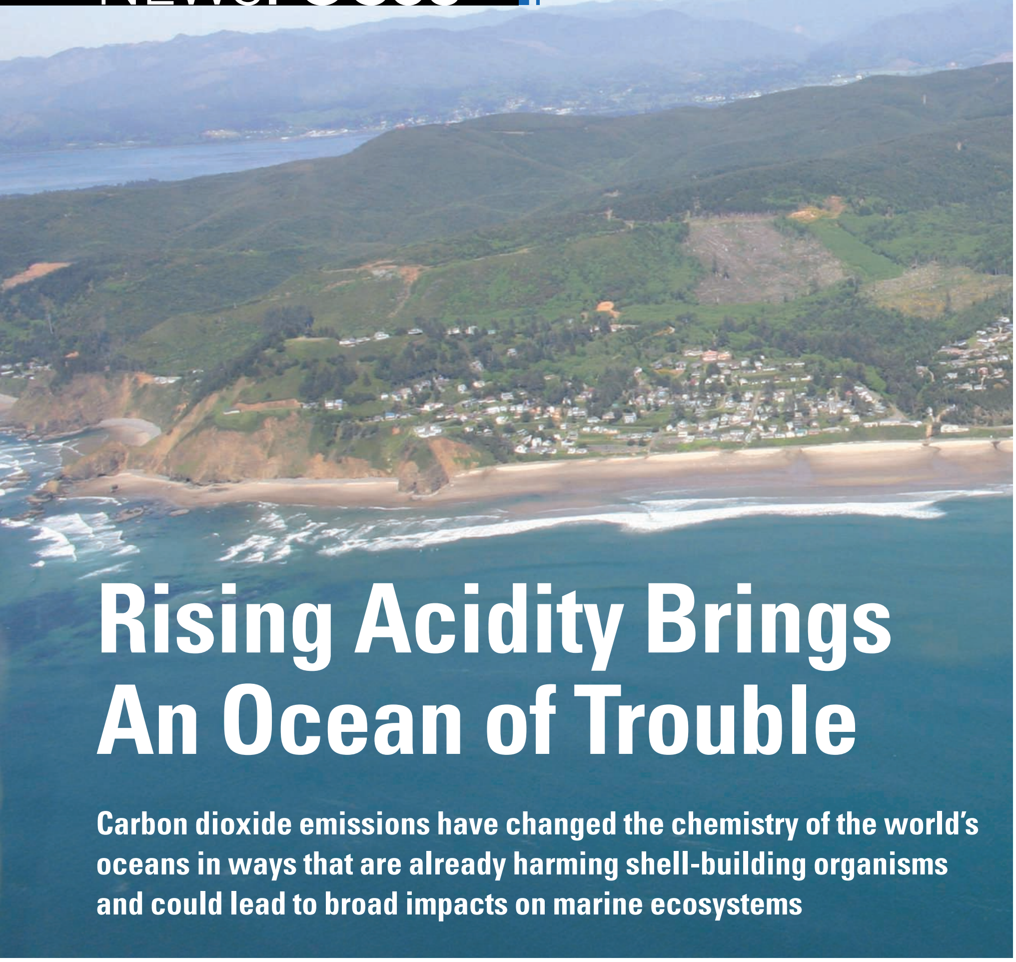

Rising Acidity Brings An Ocean of Trouble

Carbon dioxide emissions have changed the chemistry of the world's oceans in ways that are already harming shell-building organisms and could lead to broad impacts on marine ecosystems

Tip of the spear. Acidity levels in Netarts Bay, Oregon, hit levels the rest of the ocean won't see for decades.

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NETARTS BAY, OREGON—Alan Barton hates beautiful summer days. Not the warm sunshine—here on the central Oregon coast, where it is cold and rainy for much of the year, sunshine is welcome. Rather, for Barton, an oceanographer who helps run an oyster larvae hatchery here, it's the breezes he can't stand.

When the wind blows from the north as it normally does in the summer, it pushes the surface waters out to sea, drawing up cold water from the deeper ocean. That water is enriched with carbon dioxide (CO_2), given off by microbes as they metabolize organic matter that sinks to the ocean bottom. When the CO_2-rich water washes into Netarts Bay and the intake pumps and oyster larvae tanks at the Whiskey Creek Shellfish Hatchery, the excess CO_2 causes the seawater's acidity to spike and reduces the amount of carbonate ions that oyster larvae use to build their shells.

The change can kill oyster larvae instantly or stunt their growth. In 2007 and 2008, Whiskey Creek lost 80% of its annual larvae production and nearly had to close up shop before Barton, working with regional scientists, fingered rising ocean acidity as the source of the problem. Now, the hatchery copes with fluctuations in pH by making sure to draw water into its tanks only after acidity declines. But even that success has left Barton frustrated. "This is what I like to do," he says, shucking an oyster. "I hate thinking about carbonate chemistry."

The reprieve for Whiskey Creek and other shellfish hatcheries and farms along the West Coast of the United States could be short-lived. The burning of fossil fuels emits some 35 billion metric tons of CO_2 into the atmosphere every year. That has already begun to change the fundamental chemistry of the world's oceans, steadily increasing their level of acidity. On page 220, scientists in Switzerland and the United States report projections from a new high-resolution computer model showing that over the next 4 decades, the combination of deep-water upwelling and rising atmospheric CO_2 is likely to have profound impacts on waters off the West Coast of the United States, home to one of the world's most diverse marine ecosystems and most important commercial fisheries.

The new computer model is only one of several recent warning signs. Numerous laboratory and field studies over the past few years underscore rising concerns that ocean acidification could devastate marine ecosystems on which millions of people depend for food and jobs. The new results "are a major concern," says Richard Feely, a chemical oceanographer at the National Oceanic and Atmospheric Administration's Pacific Marine Environmental Laboratory in Seattle, Washington. "It's dramatic how fast these changes will take place." George Waldbusser, an ocean ecologist and biogeochemist at Oregon State University, Corvallis, says it's not clear precisely how rising acidity will affect different organisms, but the changes will likely be broad-based. "It shows us that the windows of opportunity for organisms to succeed get smaller and smaller," he says. "It will probably have important effects on fisheries, food supply, and general ocean ecology."

Nailing a killer

Concerns about ocean acidification have been ramping up for several years (*Science*, 18 June 2010, p. 1500). Although it hasn't captured the public imagination as vividly as its cousin, climate change, the "other CO_2 problem" is just as insidious. One-quarter of CO_2 in the air diffuses into the surface layer of the ocean. There, it reacts with water to create carbonic acid, which in turn splits into negatively charged bicarbonate ions and positively charged hydrogen ions that lower the water's pH. (pH measures available hydrogen ions [H+] in solution; the more hydrogen, the lower the pH value.) Bicarbonate ions lose another H+ to become carbonate ions, which oysters, clams, and other organisms use to build their shells. But as acidity increases, less bicarbonate changes into carbonate, and some of the carbonate that is around recombines with H+ to reform bicarbonate. The upshot is that lower pH means more bicarbonate and less carbonate.

Since preindustrial times, ocean pH has dropped from 8.2 to 8.1. That might not sound like much, but the pH scale is logarithmic, like the Richter scale for measuring earthquakes. The 0.1 pH unit decline therefore corresponds to a 30% rise in acidity. By 2100, ocean pH is expected to drop to about 7.8, increasing the surface ocean's acidity by 150% on average.

Even with this distinct change, strictly speaking, the world's oceans will not become acidic. For that to happen, ocean pH would have to drop below neutral pH of 7.0, something no one is forecasting will happen. An alkaline pH of 7.8 or 8.1 is more acidic than the preindustrial baseline, however, so the process is popularly known as ocean acidification.

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As the pH of seawater drops, it has other effects. The lower carbonate availability drops a measure known as the saturation state of different mineral forms of calcium carbonate, such as calcite and aragonite. Aragonite saturation is particularly sensitive to rising acidity, because that mineral form is more soluble. It also turns out to be the essential ingredient that oyster larvae rely on in their first days to build their shells. If the aragonite saturation state falls below a value of 1, a condition known as undersaturation, already-formed aragonite shells will dissolve. But trouble starts well before that. If the aragonite saturation state falls below 1.5, some organisms, such as oyster larvae, are unable to build shells during the first days of their lives, and they typically succumb quickly.

In 2008, when Barton and others were facing a full-scale collapse of their oyster hatchery, they didn't initially consider ocean pH as the culprit. Instead, they blamed a common bacterial assailant called *Vibrio tubiashii*. *Vibrio* had been a scourge of oyster hatcheries for decades, commonly asserting itself in August after the summer sun had caused widespread blooms in marine plant life, such as algae and seagrass. As those plants grow, they pull CO_2 out of the water to build their cells. That lowers CO_2 levels in the water and thus acidity levels. When the plants die and microbes gobble up the bounty, *Vibrio* moves in, proliferates, and can infect oyster larvae, hampering their development.

By the end of summer in 2007 and 2008, the number of *Vibrio* was "off the charts," Barton says. So he and his colleagues emptied their 62 larvae-rearing tanks—each of which can hold 23,000 to 76,000 liters of water—scrubbed them out, and installed filters to catch the bacteria. When they refilled the tanks, however, larvae kept dying. "After 2008, we thought we were done," says Sue Cudd, the hatchery's owner.

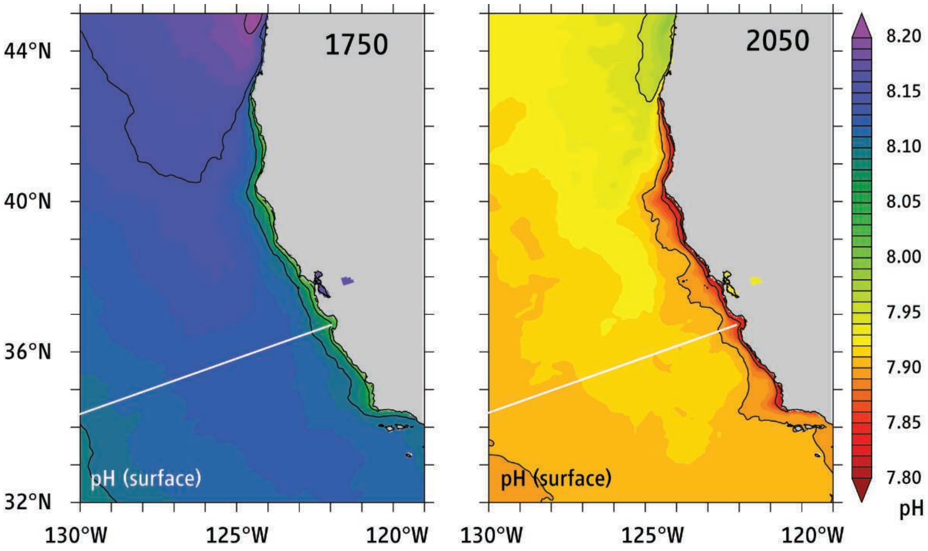
Later that year, they called in Feely, a specialist in ocean acidification. Feely, in turn, called in Waldbusser and Burke Hales of Oregon State University, Corvallis. Waldbusser and Hales brought sensitive detectors to track ocean pH as well as the partial pressure of CO_2 (pCO_2) in the water. They found that Netarts Bay was experiencing wild swings in both pCO_2 and pH. In the May 2012 issue of *Limnology and Oceanography,* they reported that the low-pH swings were the primary cause of the oyster larvae die-offs.


Poster child. Alan Barton shucks a Pacific oyster, often called the canary in the coal mine of ocean acidification.

After figuring out the source of the problem, Whiskey Creek and other oyster hatcheries in Washington state enlisted the help of Senator Maria Cantwell to secure $500,000 from the U.S. government's economic stimulus program. The hatcheries used the money to set up a network of detectors to closely monitor pH, pCO_2, temperature, salinity, and dissolved oxygen levels in Netarts Bay and two other prominent oyster-rearing grounds in Washington. "It was like putting headlights on a car," says Bill Dewey, a shellfish biologist and public affairs director for Taylor Shellfish Farms in Shelton, Washington. The detectors showed that pCO_2 levels plunged to as little as 200 microatmospheres in the afternoon, as algae and other plants pulled CO_2 out of the water for photosynthesis. Overnight, when photosynthesis stopped but respiration continued, pCO_2 levels spiked to 2800. So now the hatcheries make sure to draw their seawater into their tanks at the lowest point of the day. If a large upwelling draws in corrosive waters, they try to hold off filling the tanks as long as possible. The strategy has largely worked. Whiskey Creek is back up to 80% of its historic larvae production levels. Taylor Shellfish has done even better, getting record numbers of larvae in their hatchery, although the natural larvae there haven't had a successful spawning season in 7 years. Now, Cudd says, "monitors are tools we can't live without."

Troubled waters

But that good news looks likely to be temporary. The new computer simulations reported in this issue by a team led by Nicolas Gruber, an ocean biogeochemist at the Swiss Federal Institute of Technology in Zurich, spell trouble for shellfish in the relatively near future. Gruber and his colleagues focused on a broad region of Pacific Ocean upwelling, known as the California Current System (CCS), off the West Coast of the United States. Their regional ocean circulation model tied together the interplay of ocean and atmosphere, as well as the impacts ocean plants have in removing CO_2 from the water and microbes have in dumping that CO_2 back in when they metabolize algae and plants they eat. Because this model focused on the CCS, Gruber and colleagues could design it to study detailed changes at a resolution 400 times that of conventional global



Rising tide. Natural upwelling of CO_2-rich waters caused pH values along the West Coast of the United States to drop even in preindustrial times (*left*), a change that will increase markedly by 2050 (*right*).

CREDITS (TOP TO BOTTOM): R. F. SERVICE/*SCIENCE*; GRUBER *ET AL.*, *PHIL. TRANS. R. SOC. A*, ***369***, 1980–96, WDOI:10.1098/RSTA.2011.0003, 2011

ocean models. The researchers considered various scenarios of CO_2 emissions over the next 4 decades and compared them with CO_2 levels in the atmosphere and ocean in 1750, before global industrialization (see figure, p. 147).

They found that the buildup of atmospheric CO_2 and its diffusion into the ocean will rapidly increase the amount of waters undersaturated in aragonite in the upper 60 meters of ocean, where most organisms live. Before industrialization, undersaturation of this top layer in the CCS almost never occurred. Today, Gruber says, undersaturation conditions prevail there 2% to 4% of the time. By 2050, CCS surface waters will be undersaturated for about half of the year. Just as bad, aragonite saturation levels above 1.5—the conditions under which larvae can thrive—will largely vanish from surface waters. Moreover, as increasing acidification of surface waters diffuses into the depths, undersaturation conditions (with the saturation state below 1) will exist year-round in deep waters, making life essentially impossible for shell-building organisms there. This combination could spell doom for Pacific oysters in the northwest, a $110-million-per-year industry.

Oyster catcher. Sue Cudd of Whiskey Creek Shellfish Hatchery holds a vial containing approximately 100 million oyster larvae that will be sold to oyster farms.

“The take-home message is the closeness of some of these events,” well within the life span of an individual person, Gruber says. Dewey agrees. “We're at the tip of the spear here,” he says. Other regions won't be far behind. Ocean regions with deep-water upwelling are prevalent around the globe, including sites off Chile in South America and the West Coast of Africa. Gruber says his group will next turn to modeling impacts in some of these areas.

Even if humans manage to stop dumping CO_2 into the atmosphere, the picture won't improve for decades. Past studies that track different isotopes of carbon and other elements reveal that the deep corrosive waters that wash up along the West Coast have been circulating along the ocean bottom for 30 to 60 years. The water was last at the ocean surface and exposed to CO_2 from the air back in the 1950s and 1960s, when atmospheric CO_2 levels were only 310 to 320 parts per million, far lower than the 390 ppm today. That means even if global societies stopped emitting carbon today, CO_2-rich waters already in circulation would cause CO_2 levels in the deep ocean to continue rising. “Even if we fix it, we have 50 years of it getting worse before it gets better,” Dewey says.

Beyond oysters

Other recent experiments suggest oysters are far from the only organisms in danger. Trouble, in fact, may be brewing along the first links in the food chain. Last year, for example, researchers led by Luc Beaufort of the European Center for Research and Teaching of Environmental Geosciences at Aix-Marseille University in France reported in the 4 August 2011 issue of *Nature* that as ocean pCO_2 rises, the ability of photosynthetic phytoplankton called coccolithophores to build shells decreases markedly. The team sampled 180 regions of ocean surface water and compared them with historical records found in 555 sediment cores. The amount of calcite the coccolithophores added to their shells dropped as much as 30% when pCO_2 levels rose from about 220 to 400 microatmospheres.

Not all coccolithophores suffered. One species, called *Emiliania huxleyi*—sampled off the coast of Chile in a natural upwelling zone—fared better in CO_2-rich waters. Just how a combination of reduced coccolithophore biodiversity and supercalcifier survival will play out is unclear, the authors report.

In any case, the impacts will likely go far beyond coccolithophores. In 2009, Andrew Moy, an ice-core research scientist at the Antarctic Climate and Ecosystems Cooperative Research Centre in Hobart, Tasmania, and colleagues reported in *Nature Geoscience* that shell weights of other modern photosynthetic plankton, called foraminifera, are down as much as 35% from those in sediments dating back 50,000 years. Yet another class of plankton, called diatoms, is nearly as prolific. And in an article published online 6 May 2012 in *Nature Climate Change*, Ulf Riebesell, a biological oceanographer at the Helmholtz Centre for Ocean Research in Kiel, Germany, and colleagues reported that in the South China Sea, diatom carbon use is down by as much as 40%. So if such sinks for atmospheric CO_2 decline, it could have a powerful feedback effect in the coming decades, reducing the amount of CO_2 the oceans can absorb and thereby increasing atmospheric CO_2 levels.

Past lab studies have raised concerns about another vital link in the food chain: pteropods. These tiny sea snails are particularly abundant in polar oceans near the Arctic and Antarctica. Like oyster larvae, pteropods use aragonite to form their shells. But polar seas naturally harbor lower carbonate concentrations, reducing saturation levels. Ocean chemistry monitoring cruises have already shown aragonite saturation levels in the polar oceans dropping dramatically. If pteropods are unable to respond, that could imperil populations of salmon, krill, whales, and seals that depend directly or indirectly on their bounty. “Things are changing fundamentally in ways that are going to change the ecosystems of the ocean,” Dewey says.

A revealing look at what that change might bring comes from studies of underwater CO_2 seeps, where CO_2 bubbles out of the sea floor near volcanoes, naturally raising pCO_2 levels. Last year, researchers led by Katharina Fabricius, a coral reef ecologist with the Australian Institute of Marine Science in Townsville, reported in *Nature Climate Change* that they looked at three natural CO_2 seeps in tropical waters near Papua New Guinea with pCO_2 levels near levels expected throughout the global oceans in 2100. The biodiversity of coral species there dropped by 40%, and reef development stopped altogether in areas where the pH dropped below 7.7. In a separate study, Riebesell and colleagues found similar destructive impacts on cold-water corals.

Back along the Oregon coast, moderate north winds have returned. And Barton and his colleagues worry that conditions will once again deteriorate to levels other ocean regions won't see for decades. “I have to admit I get a little annoyed when I hear people always talking about 2050 or 2100,” Barton says. “We're already at 2050 in Netarts Bay.” It's a future that doesn't look kind.

–ROBERT F. SERVICE

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