Climate Change Could Alter Undersea Chemical Communication

Carolyn Wilke

Ocean acidification could tamper with marine animals’ sense of smell and the shape of signaling molecules.

A pair of spiny lobsters locks antennae as they battle on the gravel-strewn bottom of an aquarium. The two grapple, grabbing legs and jousting with their long spines. Their aggressive actions extend beyond the show of force: the crustaceans also fire off chemical signals by peeing at each other.

“They’re actively signaling as they’re fighting,” says Charles D. Derby, a sensory biologist at Georgia State University whose lab studies these underwater wrestling matches, along with other crustacean behaviors. Lobster urine, released from the face near the base of the antennae, contains an array of compounds, including chemical cues to an animal’s sex and social status.

Lobsters are just one of myriad marine animals that rely on molecular missives. Behaviors such as finding meals, choosing habitats, avoiding predators, seeking sex, and engaging in social encounters “are all driven by chemistry, at least in part,” Derby says. By playing key roles in how critters act and relate to each other, chemical signals affect the distribution of organisms in an ecosystem. Chemoreceptors are found not only in noses or mouths; in marine animals, they also show up on fins, limbs, or, as in lobsters, antennae that they flick back and forth.

A changing climate may make chemical communication for sea creatures more challenging. By the year 2100, the pH of the ocean—currently about 8.1—is expected to drop to 7.7 if atmospheric carbon dioxide continues to rise. Over the past decade, research has revealed how sensitive chemoreception systems are and how they may take a hit from human activities that cause pollution, warming waters, and ocean acidification. For instance, higher CO2 levels in the water cause juvenile sea bass to lose sensitivity to some smells. In the wild, that could make it harder for the fish to find food and can render them more vulnerable to predators, says Peter C. Hubbard, an electrophysiologist at the Center of Marine Sciences in Portugal. And for migratory fish, such as salmon, lowered olfactory sensitivity may mean difficulty in navigating rivers for spawning.

Many studies have reported changes to fish olfaction and behavior with increased CO2 levels. Recently, a group of marine scientists has raised doubts about the data in some of these papers and the methodology the studies used to test behavioral changes in fish due to increased CO2, a controversy that has cost the field some of its credibility.

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But many researchers agree that acidification would impact ecologically and economically important species through changes to the water’s chemistry. That makes it important to investigate the underlying mechanisms and the magnitude of the effects. Understanding such mechanisms could help make sense of confusing, difficult-to-replicate behavioral findings. So scientists continue to work to untangle the basic workings of marine chemoreception, from identifying signaling molecules to finding the receptors that they bind.

A chemical language
The molecular words that form the ocean’s chemical language present a scientific puzzle. “The language is very, very complex,” says Julia Kubanek, a marine chemist at Georgia Institute of Technology. Potentially thousands of molecules are important for conveying information to ocean organisms, she says; yet, many remain unknown.

Improved analytical techniques are helping pin down those molecules. Kubanek and colleagues have observed that when tiny predatory crustaceans called copepods are around, single-celled organisms called dinoflagellates boost their production of toxic compounds for defense. Using chemical separation techniques paired with NMR spectroscopy and mass spectrometry, the team traced the trigger for the toxicity uptick to a family of lipids in the copepods’ waste.

Since then, one of Kubanek’s collaborators, Erik Selander of the University of Gothenburg, has found that every copepod he’s studied makes these lipids. Compounds such as these had previously gone unrecognized because they’re so dilute in the water, Kubanek says. Now, “people are working on studying ocean chemistry at the single molecule level, as opposed to just bulk concentrations of types of organic compounds.”

Kubanek’s team has also used metabolomics to analyze blue crab urine, which has allowed the researchers to home in on two compounds that cause their mud crab prey to freeze up and stop foraging. Genetics and bioinformatics are also helping to decipher the vast chemical vocabulary of sea creatures, including organisms that are difficult to cultivate. “We don’t have to grow massive culture flasks,” Kubanek says. “We can just get a small sample, sequence these partial genomes, and start to infer their chemistry.”

Body and brain
In addition to identifying the chemicals that creatures send out, scientists are looking at how those molecules are sensed by other animals and trying to unveil the specific proteins that act as receptors and their roles in biological processes and behavior. Kubanek says that hundreds to thousands of mammalian receptors are known but that “we’re way behind” for aquatic animals.

Lab studies of fishes’ response to CO2, for example, have reported anxiety or strange behaviors, such as being attracted to predators’ smells. In this area, researchers aiming to replicate these behavioral studies haven’t always reached the same conclusions.

One theory to explain behavioral changes suggests modifications to the nervous system. A team—which includes members whose other papers have been disputed—put forth the idea that fish respond to high CO2 concentrations by shifting the concentration of ions in the fluid that surrounds the brain. This could change the activity of receptors for the neurotransmitter GABA and alter sensing and behavior based on chemoreception. Separately, other researchers have found evidence for this theory by using chemicals that block GABA binding. Hubbard’s team is now working to probe this theory more directly by measuring concentrations of ions in the cerebrospinal fluid and, eventually, inside fishes’ neurons.

Also, the lining of a fish’s nose links directly to the brain via the olfactory nerve. Zélia Velez of the Center of Marine Sciences, Hubbard, and colleagues monitored the response of the olfactory nerve in juvenile sea bream to elevated CO2. Unlike behavioral tests, which can be more prone to artifacts of the experimental design or even the mood of the fish, Hubbard says, these tests capture how acidification impacts physiology. Under elevated CO2 conditions, the scientists observed a decreased neural signal in response to amino acids, which are thought to serve as food cues.

At higher CO2 levels, sea bream show decreased neural response to amino acids, which serve as food cues for the fish. Credit: Joao Encarnaçao.

The team has also sought to separate the effects of increased CO2 and changes in acidity. For instance, to create acidic conditions without using CO2, the researchers add hydrochloric acid to water that flows by the fishes’ nostrils. Or, to lower the acidity when CO2 is added, they use sodium
hydroxide. Both increased CO₂ and decreased pH changed the fishes’ olfactory sensitivity to certain amino acids. The researchers were surprised to find that for some amino acids, “the effects of the CO₂ itself are higher than [the effects of] the pH,” Velez says. The mechanism behind these changes isn’t fully clear, but the scientists hypothesize that the increased CO₂ may decrease the intracellular pH of olfactory neurons by interfering with an enzyme involved in regulating pH.

This and other work suggest that climate change may have complicated impacts on animals’ sensing. “We don’t know how each species is going to react to these changes,” Velez says. Some fish, such as those that dwell near CO₂ vents, can tolerate high concentrations of CO₂. Other animals may be less resilient. Velez and her colleagues are studying more species, including top predators such as sharks, to further explore the potential impacts of acidified waters.

### Modified molecules

Climate change could alter not only animals’ ability to sense molecules but also the molecules themselves.

At a lower pH, with more hydrogen ions around, some molecules or functional groups pick up a proton. This addition can change a molecule’s conformation and charge distribution, sometimes enough that a protonated form of a molecule may not bind to a receptor in the same way as the deprotonated version.

Knowing that marine pH could drop from 8.1 to 7.7 by the turn of the century, Christina C. Roggatz, a marine chemical ecologist at the University of Hull, and her colleagues decided to investigate whether signaling molecules were sensitive to pH in this range. The team picked a few peptides that mimic molecules that female shore crabs use as cues to care for their eggs. The eggs release the molecules when they need oxygen, prompting their mother to swing them from side to side to increase ventilation. Later, the molecules trigger the female to send the eggs into the water so that all the larvae hatch at the same time, Roggatz says. The actual signaling molecules aren’t known, but the synthetic stand-ins promote the same behaviors.

NMR spectroscopy revealed that certain functional groups on the synthetic mimics become predominately protonated when the pH drops to 7.7. The scientists also determined each group’s pKₐ, the pH at which half the population of that molecule will be protonated and half deprotonated. Using quantum chemical calculations, the researchers predicted changes to the molecules’ structures and charge distributions. Neutral forms of the three peptides were more compact than the protonated forms, which were more planar and gained large positively charged regions.

Those changes correlate with crab behavior. When the crabs were exposed to protonated peptides, “the mom crabs wouldn’t ventilate the eggs as regularly,” Roggatz says. To induce the same ventilation behavior, it took up to 10 times as much protonated as unprotonated peptides, she adds.

Roggatz and her colleagues are hunting for other molecules with groups sensitive to the pH expected under acidifying conditions. Some functional groups, such as amines, phenols, and imidazoles, are particularly prone to change.

“I potentially am interested in every single molecule,” Roggatz says. “But the problem is we actually don’t know that many” molecules with defined ecological functions. Many studies use poorly characterized mixtures, sometimes extracts from marine critters or even squished-up organisms, as proxies for molecules that affect biology and behavior. The compounds could potentially be peptides, nucleic acids, or fatty acids, making identification even more difficult.

How widespread the effects on signaling molecules may be is unclear, Roggatz says. Some chemical cues may even become more potent. “What I have found so far is that when the molecule is sensitive, the changes are potentially devastating.”

Along with the changes to chemoreception and signaling molecules that may accompany acidification, creatures will likely contend with effects due to rising temperatures and hypoxia, a decrease in oxygen levels. “It’s going to be difficult
to really predict what the outcome will be," particularly for different animals, Hubbard says.

The way CO₂ is changing the chemistry of the water "might have a really, really big impact on biodiversity," Velez says. Some effects may cascade through ecosystems if top predators are impacted. By studying effects at multiple levels of the food chain, researchers hope to inform policy makers about changes in conservation efforts that can protect ecosystems. Even though scientists don’t understand all the details of the processes they’re studying, Velez adds, if people don’t act to reduce emissions, species may disappear.

Carolyn Wilke is a freelance contributor to Chemical & Engineering News, the weekly newsmagazine of the American Chemical Society.