Manganese can keep toxic hydrogen sulfide zones in check in aquatic systems

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Manganese, in trace amounts, is essential to human health. Now a research team from the University of Delaware, Scripps Institution of Oceanography, the University of Hawaii and Oregon Health and Science University has discovered that a dissolved form of the mineral also is important in waterways such as the Black Sea and Chesapeake Bay, where it can keep toxic hydrogen sulfide zones in check.

The results are reported in the Sept. 29 issue of the prestigious journal *Science* and also are the focus of the journal's "Perspectives" column, "Geochemistry: Manganese Redox Chemistry Revisited," written by Kenneth S. Johnson of the Monterey Bay Aquarium Research Institute in Moss Landing, Calif.

"This discovery will alter the paradigm on which our understanding of manganese aqueous geochemistry is based," Johnson said.

The authors of the study include Robert Trouwborst, who recently completed his doctorate in oceanography at UD's College of Marine and Earth Studies and is now a sediment and water quality consultant for Syncera Water in the Netherlands; Brian Glazer, who received his doctorate in marine biology-biochemistry from UD and is now an assistant professor at the University of Hawaii; and UD chemist George Luther, Maxwell P. and Mildred H. Harrington Professor of Marine Studies, who was Trouwborst's and Glazer's doctoral adviser.

Postdoctoral fellow Brian Clement and his adviser, Bradley Tebo, both from Oregon Health and Science University, also co-authored the study. Clement worked on the project while completing his doctorate from Scripps Institution of Oceanography.

The study is based on research that was conducted in 2003 during a month-long expedition, funded by the National Science Foundation, to explore the chemistry of the Black Sea. Nearly 90 percent of the mile-deep system is a no-oxygen "dead zone," containing large amounts of naturally produced hydrogen sulfide, which is lethal to most marine life. Only specialized microbes can survive in this underwater region.

Above this large underwater "dead zone" in the Black Sea is another aquatic layer, known as the "suboxic zone," that has both minimal amounts of oxygen and minimal amounts of hydrogen sulfide. This layer can have a thickness as great as 40 meters (130 feet) deep in the Black Sea, but only 4 meters (13 feet) deep in the Chesapeake Bay.

The scientists found that a chemical form of dissolved manganese--Mn(III)--can compose in the water or be mobilized from sediments originating from the continental slope and other sources. It can maintain the existence of the suboxic zone by reacting as a reductant with oxygen and as an oxidant with hydrogen sulfide, preventing the deadly hydrogen sulfide from reaching the surface layer of water, where most fish, algae and microscopic plants live.

The finding is surprising, Luther said, because dissolved manganese as Mn(III) was assumed not to form in the environment and thus was largely ignored by scientists.

"Now we've learned that this form of dissolved manganese [Mn(III)] can constitute almost all the dissolved manganese in suboxic water columns and can react with hydrogen sulfide and other compounds that only solid manganese(IV) phases were thought to be doing," Luther noted. "It is also more reactive than the solid phases.

"We think the role of dissolved manganese [Mn(III)] is particularly critical to the Black Sea--the largest body of water in the world containing poisonous hydrogen sulfide," Luther continued. "It also is helpful in other waterways such as the Chesapeake Bay where another element, iron, also plays a minor role in preventing hydrogen sulfide zones from reaching the surface."

During the research mission in the Black Sea, the scientists used a specialized device called an electrochemical analyzer, invented by Don Nuzzio of Analytical Instrument Systems Inc., with support from the Delaware Sea Grant College Program, to locate and map the chemistry of the suboxic zone in real time under changing salinity, temperature and depth. Nuzzio is an adjunct professor at UD's College of Marine and Earth Studies.

The sensor portion of the analyzer developed by Luther's group consists of a gold-tipped electrode encased in a protective plastic sheath that is deployed at various depths where it can then measure a host of chemicals simultaneously--a huge advance over previous sensors that could measure only one chemical at a time.

The readings taken with the analyzer at appointed depths showed the absence or presence of oxygen and different forms of sulfur in each area, which, in turn, provided a key to finding Mn(III) and other processes that might be taking place. UD scientists also have used the device in water chemistry research in the Chesapeake Bay and at hydrothermal vents nearly two miles deep in the Pacific Ocean.

"Our research shows that the impact of dissolved manganese(III) is significant in any aquatic environment, including lakes, plus sediments on the seafloor and soils on land," Luther said. "And for the public who live near the water, dissolved manganese(III) actually helps prevent naturally occurring hydrogen sulfide from getting to the surface, so it prevents both fish kills and the foul odors from this compound's telltale 'rotten egg' smell."

Source: University of Delaware

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