Finding a Drop in the Ocean

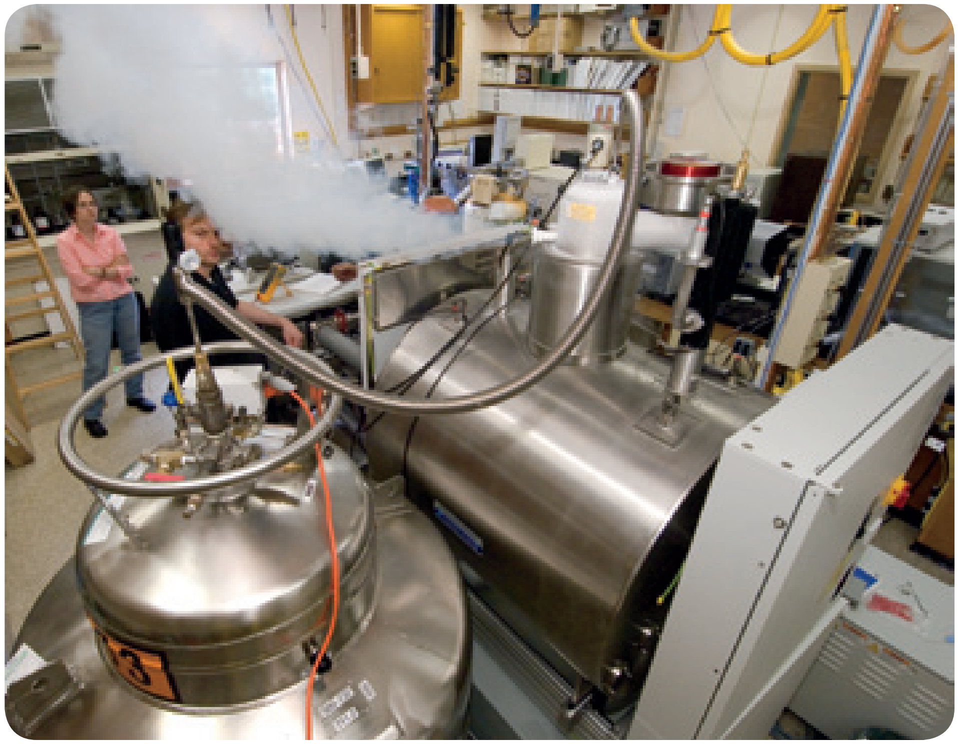
Sensitive method detects tiny traces of dispersant in the Gulf

Marine chemist Elizabeth Kujawinski had developed her analytical method for entirely different research purposes. But she recognized that it could readily be adapted to track chemical components from the Deepwater Horizon oil spill, as well as the dispersant used to try to clean it up.

Kujawinski brought into play a device with a powerful 7-tesla magnet (seven times stronger than the average MRI) and an intimidating name: a Fourier transform ion cyclotron resonance mass spectrometer, or FT-ICR-MS. It can detect and measure vanishingly tiny amounts of an individual compound in a mixture containing tens of thousands of compounds.

Kujawinski spearheaded the grant proposal to install the FT-ICR-MS at Woods Hole Oceanographic Institution (WHOI) in 2007. Since then she and WHOI colleagues Melissa Kido Soule and Krista Longnecker have been using it to develop highly sensitive analytical methods to tease out the complex mishmash of organic matter dissolved in seawater. These molecules—either made or used by marine microbes and other organisms—are like bread crumbs that can guide researchers to find key biochemical pathways that allow living things to thrive and make the entire ecosystem run.

In research published online Jan. 26, 2010, in the journal *Environmental Science & Technology (ES&T)*, Kujawinski and colleagues showed that the highly powerful mass spec and their method were also well-suited to detect, measure, and definitively identify minute quantities of chemical compounds from the Deepwater Horizon spill, including a compound in the dispersant Corexit. The dispersant has been used often on the ocean surface to break down oil clumps and make the oil easier to clean up. But never before had so much been used, and never before had the dispersant been released in the deep ocean.



Tom Kleindinst, WHOI

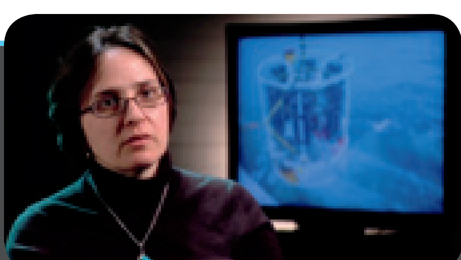
WHOI marine chemist Elizabeth Kujawinski (back left) watches the installation in 2007 of a powerful instrument with an impressive name: a Fourier transform ion cyclotron resonance mass spectrometer.

Kujawinski and colleagues' method is a thousand times more sensitive than that used by the U.S. Environmental Protection Agency to track Corexit and could be used to monitor the dispersant over longer time and distances, she said. As such, it provides a means to answer some key questions: What happened to the approximately 800,000 gallons of the dispersant released in the deep sea? Was it effective? Might it have impacts on the environment, deep-sea coral communities, and deep-water fish such as tuna?

The 'metabolomics' of the ocean

Kujawinski received samples of seawater from in and around the oil spill collected in May, June, and September of 2010 by David Valentine, a scientist at the University of California, Santa Barbara, and co-author of the *ES&T* paper. Using their technique, Kujawinski and colleagues provided a first glimpse of what happened to the dispersant. They detected one of the dispersant's key components, called DOSS (dioctyl sodium sulfosuccinate)—in concentrations of parts per million. It was present months after it was injected into the depths, indicating that the dispersant had not been rapidly biodegraded by microbes.

The researchers also detected DOSS in even lower concentrations (parts per billion) in a plume of oil and natural gas that flowed 1,100 meters deep in a southwesterly direction away from the broken well. That indicated that the dispersant did not itself become randomly dispersed, but rather



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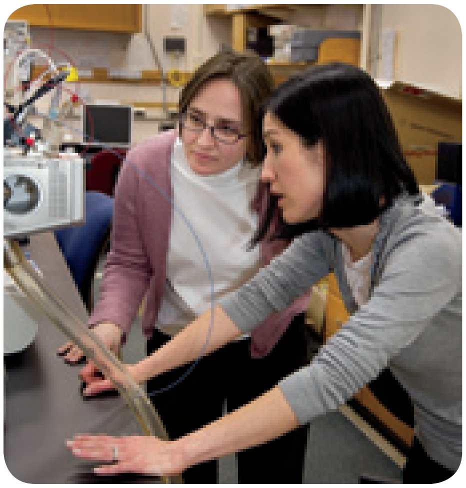
"We are adapting technology from the medical world to learn about what's going on biochemically in the ocean."
—*Elizabeth Kujawinski*



Tom Kleindinst, WHOI

Using the FT-ICR-MS, WHOI researchers Elizabeth Kujawinski (left), Melissa Kido Soule, and colleagues proved that the potentially toxic dispersant had not been quickly biodegraded by microbes but remained in the Gulf months after the spill occurred.

became trapped in the deep-water plume of oil and natural gas.

"The decision to use chemical dispersants at the seafloor was a classic choice between bad and worse," Valentine said. "And while we have provided needed insight into the fate and transport of the dispersant, we still don't know just how serious the threat is. The deep ocean is a sensitive ecosystem unaccustomed to chemical disruptions like this, and there is a lot we don't understand about this cold, dark world."

Kujawinski said FT-ICR mass specs are used in biomedicine, in a field that's gaining prominence called metabolomics, the study of metabolites made by organisms under various conditions. What cells in the body are producing at any given time offers insights into the biochemical processes going on, and FT-ICR-MSs have been used to collect metabolic profiles of highly trained athletes, heart attack victims, and pregnant women, for example.

"We are adapting technology from the medical world to learn similar insights about what's gong on biochemically in the ocean," Kujawinski said. The WHOI FT-ICR-MS, however, is one of only a handful in the world devoted to earth science.

Out to many decimal places

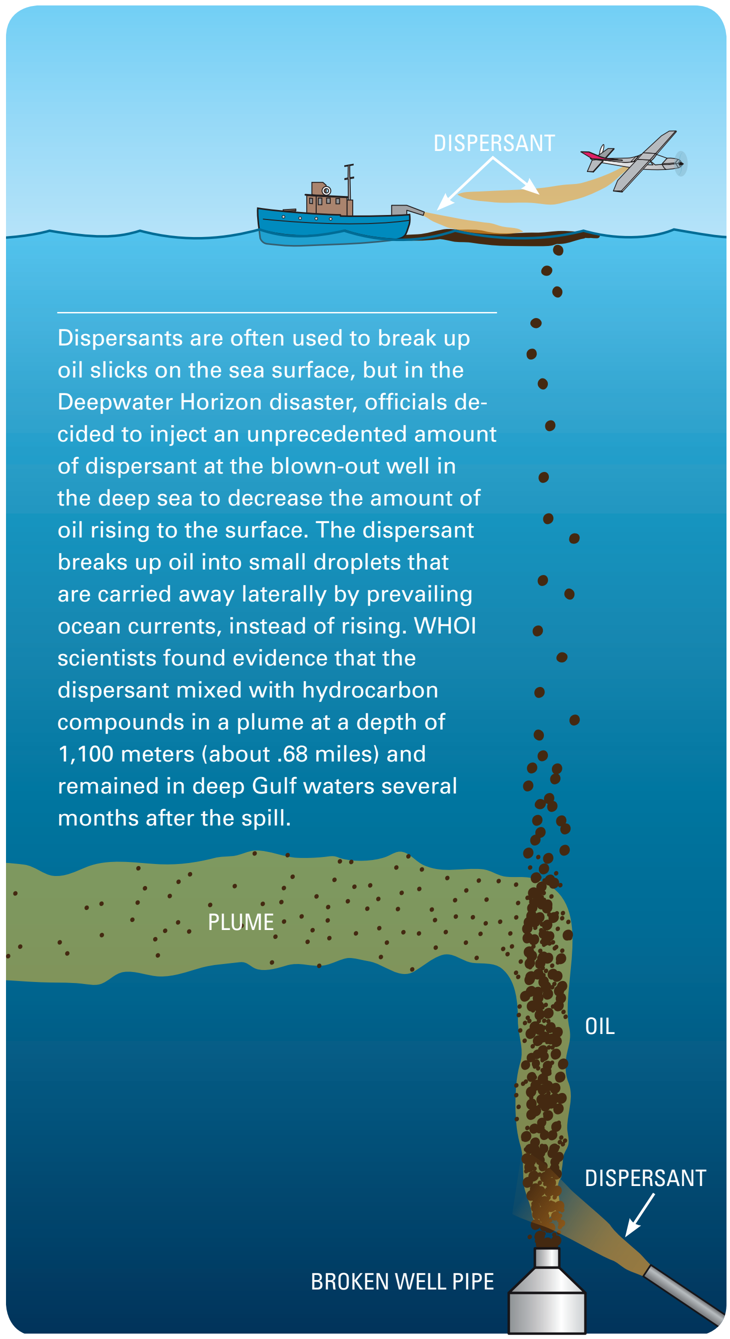
Oil can contain thousands of compounds with different physical structures, chemical properties, and molecular weights. As soon as oil from the damaged undersea Macondo well began gushing into the ocean, it no longer acted as a unified liquid; rather, individual constituents of the oil acted in their own ways. Some compounds evaporated quickly. Others were consumed by bacteria. Some persisted, and of those, some (the proverbial "oil-and-water-don't-mix" variety) remained in droplets or clumps. But other components of oil have electrical charges, and these so-called polar compounds bond with similarly polar water molecules. The FT-ICR-MS can identify and measure these hard-to-detect dissolved chemicals.

"Our goal is to identify compounds in the water that could serve as tracers of the oil in the coming months and years," Kujawinski said. That ability will help researchers elucidate what happens when oil and water *do* mix, as they have in the Gulf of Mexico.

The FT-ICR-MS accomplishes this by measuring the mass of atoms and molecules in compounds down to the fourth number past the decimal point. So while most mass specs can distinguish between compounds weighing between 407 and 408 atomic mass units (amu) and between 408 and 409 amu, for example, the FT-ICR-MS can detect a substance with a mass of 407.0259 amu. That's precise enough to identify the singular collection of atoms—the one possible compound—that could have that mass. It's like surveying a crowd of people weighing between 145 and 150 pounds and being able to find the one guy who weighs 146.3531 pounds.

—*Kate Madin and Joel Greenberg*

Kujawinski, Valentine, Kido Soule, and Longnecker were joined in the study by Angela K. Boysen, a summer student at WHOI, and Molly C. Redmond of UC Santa Barbara. The work was funded by WHOI and the National Science Foundation. The instrumentation was funded by the National Science Foundation and the Gordon and Betty Moore Foundation.



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