbon, just as is the chemistry of blood and cellular fluids. The buffering action arises from the fact that the concentrations of the various carbon species are much higher than is the concentration of H⁺ ions. If some process tries to add or remove H⁺ ions, the amount of H⁺ ions required will be determined by the amount of the carbon species that have to be converted from one form to another. This will be an amount much higher than the actual change in H⁺ concentration itself.

Most of the carbon in seawater is in the form of HCO₃⁻, while the concentrations of CO₃²⁻ and dissolved CO₂ are one and two orders of magnitude lower, respectively. The equilibrium reaction for CO₂ chemistry in seawater that most cogently captures its behavior is



where I am using double equal signs as double arrows, denoting chemical equilibrium. Since this is a chemical equilibrium, Le Chatlier's principal states that a perturbation, by say the addition of CO₂, will cause the equilibrium to shift in such a way as to minimize the perturbation. In this case, it moves to the right. The concentration of CO₂ goes up, while the concentration of CO₃²⁻ goes down. The concentration of HCO₃⁻ goes up a bit, but there is so much HCO₃⁻ that the relative change in HCO₃⁻ is smaller than the changes are for CO₂ and CO₃²⁻. It works out in the end that CO₂ and CO₃²⁻ are very nearly inversely related to each other, as if CO₂ times CO₃²⁻ equaled a constant.

Coral reefs are built from limestone by the reaction $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$, where Ca is calcium. Acidifying the ocean decreases the concentration of CO₃²⁻ ions, which by Le Chatlier's principal shifts the equilibrium toward the left, tending to dissolve CaCO₃. Note that this is a sort of counter-intuitive result, that adding CO₂ should make reefs dissolve rather than pushing carbon into making more reefs. It's all because of those H⁺ ions.

CaCO₃ tends to dissolve in the deep ocean, both because of the high pressure and because the waters have been acidified by CO₂ from rotting dead plankton. Surface waters, however, are supersaturated with respect to CaCO₃, meaning that there is enough Ca²⁺ and CO₃²⁻ in surface waters that you could give up some, and still not provoke CaCO₃ to dissolve. However, it has been documented that corals produce CaCO₃ more slowly as the extent of supersaturation decreases. This is also true for planktonic CaCO₃-secreters such as coccolithophorids and foraminifera. We should note that for coral reef communities, the acid ocean is only one problem that they face, and it's not the worst. Rising temperatures are tightly correlated with coral bleaching events, the expulsion of symbiotic algae, often followed by death of the coral. There is a terrifying time-series of temperature and coral bleaching from Tahiti in [Hoegh-Guldberg, 1999]. When you look at the temperatures that killed the coral, and project future temperatures, it looks to be all over for corals. Coral communities are also impacted by water turbidity, resulting from fertilizer runoff, and by overfishing.

Elevated CO₂ levels also affect fish and other aquatic organisms, in part because of the decrease in pH, but also because CO₂ is what heterotrophic organisms try to exhale. However, we should note that dissolved CO₂ levels were substantially higher than today in the geologic past, and organisms were able to cope with this OK, so apparently there can be some acclimation of populations to higher CO₂.

The natural pH of the ocean is determined by a need to balance the deposition and burial of CaCO₃ on the sea floor against the influx of Ca²⁺ and CO₃²⁻ into the ocean from dissolving rocks on land, called weathering. These processes stabilize the pH of the ocean, by a mechanism called CaCO₃ compensation. CaCO₃ compensation works on time scales of thousands of years or so. Because of CaCO₃ compensation, the oceans were probably at close to their present pH of around 8 even millions of years ago when atmospheric CO₂ was 10 times the present value or whatever it was. The CaCO₃ cycle was discussed briefly in regards to the uptake of fossil fuel by the ocean, **here**. The point of bringing it up again is to note that if the CO₂ concentration of the atmosphere changes more slowly than this, as it always has throughout the Vostok record, the pH of the ocean will be relatively unaffected because CaCO₃ compensation can keep up. The fossil fuel acidification is much faster than natural changes, and so the acid spike will be more intense than the earth has seen in at least

800,000 years.

There are several feedbacks between decreasing the rate of calcification that organisms do in the ocean, and the carbon cycle. Removing CaCO_3 from surface waters tends to raise the CO_2 concentration of the waters (it should be possible for you to work that out for yourself based on the chemical reactions above). This is a negative feedback, tending to remove excess CO_2 from the atmosphere, but it is a small effect. Decreasing the flux of CaCO_3 to the sea floor tends to diminish the amount of CaCO_3 that gets buried in sediments, which hastens the pH-recovery from the CaCO_3 compensation mechanism. This may not be a small effect at all, but it is a slow effect: thousands of years.

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