SICK SEAS

The rising level of carbon dioxide in the atmosphere is making the world's oceans more acidic. Jacqueline Ruttimann reports on the potentially catastrophic effect this could have on marine creatures.

t's not hard to imagine a tonne of water: it is a week's worth of not-very-deep baths. Getting to grips with a billion tonnes of water is more of a challenge. That would be a similar bath for every man, woman and child on the planet; a week's worth of flow for the Nile. To really expand your mind, go further still, to a billion billion tonnes - enough water to give every human a day's worth of the Nile instead of a shallow bath. There are dwarf planets that weigh less than a billion billion tonnes. Yet Earth's oceans weigh more.

If it is hard to imagine something so vast, it is perhaps even harder to imagine changing it. But humanity is changing the oceans. From the tropics to the Arctic, the seas are sucking up human-driven emissions of carbon dioxide - about half of the excess belched into the atmosphere over the past two centuries from fossil-fuel burning and cement manufacturing plants¹. When carbon dioxide dissolves in water, carbonic acid is produced: as a result the oceans are becoming more acidic. "It's basic chemistry," says Joanie Kleypas, a marine ecologist at the National Center for Atmospheric Research in Boulder, Colorado. "It's hard to say that this is not happening."

Over the past few years, scientists have documented how increasingly acidic seas could eat away the armour of many creatures - blunting the spikes on sea urchins and

dissolving the covering on corals. In artificially acidified waters, some animals, such as squid, have problems swimming because the corrosive water affects their respiration rate. Others, particularly tiny organisms with carbonate shells, lose their protective shields as the acid eats away at them². But research into low-pH oceanography is, as yet, sparse. "We're just starting to grapple with what low pH will mean for ocean communities," says Jim Barry, a marine biologist at the Monterey Bay Aquarium Research Institute (MBARI) in Moss Landing, California.

This ocean acidification is unlike the atmospheric warming also being caused by carbon dioxide in that it is fairly predictable; plotting its future course requires little more than school chemistry, as opposed to sophisticated modelling. The rate of acidification is pretty much unprecedented. Before the industrial revolution, the rise in the level of carbon dioxide in the atmosphere was relatively slow - giving oceans time to circulate the waters being made more acidic in the shallows with acid-neutralizing carbonate sediments in the depths.

In the past few decades, carbon dioxide has been building up far more quickly, and the ocean is becoming acidified at a rate that outpaces the action of sedimentary antacids. The rate of change is perhaps 100 times anything seen in the past hundreds of millennia, as suggested by isotope studies of ancient sediments. In the century to come, sea creatures will find themselves in conditions that their ancestors never had to face. These organisms have never been forced to adapt to lower pH, says Ulf Riebesell, a marine biogeochemist at the Leibniz Institute for Marine Sciences in Germany. "They've never seen this before in their evolution."

Acid attack

The acidified waters eat away at the carbonate skeletons that protect many marine organisms. By some estimates, calcification rates will decrease by up to 60% by the end of this century. If so, carbon dioxide in the ocean could represent a chemical threat to the biosphere as severe as that posed by the build up of carbon

dioxide in the atmosphere.

A 2005 report from the Royal Society in London called for more research to help quantify the threat. Another report, released last month by three US research agencies, the National Science Foundation, the National Oceanic and Atmospheric Administration, and the US Geological Survey, laid out research strategies for tackling the problem. And

the Intergovernmental Panel on Climate Change (IPCC) — the international body tasked with quantifying the effects of climate change — is flagging ocean acidification as a problem for the first time in its next report, due in early 2007

In 1800, the carbon dioxide in the atmosphere was 280 parts per million, and the oceans' pH averaged 8.16. Today there are 380 parts per million of carbon dioxide in the atmosphere, and the pH of the oceans is on average 8.05.



Estimates suggest the pH could drop to 7.9 by the end of the century. The drop from 8.16 to 7.9, says Kleypas, "doesn't sound like much, but it's a lot." Each one-step change on the pH scale indicates a tenfold change in acidity.

Just as terrestrial ecologists experiment by growing plants in high concentrations of carbon dioxide, so marine biologists are beginning to investigate what life in the less-alkaline ocean may be like.

In a fjord in southwest Norway, Riebesell has set up an outdoor laboratory consisting of a raft with what look like giant milk cartons moored to it. The containers, known as 'mesocosms', are 50-litre vessels filled with coccolithophores - photosynthesizing plankton, or phytoplankton, with carbonate coverings. Riebesell immerses the coccolithophores into tanks that are aerated with the projected levels of carbon dioxide in the next 50 and 100 years. He calls them "the oceans of the future".

The coccolithophores' outer casings — tiny hubcaps known as coccoliths — are made of the carbonate mineral calcite. Riebesell found that exposing coccolithophores to three times the present-day atmospheric level of carbon dioxide caused nearly half of their protective coating to disintegrate³.

Such changes don't bode well for one of the ocean's most abundant types of phytoplankton,



Fragile lives: acidified seas could dissolve corals and blunt the spines of sea urchins (left).

and what's bad for phytoplankton is likely to be bad for the food webs they sustain. By aggregating on the surface of waste from the upper levels of the ocean (mainly fish droppings), the coccoliths help it to sink down to the seabed communities, which recycle its nutrients into the ocean. Weakening the coccoliths could have knock-on effects on nutrient cycling.

Most at risk

Riebesell is now looking at the effects of increasing acidity on plankton eggs and larvae; other researchers are studying the dangers posed to larger animals, such as sea urchins and snails. In one experiment, marine biologist Yoshihisa Shirayama, at Kyoto University in Japan, placed sea urchins and snails separately into 30-litre tanks filled with water containing 550 parts per million of carbon dioxide. Within three months, the creatures dropped in weight by roughly 8%. Their calcite spines became blunted, says Shirayama, and so brittle that they broke off easily when handled.

If carbon dioxide levels in the tanks were quickly lowered, the animals eventually recovered. If they were exposed to high levels over the long term, such as for a year, most of them died⁴. "It's obvious that animals cannot adapt to large change in carbon-dioxide concentration," says Shirayama.

Other disturbing news comes from experiments led by MBARI's Barry. For most of his career, carbon dioxide has just been a tool: he used to carry a fire extin-

guisher to intertidal zones so he could bubble the gas through the sea water, put the animals living in it to sleep and thus capture them more easily. Now he's looking at carbon dioxide as a threat.

Working with his postdoctoral fellow Eric Pane, Barry has been studying how

two crab species respond to elevated levels of carbon dioxide. Preliminary results suggest that the shallow-water Dungeness crab, (*Cancer* species), does much better than the deep-sea Tanner crab (*Chionoecetes* species), as measured by how long it takes their metabolism to recover from a high dose of carbon dioxide. That difference points out a key point about the acidifying oceans, says Barry: "Deep-sea animals are probably much more sensitive to changes than animals found in shallow water."

Barry and Pace presented their findings on

the crab studies in July, at a deep-sea biology symposium in Southampton, UK. In related work, Barry has found that microscopic animals living in seafloor sediments seem to decline after being exposed to a drop in pH of just 0.1 for one month. Oddly, they seem to recover after a week or two — perhaps, Barry says, because fewer of them are being eaten by larger animals, which may have died off, or because they have more to eat themselves as the dead bodies of other small creatures, killed by the pH change, drift to the sea floor.

Mass die-off

Also at risk in the deep sea are cold-water corals, some of the slowest growing corals on Earth. Corals are particularly vulnerable to acidification because reefs are built out of aragonite, a carbonate mineral that is more soluble than the calcite used by coccolithophores and sea urchins. "Deep-water corals could soon be in trouble," says James Orr, an oceanographer at the Laboratory for Climate and Environmental Science in Gif-sur-Yvette, France. By the end of the century, two-thirds of deep-water corals — as opposed to virtually none today — could be exposed to sea water that is corrosive to aragonite⁵.

Because carbonate is more soluble in high pressures and cold water, increased acidity has a greater effect at depth. But Orr's studies suggest that aragonite will be unstable at all depths throughout the Southern Ocean by 2100. Once the corals go, so too may other species that rely on them for resources such as shelter.

Despite such dire models, not all scientists are convinced that ocean acidification will be a major problem. In May, a paper in *Geophysical Research Letters* suggested that the rising carbon dioxide would have minimal biological impact in the ocean⁶. Hugo Loáiciga, a hydrologist at the University of California, Santa Barbara, argued that sediment carbonates would be able to buffer the predicted acidification.

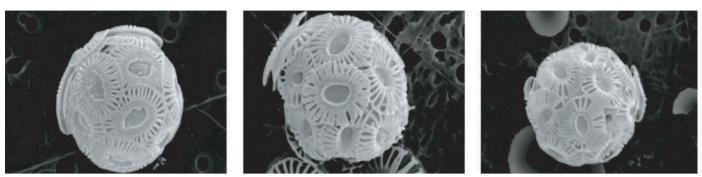
> But it seems most experts disagree. A response, signed by 25 leaders in the field of ocean acidification, rebutted each of Loáiciga's points in detail. The experts also argued that many marine organisms would be sensitive to a drop of 0.2 pH units — a change Loáiciga had said would be essentially unimportant.

Ken Caldeira, an Earth-systems modeller at the Carnegie Institution of Washington in Stanford, California, who led the response, says the public needs to know now that this is a problem, and that it is unprecedented in its scale. In one model, Caldeira and his colleague Michael Wickett from the Lawrence Livermore National Laboratory, California, simulated the effects of an unregulated pulse of fossil-fuel burning that peaks around the year 2100.

The atmospheric carbon-dioxide level peaks shortly after the highest rate of burning. Then

"People should know that the consequences of what we're doing in the next decade will last for thousands of years." — Ken Caldeira





Lost protection: making sea water more acidic (centre and right) dissolves the outer casings of coccolithophores, tiny plankton that form the basis of food webs.

it slowly subsides as the carbon is picked up by the ocean — which slowly becomes more acidic at depth. At the surface, the pH might stop falling by 2750. A kilometre or so deep, however, the pH would still be dropping at the beginning of the next millennium⁷. "People should know that the consequences of what we're doing in next decade will last for thousands of years," says Caldeira.

In the meantime, researchers have a great deal to do trying to understand what the first decades of change could bring about. "So few studies have been done," says Victoria Fabry, an oceanographer at California State University in San Marcos. "We've really just scratched the surface." As an example, Fabry says lab studies on calcifying plankton are in such short supply that researchers have investigated only about 2% of all species.

The July report produced by the US research

agencies suggests paths for future studies. These include merging experiments done in the laboratory with those in the field, as well as identifying the effects of acidification on keystone species such as coral and plankton and how changes to such species could affect the rest of the ecosystem. The report also notes the need to study the problem at all spatial scales; currently, most studies are focused on either the large-scale biogeochemical level or effects on individual organisms. Studies of ecosystems are in short supply.

A world of problems

To try to rectify that, some researchers are pushing for large-scale field experiments, such as marine versions of the open-air experiments in carbon-dioxide enrichment that have been taking place in forests for many years. Barry and his MBARI colleagues are working to

Artificially acidified tanks of sea water are shedding light on the effects of lower pH on sea creatures.

develop one of these experiments in the free ocean — it will be essentially a deep-sea cage set in a plume of water enriched in carbon dioxide.

In addition, disciplines are starting to merge. Oceanographers are beginning to collaborate with chemists to quantify the acidification reactions, and with engineers to develop robotic submersibles to collect deep-sea organisms for study. Social scientists are starting to get involved as well. The next Pacific Science Congress, to be held in Okinawa, Japan, in June 2007, will bring together natural scientists and social scientists to discuss how residents of coastal areas might adapt.

With more attention on the problem, a new possibility has raised its head. Ocean acidification might not just run in parallel with global warming — it could amplify it. The chalky coccolithophores, when blooming, lighten the surface of the oceans, which means more sunlight is reflected into space. Reduce their number and even if other phytoplankton take their place, that lightness will be gone.

Coccolithophores are also responsible for many of the clouds over oceans. They produce a lot of dimethylsulphide, which accounts for much of the aerosolized sulphate in the atmosphere above the oceans. Sulphate particles act as 'seeds' around which cloud droplets grow⁸. Remove them, and you could remove a significant fraction of the world's clouds, warming the planet yet further⁹.

Human imagination cannot easily cope with the vastness of the oceans, or the complexities that change within them can bring about. But human industry faces no such obstacle in making change unavoidable for centuries to come.

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Additional reporting is by Alexandra Witze.

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