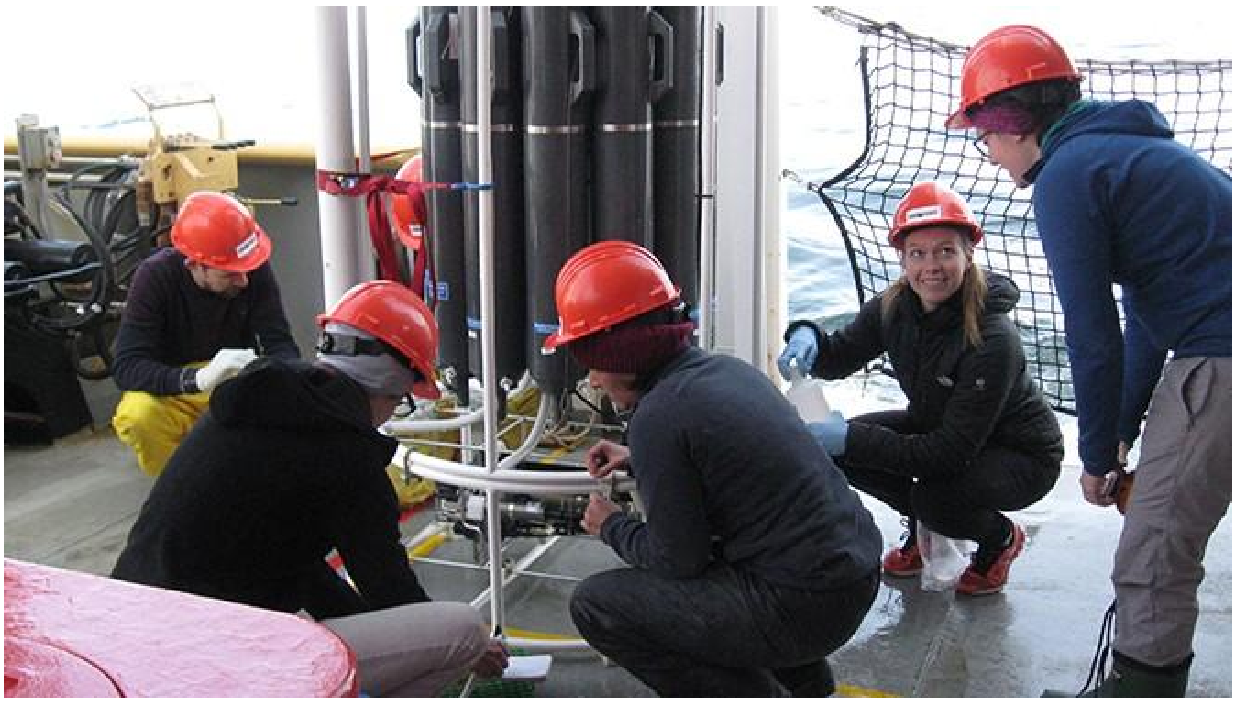
Researchers put manganese's role in coastal waters under the microscope

June 24 2016



University of Delaware doctoral student Veronique Oldham (second from right) takes water samples along the St. Lawrence. Credit: George Luther, University of Delaware

The St. Lawrence Seaway extends more than 2,300 miles from the Atlantic Ocean to the top of the Great Lakes, connecting Canada and the United States.

It has been called the "gateway to North America," serving as an industrial transportation corridor for commodities like iron and coal, grain, machinery and more, as well as a recreational waterway for boaters and anglers.

But the St. Lawrence Seaway also is a prime ecosystem for studying changes occurring in the ocean as a result of the synergistic impacts of climate change.

According to the University of Delaware's George Luther, over the last century the waters of the St. Lawrence have changed as documented by his Canadian colleagues including Alfonso Mucci, a professor in the Department of Earth and Planetary Sciences at McGill University.

"Oxygen-rich water coming down from Iceland has been feeding the St. Lawrence for many years, but now the water circulation patterns have changed and the water is coming from the Atlantic, which has lower oxygen concentrations than Icelandic waters, creating bottom waters that are nearly hypoxic or less than 20 percent oxygen saturated," said Luther, Maxwell P. and Mildred H. Harrington Professor of Oceanography in the School of Marine Science and Policy in UD's College of Earth, Ocean, and Environment.

Luther explained that there is growing concern over low or depleted oxygen zones (called oxygen minimum zones) in water, particularly in coastal regions, because these dead zones cannot support marine life such as fish, crabs and other important species.

Mighty manganese

Luther and longtime collaborator Bradley M. Tebo from Oregon Health and Science University recently received $870,000 from the National Science Foundation's Division of Ocean Sciences to continue investigating the important role that manganese plays in the biogeochemistry of ocean and coastal waters.

Manganese is a trace nutrient important to the growth of humans, plants and animals. Among other things, manganese helps facilitate digestion in humans and it is the key metal involved in forming oxygen during photosynthesis. It is also crucial to the growth and survival of marine organisms in the aquatic environment.

Manganese is present in the environment in three forms—manganese(II), manganese(III) and manganese(IV).

When the element loses or gains an electron, the oxidation state—or number of electrons present— changes in a "redox reaction," like when iron rusts or clothes fade by losing electrons to oxygen in air.

Luther's previous research showed that soluble Mn(III) is far more prevalent in ocean environments than previously known. Recent work in waters and sediments with little or no oxygen has shown that soluble Mn(III) can be the dominant form of manganese and can even be present in oxygenated water if attached to specific organic molecules called ligands.

Understanding how Mn(III) reacts with organic molecules in the presence or absence of oxygen may help scientists understand manganese availability to marine organisms. In particular, the scientists want to understand whether organisms present in the water are helping manganese transition between different states, and if so, what that means.

Fieldwork in the Lower St. Lawrence

Luther studied two sites in the St. Lawrence in 2014 and he knows that sediments on the seafloor release some of the manganese found in the water column. As the manganese is released, it oxidizes in the water column. This is typically mediated by bacteria in the water that set off a chain of chemical reactions.

"During photosynthesis, manganese produces oxygen needed for normal marine life, but you don't need as much manganese as you do iron, which acts like fertilizer in the water as it is taken up by plankton at the base of the food chain to perform a variety of biological functions," Luther said.

The problem is that there is always more manganese in the marine environment than iron, particularly in surface waters. In the Broadkill River Estuary in Delaware, for example, there are salt marsh plants as well as surface waters containing algae, which can create natural organic ligands that bind metals. If these natural materials can react equally or better with manganese than with iron, Luther said, it could upset other metal cycles in the water, like the iron cycle that helps plankton access iron as food.

"This could have an effect on biological growth of marine organisms at the base of the food chain," Luther said.

At the invitation of his Canadian colleague Mucci, Luther returned to the Lower St. Lawrence Estuary (LSLE) in May and spent two-weeks taking water and sediment samples throughout the estuary. The largest estuary in the world, LSLE is considered a model system for understanding the development of low oxygen or oxygen minimum zones and manganese biogeochemistry and cycling because its bottom waters are situated between hypoxic (oxygen-depleted) and oxic (oxygen-rich) conditions.

During the trip, Luther and Veronique Oldham, a UD doctoral student, measured manganese and iron throughout the water column and used sensors to measure oxygen, salinity, depth, pressure, temperature, water turbidity, and chlorophyll concentration, which tell the researchers something about plankton growth prior to the measurement.

At the same time, Tebo, a microbiologist, and his research team cultivated for micro-organisms performing the oxidation, hoping to reveal a connection between the oxidation and the biological content in the water.

Over the next two years, Luther will take similar measurements in the seasonally anoxic Chesapeake Bay, and in the Broadkill River, which is characterized by high surface oxygen levels, high nutrient load and high bacteria counts.

"The amount of oxygen in any given body of water varies seasonally and over time based on the amount of oxygen coming into the water from the atmosphere or from the mixing of different water masses and the chemical or biological processes that produce or consume the oxygen in situ," Luther said.

"We are trying to figure out which processes are more important in one location than another, and if so, why; are they related to low oxygen or are they related to something else?"

Provided by University of Delaware