This is Wisconsin Water News, a production of the University of Wisconsin Sea Grant Program. I'm your host, Marie Zhuikov. Today's episode is:

## Freshwater steel corrosion occurring beyond Lake Superior harbors

## {insert ship salute}

That's the sound of the last ship of the season entering the Duluth-Superior Harbor on the western tip of Lake Superior. The Paul R Tregurtha closed the local shipping season on January 15, 2021. Visitors to the Superior and Duluth ship canals enjoy watching these ships come and go. What they may not realize is that the structures supporting these ships – such as docks and breakwalls -- are under a silent and slow attack.

The culprits are microbes, which are corroding underwater steel structures at an accelerated rate. The problem was first noticed in 1998. Researchers funded in part by the Wisconsin and Minnesota Sea Grant programs eventually discovered that the microbes are working in a complicated interaction between water and the steel. Bacteria form small lumps, or tubercles, on the steel. The lumps limit oxygen and allow small amounts of copper in the water to interact with and dissolve the steel, which results in pockmarks and holes that compromise steel structures.

In addition to the Duluth-Superior Harbor, the corrosion was found in other Lake Superior Harbors located in Wisconsin, Michigan, Minnesota and Canada.

Along with partners, Gene Clark, retired Wisconsin Sea Grant coastal engineer, devoted considerable energy into ferreting out the causes of and ways to mitigate <u>this corrosion</u>, which can lead to costly harbor infrastructure replacement.

A group of experts brought together to investigate the issue in 2004 blamed water chemistry specific to Lake Superior. However, those still tracking the issue have discovered this microbially influenced corrosion problem is more widespread. It's being found in inland lakes in northern Minnesota and in the St. Louis River, far upstream from Lake Superior.

Chad Scott, principal at AMI Consulting Engineers, initially alerted harbor industries about the corrosion in 1998 when he was a diver inspecting structures in the Duluth-Superior Harbor. Scott said during the past few years his company has worked with the U.S. Army Corps of Engineers to place steel samples (or coupons) in the St. Louis River at the Thompson Dam, the Minnesota towns of Scanlon, Cloquet, and Cotton. Scott reports what they found:

"At every single location along the river, the steel had the same tubercles on them. So, what that tells me is, what's coming to the harbor is coming down naturally from inland in Minnesota."

Scott said his firm designed and oversaw replacement of gates on the Fond du Lac Dam and the Sappi Dam along the St. Louis River in Cloquet.

## "They were all heavily pitted. It looked just like harbor corrosion."

He's also had friends report biocorrosion on their docks on Fish Lake, Island Lake and Grand Lake. He's seen firsthand the dock posts covered by corrosive tubercles on those lakes.

Randall Hicks, professor emeritus at the University of Minnesota Duluth, has worked for years to understand the microbiology behind the corrosion. He said he has seen the tubercles on his own dock on Barrs Lake near Two Harbors. He has also identified them in photos from a dock on Wilson Lake near Cotton.

"I don't think it's just a regional problem. I think it's been happening all along for a long time in places where conditions are right."

Those conditions include the presence of sulfate-reducing bacteria and iron-oxidizing bacteria, a source of dissolved sulfate and iron, and low-oxygen conditions such as those sometimes found in spring water.

Hicks described how the process begins when a clean sheet of steel is placed in water.

"Different bacteria will attach to the surface and form a biofilm first."

Dental plaque is a common example of a biofilm. Microorganisms multiply and create a thin but tight layer on teeth. In this case, the biofilm layer is on steel.

"As that biofilm grows, we see a lot of iron-oxidizing bacteria – they're aerobic microorganisms. He explained that as the iron-oxidizing bacteria next to the steel surface use up oxygen, sulfate-reducing bacteria, bacteria that can live without oxygen, become common. "It's really their activities in combination with activities of the iron-oxidizers in the biofilm that accelerate the loss of steel from the surface of the metal."

Jim Sharrow, retired director of planning and resiliency with the Duluth Seaway Port Authority, said the corrosion bacteria are not an invasive species.

"They're indigenous to this area. They're all over."

Previous research identified <u>coatings that can be used to protect steel</u>. Hicks is now working on ways to fool the bacteria in the first place. He and Mikael Elias, associate professor from the University of Minnesota Twin Cities, have found that adding a lactonase enzyme into a steel coating can <u>reduce the biofilm produced</u>, <u>change the biofilm community and reduce the amount of corrosion</u>. The lactonase enzyme works by destroying signaling molecules that the bacteria on steel produce to sense each other – in essence, fooling the bacteria into thinking they are alone, so they don't turn on genes to produce a biofilm.

The nontoxic coating enzymes only last a month or two before degrading or diffusing out of the coating but Hicks said that, compared to untreated steel, the enzymes have reduced corrosion by 50% for at least two years, which was the length of their study.

"Hopefully, these enzymes can have an impact even farther out. If you're in the shipping business and you expect a steel structure to last 100 years, then all of a sudden you have to replace it every 50 years because of the corrosion, that's a big economic impact – and that's just with doubling the corrosion rate. If we can reduce the rate, we don't need to have a big impact to really extend the lifetime of structures quite a ways down the road."

The University of Minnesota has <u>applied for a patent</u> for the lactonase enzyme coating. Hicks and Elias have also conducted tests in Lake Minnetonka and the Mississippi River to see if the same mechanism in

the enzymes that inhibits biofilms from forming on steel inhibits larger invasive and nuisance organisms like zebra mussels and barnacles from attaching to underwater structures.

Elias said their experiments, funded by the Minnesota Environment and Natural Resources Trust Fund, were successful. More recently, they added sites in sea water. Their pilot experiments in Florida show promise.

Until the lactonase enzyme coating becomes commercially available, what should cabin dock owners do to protect their steel from biocorrosion? Sharrow has some suggestions:

"Basically, what we found is, all you need to do is keep paint on your dock. You need to keep the water from touching the steel. You can use epoxy, but if you take your dock out every fall, you could probably use Rustoleum or something like that."

Beyond docks, enzyme technology might also work on farm crops and even in people. Elias said he is testing whether a lactonase enzyme spray can protect corn from a common bacterial infection called Gross's wilt. Cystic fibrosis patients are prone to bacterial pneumonia, which forms in a biofilm.

"One of our goals is to potentially use this enzyme as an aerosol to prevent biofilms in the lungs. . . It appears from our experiments that everywhere microbes are creating some sort of nuisance, this enzyme, because it changes the behavior of bacteria, can be helpful. We have a lot of different investigations to do and we are trying our best to pursue some of them as hard as we can."

Hicks gave credit to the first groups that paid attention to the biocorrosion.

"This all grew out of those initial corrosion studies funded by Sea Grant and the work we did with Gene Clark and the other people in the corrosion study group."

Other organizations involved include the U.S. Army Corps of Engineers and the Great Lakes Maritime Research Institute.

That's it for this episode of Wisconsin Water News, just one of the ways that Wisconsin Sea Grant promotes the sustainable use of Great Lakes resources through research, education and outreach. Listen and subscribe to us through Spotify, I-Tunes and Google Play or at seagrant.wisc.edu. Thank you to Jim Sharrow, Randall Hicks, Chad Scott, and Mikael Elias, and thank you for listening.