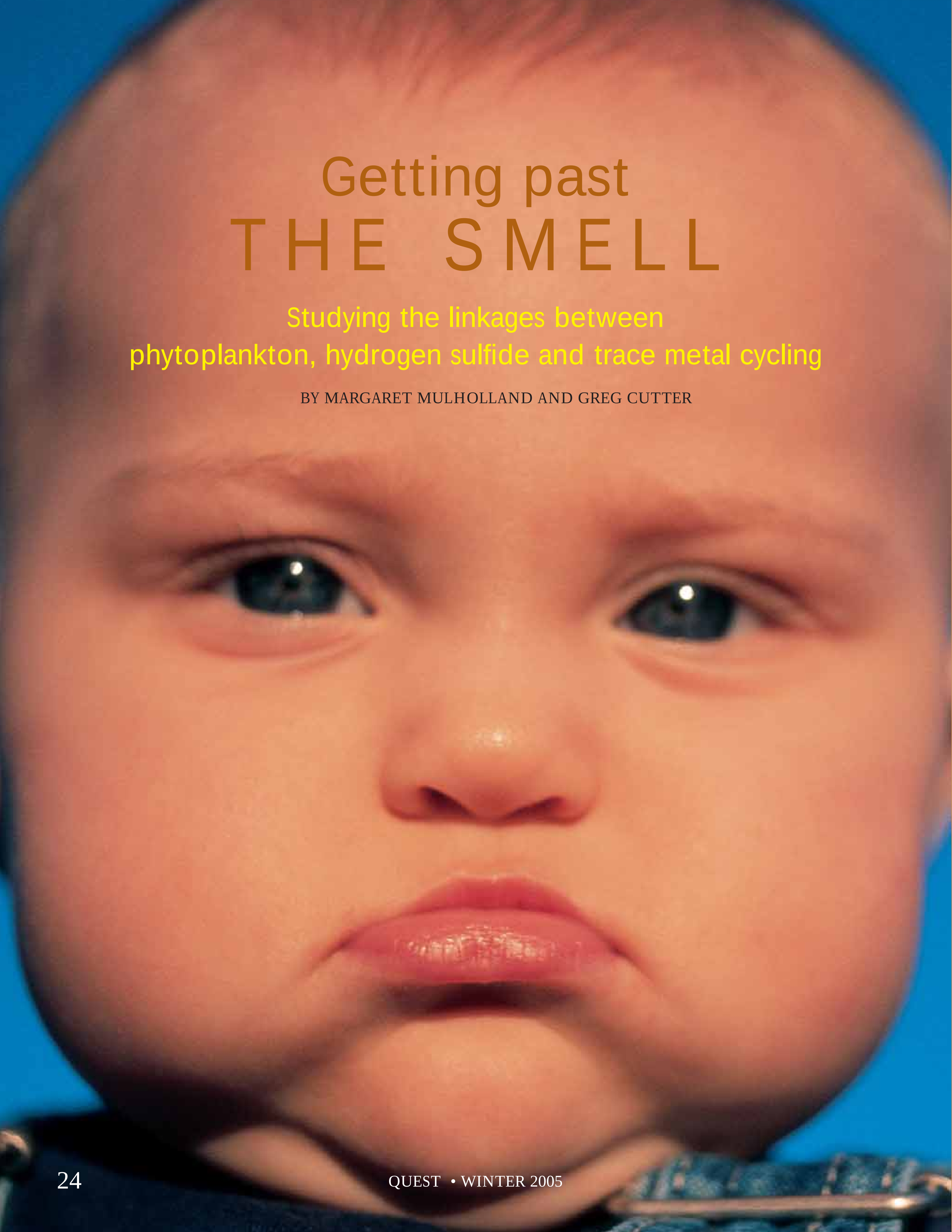

Getting past THE SMELL

Studying the linkages between phytoplankton, hydrogen sulfide and trace metal cycling

BY MARGARET MULHOLLAND AND GREG CUTTER

Why would anyone want to study hydrogen sulfide, the smelly gas that most people associate with rotten eggs or mud flats? Actually, scientists are quite interested in this gas which is released by microscopic plants, or algae, called phytoplankton that live in the ocean's surface waters. The National Science Foundation (NSF) is funding such a study to find out how and why phytoplankton produce this stinky product.

It turns out that hydrogen sulfide reacts with many trace metals that can be essential (like iron or zinc) or toxic (like copper or mercury) to phytoplankton. These reactions can make trace metals unavailable to phytoplankton or even make them insoluble in seawater and cause them to precipitate. This not only affects the way some metals are cycled in the ocean, but also could be a way that phytoplankton affect and even control their chemical environment. Phytoplankton processes can also affect another gas, carbonyl sulfide, which is associated with the production of hydrogen sulfide. This gas affects the radiation balance of the planet by diffusing into the stratosphere and producing particles that block radiative energy from reaching the Earth's surface.

Our research seeks to determine whether hydrogen sulfide production by phytoplankton in the surface ocean is a significant factor in trace metal cycling and in the planetary sulfur cycle. We are conducting laboratory experiments and fieldwork to test more specific hypotheses. In the laboratory, phytoplankton can be grown under controlled conditions to determine which species of these algae can produce hydrogen sulfide. This work provides a "yardstick" with which field results in the real world can be interpreted.

During laboratory studies to date, phytoplankton from almost all taxonomic groups found in the ocean produce H2S (hydrogen sulfide) to some extent. These include species that occur in the Chesapeake Bay, where there is a broad range of nutrient and trace metal concentrations, and the open ocean, where nutrients and trace metals are often at the limits of analytical detection and where they are thought to limit biological productivity, or growth. In general, the lab results show that the smallest of the small phytoplankton, the "blue-green algae," or cyanobacteria, produce the most, while the diatoms that make skeletons out of biogenic silica (also known as opal) and are 100 times as large as the cyanobacteria, produce the least. Adding more metals such as zinc to the culture solutions also increases the relative amounts of hydrogen sulfide produced.

Laboratories at Sea

To put these lab results in context, we conducted two major field expeditions during contrasting seasons, August 2003 and March 2004. Both trips followed the same route, leaving Norfolk to sample waters at the edge of the continental shelf where nutrients, phytoplankton and trace metals are abundant. Our science team then traveled out into the Sargasso Sea (western North Atlantic) near Bermuda, where there are low nutrient, trace metal and phytoplankton concentrations for a temperate open ocean station. Finally, we transected approximately 1,500 miles southeast (800 miles east of Barbados) and repeated sampling experiments in warmer subtropical and tropical seas where the types and species of phytoplankton are different, but where nutrient, trace metal and phytoplankton concentrations remain low. Measurements were made in the uppermost portion of the water column (to 500 meters), where phytoplankton are abundant, and the concentrations and distributions of metals, hydrogen and carbonyl sulfide, and phytoplankton species in these waters were determined. In addition to this work, water was collected and used for incubation experiments to measure the rates of, and factors controlling, hydrogen sulfide production by the natural resident phytoplankton. In these shipboard incubation experiments, hydrogen sulfide production was monitored over time, along with the abundance of particular phytoplankton species.

During August 2003, we used the R/V Cape Hatteras, a member of the NSF research fleet and operated by Duke University and the University of North Carolina, for our fieldwork. We had 12 scientists aboard from Old Dominion University (graduate students, technicians and three faculty) and the University of Maryland (graduate student, postdoctoral researcher and a faculty member). We focused on obtaining data on the concentrations of trace metals and hydrogen sulfide in the water column and their interactions. Although John Donat, ODU associate professor of chemistry and biochemistry, is still analyzing the collected trace metals in his lab at the university, one interesting on-board finding was that hydrogen sulfide and mercury strongly interact, and much of the dissolved mercury in the Sargasso Sea appears to be complexed, or bound, by hydrogen sulfide, which affects its cycling and even toxicity.

Other "highlights" of the August expedition were the two major hurricanes we had to avoid. One was Fabian, which caused us two days of lost ship time and went on to inflict substantial damage to Bermuda. The other "missed" hurricane on our way south was Isabel, which hit Norfolk after we returned.

Research Team Tries Something New

In March 2004, we went out on the R/V Endeavor, another NSF research vessel, operated by the University of Rhode Island. This time, graduate students from the University of Southern California and Scripps Institution of Oceanography joined our group. While no hurricanes bothered us, strong winter storms whipped the seas, making work aboard the ship challenging. The scientific focus of this trip was on performing field incubations of resident phytoplankton to determine the rates of hydrogen sulfide production and to examine the effects of trace metal additions. The

Cutter group also brought along a newly developed automatic system to measure hydrogen sulfide concentrations in the surface ocean every 25 minutes, something never before attempted because it requires a group of analysts working in shifts to cover 24 hours a day for days at a time. Such a “time series” allows the integration of all the processes producing and removing hydrogen sulfide to be observed, which cannot be easily duplicated in the laboratory on land.

In the ocean waters east of Barbados, we found that hydrogen sulfide concentrations were maximal in the early morning after sunrise, but then decreased through the day and into the night. This is consistent with production by phytoplankton as part of photosynthesis (which requires energy from sunlight).

Hydrogen Sulfide’s Role in Our Changing Global Climate

The field incubation work obtained data that are spurring new efforts for the Old Dominion lab studies. Surprisingly, the phytoplankton that produced the most hydrogen sulfide in the field were the larger diatoms and not the very small cyanobacteria – exactly the opposite of previous lab results. Furthermore, the addition of metals seemed to have little effect on phytoplankton growth and their production of hydrogen sulfide. This is consistent with what has been found by other researchers working in the North Atlantic (i.e., metal additions do not stimulate the growth of larger phytoplankton), but its relevance to the hydrogen sulfide-phytoplankton connection will have to remain a puzzle for the moment. Nevertheless, further laboratory experiments are being done to confirm that these species produce hydrogen sulfide in a controlled, unialgal, laboratory setting.

Why is this important? As noted, hydrogen sulfide can play an important role in trace metal availability in the oceans, and as such, act as an intermediary between the phytoplankton producing it and the trace metals affecting them (pro and con) in their aquatic habitat. In our changing global climate, we are already observing changes in algal species distributions in the coastal and open oceans around the world as a result of man-made nutrient and trace metal inputs. Changes in ocean temperature and pH (acidity from atmospheric carbon dioxide entering surface seawater) will also elicit changes in species composition and the resultant cycling of bioreactive elements in the sea. Hydrogen sulfide will have a role in these global changes, ameliorating some effects, while exacerbating others.

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