

Major source of methanol in the ocean identified

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Finding the right laboratory conditions to culture phytoplankton can be challenging. Phytoplankton are mostly microscopic, single-celled photosynthetic organisms that live suspended in water. Like land plants, they take up carbon dioxide, make carbohydrates using light energy, and release oxygen. They are what is known as primary producers of the ocean -- the organisms that form the base of the food chain. Credit: Tracy Mincer, Woods Hole Oceanographic Institution

As one of the most abundant organic compounds on the planet, methanol occurs naturally in the environment as plants release it as they grow and decompose. It is also found in the ocean, where it is a welcome food source for ravenous microbes that feast on it for energy and growth. While scientists have long known methanol exists in the ocean, and that certain microbes love to snack on it, they've been stymied by one key question: where does it come from?

Researchers at the Woods Hole Oceanographic Institution (WHOI) have solved this mystery through the discovery of a massive - and previously unaccounted for - source of methanol in the [ocean](#): phytoplankton. The study found that these microscopic, plant-like organisms, which form the base of the marine food web, have a unique ability to biologically produce methanol in the ocean in quantities that could rival or exceed that which is produced on land. The results, published in the March 10, 2016, issue of *PLOS ONE*, challenge previous thinking on sources of methanol in the ocean, and help fill important knowledge gaps about ocean microbiology and the amount of methanol generated on our planet. The discovery may also spur research leading to biofuel applications in the future.

"Methanol can be considered a 'baby sugar' molecule and is rapidly consumed in the ocean by abundant bacteria - called methylotrophs - which specialize in this type of food," said Dr. Tracy Mincer, WHOI associate scientist and lead author of the paper. "However, up until now, the thought was that methanol in the ocean came from an overflow of terrestrial methanol in the atmosphere. So, this discovery reveals a huge source of methanol that has gone completely unaccounted for in global methanol estimates."

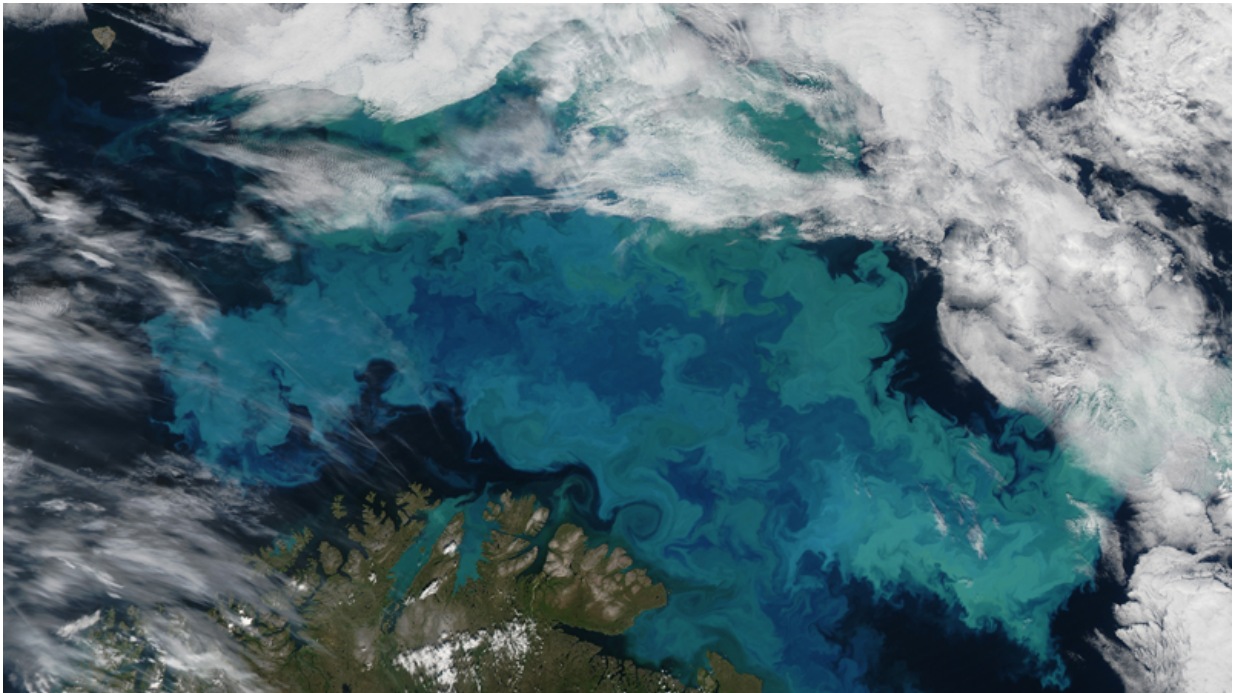


Microbiologist Tracy Mincer with one of the hundreds of cultures of marine microbes that is maintained at WHOI. Credit: Tom Kleindinst, Woods Hole Oceanographic Institution

"Mincer first became interested in the idea of biologically-produced methanol in the ocean through previous work where he found methanol-nibbling bacteria in a phytoplankton culture he was growing. Intrigued, he extracted the microbe's DNA and its barcodes matched up with a well-known methylotroph in the ocean. "Once we were able to characterize this bacteria, I wanted to explore the idea of plankton-produced methanol," said Mincer. "I began reviewing literature and found a paper where a student, as part of his dissertation, had reported some measurements of methanol from phytoplankton. At that point, I knew something was really going on there. It was like a fist coming right out of the computer screen and punching me in the face." Growing pains

As Mincer set out to explore things further, he quickly learned that trying to measure methanol from marine phytoplankton wasn't easy. "I asked a number of colleagues how to measure methanol in seawater and no one had done it before," said Mincer. "There didn't appear to be any methods to directly measure it, so we had to develop our own." Given the high solubility of methanol, extracting samples proved challenging. Mincer and his lab team had to separate out methanol from the salts in seawater by bubbling helium through it to push the volatile organic compounds out. This made it possible to get the samples onto an instrument to be separated and detected. But then they discovered that, instead of producing methanol steadily over time, phytoplankton release it in quick episodic pulses, and only during certain stages of growth. So, they had to be there at the right time to see it.

"As we were growing the phytoplankton cultures, we measured like crazy during the first week and didn't detect anything," he said. "But after about ten days, they started to run out of nutrients and hit a plateau, which is when we saw that initial pulse of methanol." Strength in numbers One of the most noteworthy aspects of the study, according to Mincer, was the amount of methanol plankton were able to produce. Based on lab measurements, he estimates that at least a million tons of the compound is produced in the world's oceans each year - which could exceed the amount found in the atmosphere. "In our cultures, we were surprised to see so much methanol being produced," said Mincer. "The fact that the quantities in the ocean could rival or exceed levels on land indicates that the abundance of methylotrophic microbes - and the overall metabolic demand for methanol - is higher than previously thought." According to Dr. Brian Heikes, a professor and atmospheric chemist at the University of Rhode Island's Graduate School of Oceanography, the findings help shore up previously hypothesized - but unquantified - oceanic sources of methanol.



Satellite imagery captures a massive bloom of microscopic phytoplankton exploding across the Barents Sea. Among the most abundant organisms in the sea, phytoplankton, scientists find, are able to biologically produce methanol -- and in quantities that could rival or exceed that which is produced on land. Credit: NASA MODIS

"Up until now, in situ oceanic methanol sources have been speculative. This study is significant because it shows there is a system that can make and consume methanol biologically in the ocean in large quantities. That wasn't fully appreciated before," said Heikes. Fast food of the ocean While volumes may be high, methanol in seawater doesn't hang around. Like burgers at a fast food joint, high production is quickly offset by fast consumption: most of the methanol is scavenged within a day or two. This, combined with its high solubility, makes the prospect of methanol escaping up into the atmosphere in significant quantities questionable. But according to Mincer, methanol can head towards the

ocean floor.

"We believe that when phytoplankton die and sink, they emit methanol," he said. "This can fuel deeper populations of bacteria in the ocean, and helps answer the question of where methylotrophs in the deep ocean are getting the methanol from." Food source to fuel source Methanol is a key food source that energizes ocean microbes, but could it be harvested from plankton to fuel other things? According to Mincer, there may be opportunities to turn the vast resource into biofuel. "Like terrestrial plants, we believe phytoplankton produce methanol enzymatically, so if we can obtain the enzymes involved and use them to digest their biomass, we may be able to extract useful methanol from them. Methanol is a waste product of these organisms, and they can produce a good amount of it. So when those pulses come out, they could be taken advantage of and harvested from cultures.

"New questions While the findings fill a number of important knowledge gaps, Mincer feels the study has opened up a new set of research questions that need to be addressed. In future work, he hopes to understand, for example, if methanol can tell us anything about phytoplankton growth patterns, what the "chemical currency" is in terms of what, if anything, microbes give back to the [phytoplankton](#) community, and what the velocity of the [methanol](#) consumption loop is in the ocean. "Sometimes in research you have a finding that's bigger than you or your lab can tackle," he said. "If we can answer these questions, we will understand the whole relationship of microbiology in the oceans better and be able to treat this layer of life in the upper ocean like a layer of skin. We'll know when it's healthy, when it's not, and how it functions. Understanding how our planet works at those fundamental levels is critically important.

"The work was supported by the National Science Foundation. Woods Hole Oceanographic Institution is a private, non-profit organization on

Cape Cod, Mass., dedicated to marine research, engineering, and higher education. Established in 1930 on a recommendation from the National Academy of Sciences, its primary mission is to understand the ocean and its interaction with the Earth as a whole, and to communicate a basic understanding of the ocean's role in the changing global environment.

Provided by Woods Hole Oceanographic Institution

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