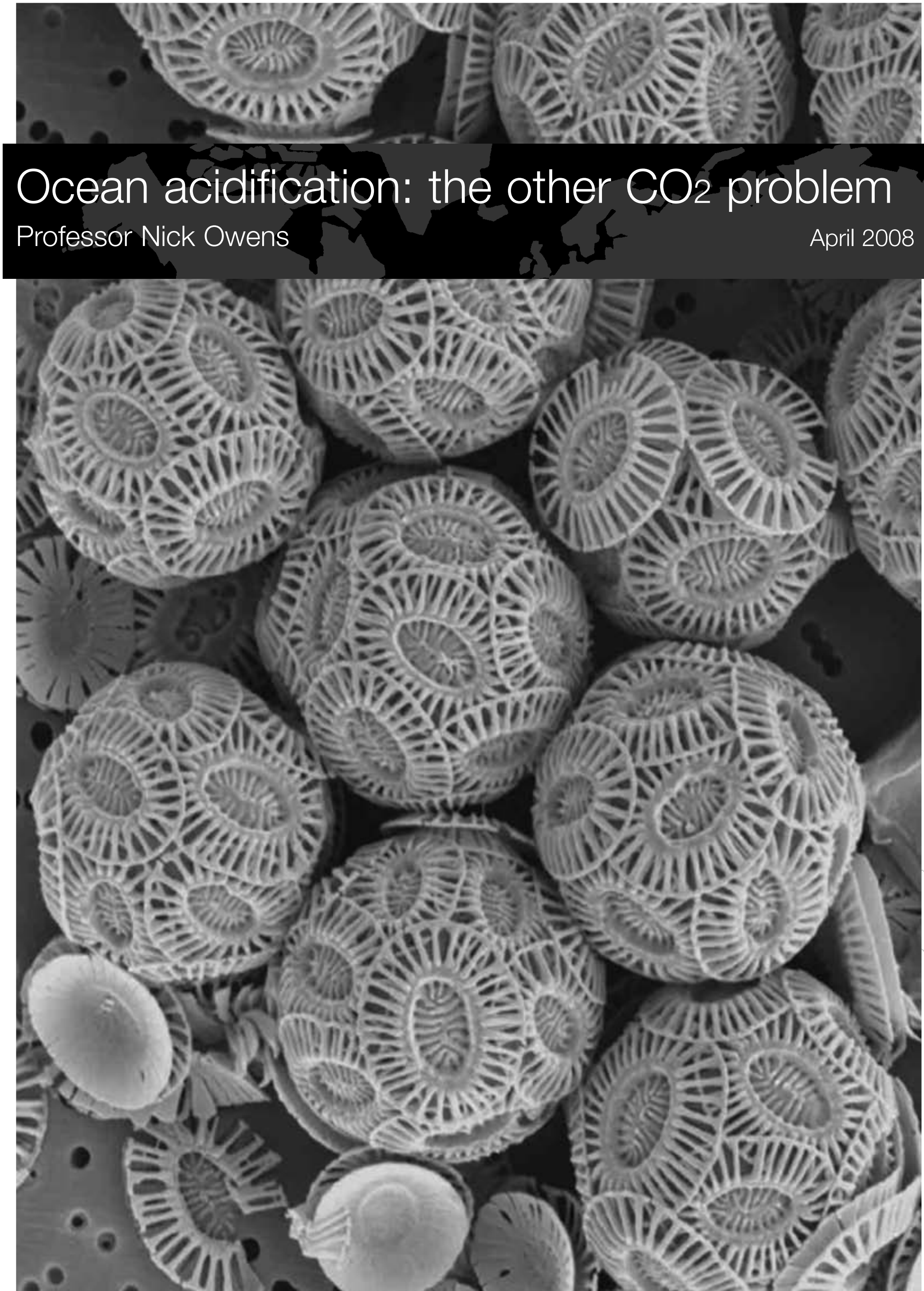

Ocean acidification: the other CO_2 problem

Professor Nick Owens

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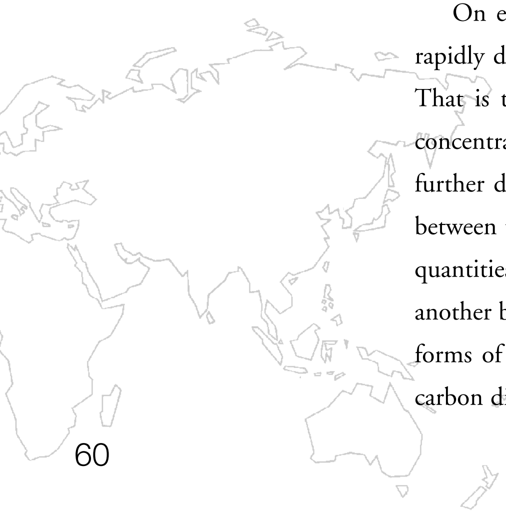
Everybody has heard of the ice core records – going back 800,000 years – showing repeat patterns of rising atmospheric carbon dioxide concentrations and rising global temperatures. Climate change is a hot topic. But the other CO_2 problem – the acidification of the oceans – still goes largely unrecognized. Neither the scientific literature nor the more popular variety has offered much coverage of the issue. A quick trawl through Times online throws up more than 5,000 hits for the words 'climate change', but only a dozen for 'ocean acidification' (April 2008). This is a totally unscientific indicator, of course, but it is nonetheless a reasonable measure of what is going on in terms of our understanding, and indeed basic awareness, of this other big CO_2 problem.

Through the natural carbon cycle – which everybody learns about at school – there are continual fluxes of carbon between the atmosphere and the oceans, and Henry's Law on the partial pressure of gases ensures that the relative amounts are maintained in equilibrium. Since the dawn of the Industrial Revolution, however, we have massively increased the amount of CO_2 in the atmosphere through our use of fossil fuels, the formation of cement from limestone, and so on. So ocean uptake of CO_2 has increased, with a net inward direction of carbon from the atmosphere into the oceans of approximately 2 billion tonnes of carbon per year. This is roughly a third of all the CO_2 produced by human activities. So ocean uptake has actually slowed the build-up of carbon in the atmosphere, a process which to some extent is reducing the rapidity of climate change.

But what does it mean for the marine environment?



On entering the ocean, CO_2 combines with seawater to produce carbonic acid (H_2CO_3). This rapidly dissociates into carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_{3-}) and hydrogen ions (H+). That is the very simple first step and it is unequivocal. We know that it happens. And it is the concentration of hydrogen ions that determines acidity or alkalinity – the more hydrogen ions, the further down you go on the pH scale from alkaline to acidic. What comes next is a rapid reaction between the hydrogen ions and carbonate ions present in the seawater. Now the ocean has very large quantities of carbonate ions from various sources, and the hydrogen ions react with these to produce another bicarbonate ion; they are effectively mopping up the carbonates. The relative balance of these forms of inorganic carbon in seawater changes, leaving you with very small quantities of dissolved carbon dioxide, rather more carbonate, and a very great preponderance of bicarbonate.

One of the things that is of really great importance to marine organisms – for growing and maintaining their skeletons or hard structures – is the presence of calcium carbonate ($CaCO_3$), which includes familiar minerals like calcite and aragonite. Carbonate minerals form through the reaction of calcium ions (Ca_2) with carbonate ions (CO_3^{2-}). Conversely, when the carbonate ions are removed – as happens when they are 'mopped up' by the hydrogen ions – the calcium carbonate essentially dissolves into its constituent forms.

One important feature of this mineral formation or dissolution process is that the global distribution of carbonate in the oceans is affected by temperature and pressure. More minerals are present where the water is warm and shallow, while there is a tendency towards the dissolution of the carbonate in deeper cooler water where pressure is higher. So surface waters and lower latitudes are higher in carbonate minerals, and deeper or higher-latitude waters have an undersaturation of the mineral. It is that natural distribution of carbonates that is being seriously disturbed by the increased ocean uptake of CO_2.

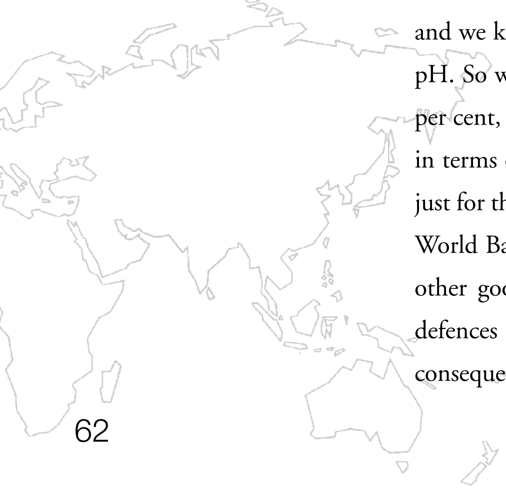
On average the pH of the world's ocean is around 8.1. It varies from place to place, partly due to the amount of plant life, partly due to temperature and pressure. Now if we assume that we will continue to burn fossil fuels until they have effectively run out, we will get an ongoing accretion of atmospheric carbon up to 2250 or thereabouts, and this will then decay only very very slowly. The ocean will continue to absorb CO_2 long after we stop producing it, slowly pushing seawater down the pH scale and reducing alkalinity by as much 0.7 pH units. Now, 0.7 may not sound like very much, but when you consider that pH is a logarithmic scale, it is a very significant number. In fact we have already shifted the pH of the ocean, reducing it by 0.1 of a pH unit since preindustrial times in the surface waters, and we are beginning to see penetration down into deeper water as well. Now 0.1 of a pH unit may seem a very trivial amount, but it represents a 30 per cent increase in the quantity of hydrogen ions in the ocean – already. Should we continue to burn fossil fuels at the present rate we will see levels of hydrogen ions right down through the ocean water column that have not been seen for at least 55 million years and possibly longer. This is a very significant and major perturbation to the Earth's system.

Unlike climate change predictions, of which there are many and they are uncertain, the chemistry and physics involved in ocean acidification is very simple and very certain. One of the uncertainties about climate, for example, is how clouds operate, or perhaps the way that ice shifts and moves. These are

complicated dynamic systems that are very difficult to predict. But what we are talking about here is straightforward unequivocal ocean chemistry and the simple physics of pumping CO_2 into the ocean. Of course we cannot be certain how high the concentrations of atmospheric carbon will go before they begin to flatten out. We might even manage to keep them at 500 parts per million, but even that, in 100 years or so, will inevitably take us to an ocean pH that the world has not seen for 25 million years. Some people have suggested that we are heading for an ocean pH that hasn't been seen for 300 million years.

Back to the minerals now, because this is where we are starting to have the interaction with the biology. Measurements and predictions of aragonite saturation levels show an alarming picture: during the pre-industrial period, the majority of the ocean's surface waters, stretching from (very roughly) around 40° North to 40° South, were classed as adequate to optimal for the existence of calcifiers. In the 1990s, this band stretched, perhaps, from only 30° North to 30° South, though it was still a substantial part of the ocean. By mid-century, however, only small pockets of adequate saturation are expected to remain, with the vast majority of the ocean ranging from 'marginal' to 'low', and by the dawn of the next century, there will remain only small areas of marginal saturation, with most of it 'extremely low'.

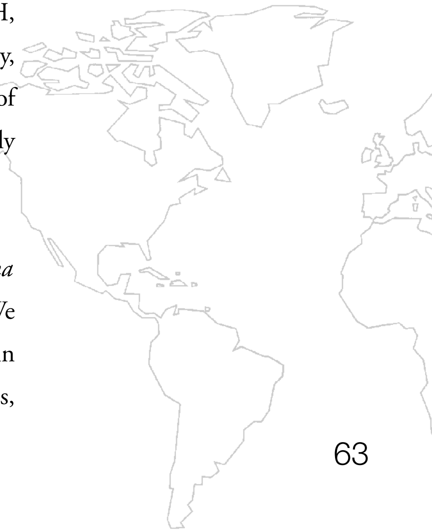
So what does all this mean for the ocean and the organisms that live in it? There is a whole range of organisms that use calcium carbonate minerals to make their hard structures, the most obvious among them being the reef-building corals. It is no coincidence that corals are particularly abundant in warm, shallow waters where the mineral aragonite is very abundant. They cover around 1.28 million square kilometres, which is less than 1.2 per cent of the world continental shelf area, but are highly biologically diverse, harbouring some 25 per cent of known marine species. Corals are fairly easy to experiment on, and we know that they cannot secrete stable forms of calcium carbonate (especially aragonite) at a low pH. So we are getting a very marked reduction in the rate of coral skeleton formation – of around 20 per cent, rising to 40 per cent over the coming decades, as a result of what we have experienced already in terms of reduction of pH. At one level, of course, no one would wish to see the reduction of corals just for their own sake. But they are also enormously important around the world. Recent data from the World Bank estimate that over half a billion people fundamentally rely on healthy corals for food and other goods and services, with an estimated value of $375 billion. Corals also provide natural sea defences for low-lying islands, usually rather poor islands at that, so there are massive socio-economic consequences associated with coral destruction.



There are also some very extensive cold corals that tend to be in deep water. They have only been discovered relatively recently and they have been very little studied compared with their warm water cousins. But they are clearly very abundant, with new colonies being discovered all the time. They are found everywhere in deep cold water and are particularly important off the coast of the United Kingdom. They can form very large structures of as much as 20 metres in depth and 100 metres across, and some are perhaps 8,000 years old, and are havens for biodiversity, harbouring extensive fish stocks which use them as feeding grounds and for shelter. Now bearing in mind that these deeper cold-water environments are already low in minerals, then the introduction of CO_2 and the lowering of pH will reduce those levels even further, thus putting deep-water corals under extreme pressure. The depth below which mineral desaturation occurs – where there are insufficient minerals for marine calcifiers to thrive – is know as the 'saturation horizon', and shallowing of the aragonite saturation horizon will be greatest in the higher latitudes, making these ecosystems very vulnerable.

Molluscs, of course, require calcium carbonate in mineral form to make their shells, and a whole range of responses to changing pH has been observed in experiments with these organisms done at Plymouth. A lowering of the pH to 7.3 results in a 50 per cent reduction in growth, and at a pH of only 7.0 (ie neutral), scallop mortality was found to be at 100 per cent. Juveniles and spat (larvae) tend to be particularly sensitive. So there are some very real concerns about the natural communities of molluscs, but also again about the economic consequences for commercial shell fisheries. Echinoderms such as sea urchins, sea stars and sea slugs are particularly sensitive to lowering pH because they have no impermeable barrier between the ambient seawater and their internal body cavity, so have little ability to control the acid-base chemistry within their bodies. The heart urchin (*Echinocardium cordatum*), when exposed to reductions in pH, showed considerable deterioration of the digestive tract, affecting nutrient uptake, growth and, ultimately, reproduction. Again, echinoderms are very important for the ecosystem, providing services in terms of turning over material in sediments and so on, and as food for fish species. Many of them are commercially important too, both in themselves and in supporting active fisheries.

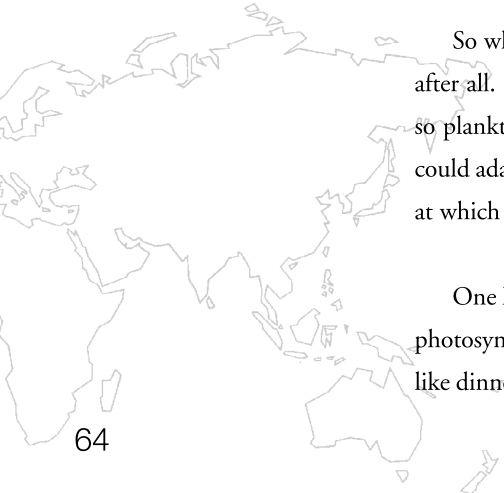
There are also some quite quirky things happening here. Take the edible periwinkle (*Littorina littorea*), and its survival mechanisms when threatened by the green shore crab (*Carcinus maenas*). We have known for some time that there is considerable communication between these two organisms in the form of chemical cues being picked up by the periwinkles. When they detect the presence of crabs,



they lay down much thicker shells. In a future ocean where the availability of carbonate ions is reduced, snails may be less able to thicken their shells and could therefore be more vulnerable to predation.

There are likely to be all sorts of unexpected consequences for the ecology of these sorts of organisms, particularly in the smaller plankton species, and there is currently very little idea of the subtleties that may occur. But what experiments have been done show that these organisms are very sensitive. There is evidence to indicate that one might expect reduced reproductive rates in undersaturated waters, and that marine zooplankton passing through plumes of CO_2-enriched seawater suffer high mortalities.

There is also some debate on the relative importance of some of these organisms. Take, for example, *Limacina helicina*, a shelled pteropod found in polar and subpolar waters of both the northern and southern hemispheres. They are basically little winged snails that float and flap around in the plankton, and are believed by some to be a very important component of the food chain. There have been instances where these things have shown up in vast quantities in sediment traps, and there are areas of the world ocean where the sediment is made up primarily of the remains of these organisms, so it is almost certain that they have an important role to play. And it is also certain that they need high levels of aragonite saturation to make their shells. But current scenarios for ocean acidification indicate that by 2050 there will be few areas where these pteropods can survive, and by the end of this century almost all the ocean – and particularly polar waters – will be so undersaturated that the pteropod shells will simply dissolve.



So what will these pteropods do? There is a possibility that they will just move: they are planktonic after all. But there are quite potent and marked frontal boundaries which isolate the Southern Ocean, so planktonic movement seems unlikely. There are some indications that, given time, some organisms could adapt through genetic selection and adjust to the lowering pH. The concern, however, is the speed at which acidification is happening, almost certainly precluding sufficiently rapid evolutionary change.

One kind of organism that has been under study is coccolithophores. These are in fact a plant – they photosynthesize – and are quite beautiful under the microscope, like little footballs with round plates like dinner plates – actually shells make of calcium carbonate. And so of course they need these minerals in saturating quantities. Not only are they beautiful; they are important components of the ecosystem and are believed to have been so over geological time scales. Their story is quite fascinating. They are miniscule – about 2 microns (millionths of a metre) in diameter – but occur in such vast quantities that you can actually see coccolithophore blooms from space, appearing as milky white swathes hugging the land masses, particularly around Europe and northeast America, the South Pacific and the Southern Ocean. Their numbers are absolutely unimaginable. So you have got this tiny little thing in such quantities that it can be seen from space. And they have been produced in these enormous quantities over such long geological time periods that where they sediment out, all their chalky plates have combined to form features such as the White Cliffs of Dover. This is quite a challenge to one's thinking about scale – to have something 2 microns in diameter that can be seen from hundreds of kilometres off in space and that has produced solid rock many metres thick.

Another interesting feature is that as the coccolithophores die they release a volatile sulphur compound which eventually gets out into the atmosphere as dimethyl sulphide (DMS). Now one of the interesting things about DMS is that once in the atmosphere it oxidizes to sulphur dioxide (SO_2) aerosol particles, around which clouds form. So it is possible that coccolithophores are a natural temperature regulator that may have played an important role in this way over geological time scales. Their very presence in the ocean also results in a lowering of the sea temperature, as their high reflectivity reflects sunlight back out to space (which, of course, is what makes them visible from so far away). If you measure seawater temperatures within these blooms of coccolithophores you find the water temperature is cooler than outside them, so you have a double cooling effect from these creatures.

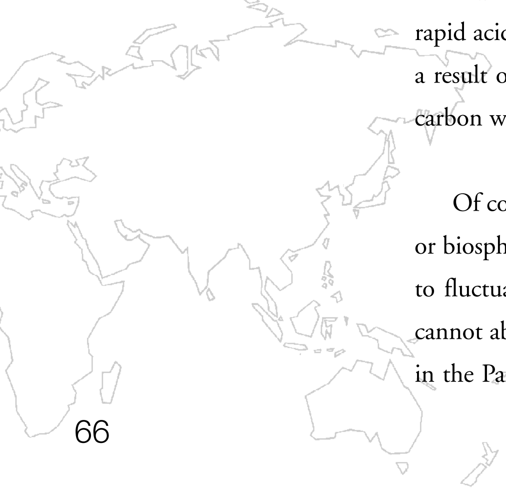
There has been some pretty good evidence of what happens when you expose carbonate-dependent organisms to a lowering of seawater pH associated with the sorts of atmospheric CO_2 concentrations that we are almost certainly committed to. And it seems pretty convincing. Or at least it did – until the appearance of an article in *Science* in April 2008 that has rather turned this simple notion on its head. It has not totally discredited theories about the negative impacts on marine life of ocean acidification, but it does mean that things are more complicated than we thought. The paper in *Science*, by Iglesias-Rodriguez and others, explored the findings of an investigation into the effects of CO_2 on the coccolithophore species *Emiliania huxleyi* in its formation of calcite plates. Contrary to expectations, they found that raising CO_2 and lowering pH actually led to the plates getting bigger and thicker.

Production of the mineral was in fact stimulated by an increase in CO_2. So it is thought that certain types of coccolithophores might actually do quite well in a high-CO_2 environment. This is clearly more complicated than we at first thought and, like all good papers, the final paragraph said 'we need more research'. It is an interesting tale that is developing all the time.

One of the features of changing pH relates to the availability of key nutrients for phytoplankton and bacterial growth. There are many ionic compounds in seawater that have different forms depending upon the pH. Different forms of nitrogen, in particular the ions ammonia and ammonium, for example, change their quantities and proportions depending on pH. Different inorganic phosphate ions also shift their balance as pH falls. Changes in the relative proportions of these nutrients may well have an effect on plankton diversity. Colleagues in Plymouth have modelled what might happen in the North Sea if we assume 'business as usual' in the burning of fossil fuels, with atmospheric CO_2 concentrations moving from the current level of around 380 parts per million (ppm) to 700ppm or beyond. Their work suggests that by 2050 some areas of the North Sea will have a different pH range from today's, and by 2100 most of the region will have undergone a drop on the pH scale of 0.3 units or more. This will lead to a change in the ratio of nitrate to total nitrogen (raising the nitrate), with potential effects on denitrification and eutrophication, and as yet under-researched physiological impacts on fauna.

Looking at the fossil record going back 600 million years, the planet has experienced very high CO_2 concentrations during interglacial periods, while through times of glaciation the CO_2 has been low, if with some temporary hotspots. During the Paleocene-Eocene thermal maximum, there was a big spike of CO_2 into the atmosphere, a corresponding increase in global temperature, and almost certainly a very rapid acidification event in the ocean, much as we are experiencing today. The CO_2 probably spiked as a result of a release of methane from the thermafrost, rapidly oxidizing into CO_2. And much of that carbon was absorbed into the ocean.

Of course there is a massive amount of carbon stored in the ocean, far more than in the atmosphere or biosphere, and over long time scales this has formed carbonate sediments that have acted as a buffer to fluctuating seawater acidity. But where you have a very rapid increase in CO_2 uptake, the ocean cannot absorb it and so you get a big slide down the pH scale. The amount of CO_2 entering the ocean in the Paleocene-Eocene thermal maximum was so rapid that the ocean was incapable of buffering it.



Sediment cores taken from the Weddell Sea from that period show a marked change in the colour of the sediment resulting from a fundamental and profound shift in the composition of the organisms in the oceans. It is estimated that something over 50 per cent of the calcifying organisms in the ocean at the time became extinct. This is very graphic evidence of what happens when you have a rapid shift in the acidity of the ocean, and it is rather chilling to think that as far as we are aware, the rate of change in the acidity of the ocean today as a result of human activity is faster than occurred during the the Paleocene-Eocene thermal maximum. There is no doubt whatsoever that there was a major extinction in the oceans at that time and this is part of the concern today.

I thought I would finish by asking whether the ocean could come to our aid. As we know the ocean is soaking up CO_2 through natural processes. Roughly half of the carbon that has been mobilized by humans since the industrial revolution has ended up in the ocean. Could the ocean be manipulated further to help solve the problems we have caused – not only the acidity problem but also the climate change problem?

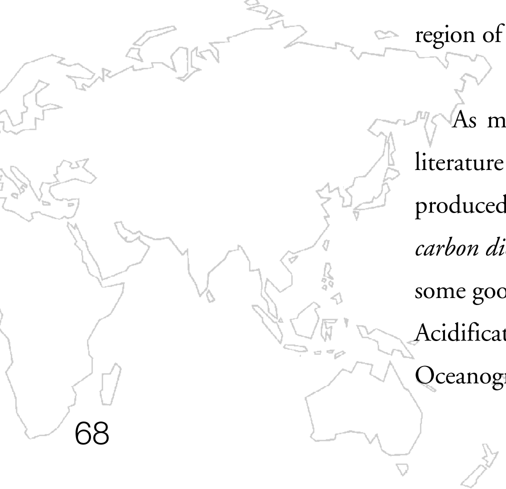
There are very large areas of the world ocean which, on the face of it, should have greater quantities of plant life than they currently do, with plenty of nitrogen and phosphorous and so on. These are called high-nitrogen low-chlorophyll areas, and they occur in different parts of the world. The Southern Ocean certainly has a big one, the equatorial Pacific another. It has been suggested that if you fertilize these areas of the ocean with iron you can stimulate the plant life and thereby get a greater CO_2 uptake from the atmosphere. Experiments with iron fertilization in the Southern Ocean have indeed achieved phytoplankton blooms large enough to be observed from space. So people have begun to think very seriously about fertilizing the ocean. But there are many problems with potentially serious consequences. First, to have any real impact on atmospheric CO_2 concentrations, you would have to do it on a vast scale – the size of the entire ocean, not just a patch of it. The time scales involved are vast, bearing in mind that the carbon we are burning in the form of fossil fuels was laid down in part by these kinds of plankton blooms over millions of years, not just a few hundreds. They happened over geological time, and it would be impossible to stimulate the system to soak up that quantity of carbon over the sort of time scales that we require. We also know that plankton blooms give off compounds like methane and nitrous oxide, both highly potent greenhouse molecules in their own right. Thus we would be up against a major perturbation of the natural system with some very serious consequences.

Unfortunately, there are several companies who are lured by the carbon trading notion and are planning on doing this sort of thing right now. Personally, I think this is utterly insane – and you don't often get scientists being as bold as that.

Closer to the realms of the possible, perhaps, is scrubbing out the CO_2, pressurizing it and turning it into liquid, and piping it to the deeper parts of the ocean. The Monterey Bay Aquarium has done some experiments with putting liquefied CO_2 into the ocean, where it basically just rolls around on the seabed. Now this is a good way of 'burying' carbon dioxide, but only temporarily. It will eventually dissolve into the seawater, making it more acid. A more realistic possibility is the near-permanent burial of CO_2 in the rock formations from which oil and gas have been extracted. This is so-called geological sequestration. CO_2 is captured at source, compressed and injected back down into the rock strata. There are some experimental sites where this is already going on, including at an oil field in Norway. The United Kingdom, too, is considering this as a serious option. An assessment of the types of rock formation suited to this type of carbon storage concludes that there are plenty of appropriate sites around the world, including opportunities in the North Sea.

There are, however, many issues yet to be addressed, not least leakage and whether this might give rise to a serious acid event in the locality of the carbon storage site. Modelling work that has been done on this suggests considerably different responses at different times of the year. If you get a release in the early part of the year before the ocean has had a chance to stratify, you might get slight acidification but it would be short-lived and much of the carbon would go straight out into the atmosphere. If, however, you get a leak later on in the year when the ocean is firmly stratified, you would get quite significant acidification in that region of the ocean. So there are some serious decisions to be made if we go down this route.

As mentioned earlier, not much has been written on ocean acidification relative to the mass of literature on climate change. But there are a couple of good sources of information: the Royal Society produced a report on the topic a couple of years ago (*Ocean acidification due to increasing atmospheric carbon dioxide*, available on the web, http://royalsociety.org) with very easily accessible information and some good references to primary sources. There are also some interesting websites, including the Ocean Acidification Network, a very serious and highly erudite site run by the UNESCO Intergovernmental Oceanographic Commission and the Scientific Committee on Oceanic Research.



I am sure we all have our own personal views on whether concerns about ocean acidification are simply another distraction. But there is no doubt that by burning fossil fuels we have reduced the ocean's surface alkalinity, and the longer we go on pumping CO_2 into the atmosphere, the longer this process will continue and the deeper it will go. The chemistry behind it is unequivocal, even if the biological responses are complex and largely unknown. Alongside climate change, this is a very strong argument indeed for curbing our emissions, not just mopping up after ourselves.

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