
Assessing the Role of Microorganisms in the Accelerated Corrosion of Port Transportation Infrastructure in the Duluth-Superior Harbor

by *Randall E. Hicks*



Photo courtesy of Visit Duluth and Sequest Productions

A ship docked in a canal in Duluth-Superior Harbor.

The economies of coastal communities around the Great Lakes have historically been dependent upon maritime transportation. Urban ports and waterways continue to accommodate expanding trade, growth of tourism, and recreational boating. Even in this challenging economic period, planned expansions in the iron-ore, slab-steel, low-sulfur coal, and nonferrous metals industries and growing tourism indicate that the need for adequate port infrastructure will increase and become even more important to Minnesota's economy over the next decade. Yet, Lake Superior harbors and the maritime industry are facing a

serious problem: accelerated corrosive loss of port infrastructure.

Steel sheet- and H-pilings used for docks, bridges, and bulkheads have been reported to be corroding at an accelerated rate in the Duluth-Superior harbor. The increased rate of corrosion appears to have begun in the late 1970s, and will require expensive replacement of port facilities if the cause and possible remedies cannot be identified. Approximately 20 kilometers of steel sheet-pilings appear to be affected in the Duluth-Superior harbor, which may cost more than \$200 million to replace. When Lake Superior water levels dropped in 2007, the extent of

piling corrosion was clearly visible on numerous steel structures in the harbor.

This article highlights the extent of corrosion of port transportation infrastructure in the Duluth-Superior harbor and describes the methodology and findings from our laboratory's initial studies of the possible role of microorganisms in this corrosion. Our goal was to determine if differences in microbial communities between two corroding structures and a less-affected site indicated the participation of bacteria in this accelerated corrosion process. Our research group is continuing to actively investigate the cause of this problem through field and laboratory studies.

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First Observations of Corrosion on Duluth-Superior Harbor Port Pilings

Chad Scott, from AMI Consulting Engineers in Duluth, Minnesota, was one of the first persons to recognize the corrosion problem in the Duluth-Superior harbor when he saw football-size holes in steel pilings at the U.S. Coast Guard dock during 1998. In September 2004, the U.S. Army Corps of Engineers, the Duluth Seaway Port Authority, and the Minnesota and Wisconsin Sea Grant Programs convened an expert panel from the U.S. Army Corps of Engineers, universities, consulting firms, and the Naval Research Laboratory to evaluate this corrosion issue. This panel described the corrosion as "pock marks primarily in the 4 feet just below the water surface" extending "down to about 10 feet, but decreasing from 4 feet below the surface to 10 feet. The corroding pock marks are covered by an orangish coating that tends to cover the corroded pit." The workshop culminated in a report for the U.S. Army Corps of Engineers that recommended a course of action for addressing the problem.¹

This expert panel identified and ranked 12 possible causes of the corrosion (Table 1), and concluded that water chemistry, dissolved oxygen content, and dissolved chlorides from de-icing salts appeared the most likely of the 12 causes discussed to be responsible for the accelerated corrosion. A lack of data made it unclear whether microbiological factors or functional harbor changes were unduly influencing corrosion in the harbor. The panel recommended "immediately quantifying the corrosion rate, conducting a water chemistry analysis, checking for microbiologically influenced corrosion, testing for stray DC currents, and assessing the condition of critical steel structures."

The U.S. Army Corps of Engineers formed a working group of governmental, private, and university partners

¹ C.P. Marsh, J. Bushman, A.D. Beitelman, R.G. Buchheit, and B.J. Little. *Freshwater Corrosion in the Duluth-Superior Harbor-Summary of the Initial Workshop Findings*. Special publication ERDC/CERL SR-05-3, U.S. Army Corps of Engineers, 2005.



Corroding steel sheet-piling (and close-up) on the foundation of a navigation aid in the Duluth-Superior harbor, exposed during low water levels in 2007.



in 2005 who were concerned about this problem. I became part of this working group in late 2005 at the request of the Duluth Seaway Port Authority and the Minnesota Sea Grant Program. Subsequently, the federal government awarded funding to the U.S. Army Corps of Engineers, and the State of Minnesota awarded funds to the Duluth Seaway Port Authority, to study this problem further. These groups used much of the

initial funding to assess the condition of federal and private structures in the harbor, but also measured instantaneous corrosion rates and some water chemistry parameters, tested for stray DC currents, and collected preliminary samples for microbiological analysis. Since then, stray current from high-voltage DC power lines has been eliminated as a possible cause of the corrosion.

Table 1. Estimated Importance of Possible Causes of Harbor Corrosion

Possible Causes of Corrosion	Assessment of Significance
Water chemistry	Significant
Temperature	Not significant
Dissolved oxygen content	Significant
Dissolved chlorides from de-icing salts	Significant
Microbiologically influenced corrosion	Not clear (further analysis)
Stray current corrosion	Not significant (but check)
Storm water runoff/sewage discharge (related to water chemistry)	Not significant (of itself)
Ballast discharge	Not significant
Zebra mussels	Not significant
Metallurgy of steel	Not significant
Water electrolysis from power distribution	Not significant
Functional changes within the harbor	Not clear (bear in mind)

Source: C.P. Marsh, J. Bushman, A. D. Beitelman, R. G. Buchheit, and B. J. Little. *Freshwater Corrosion in the Duluth-Superior Harbor-Summary of the Initial Workshop Findings*. Special publication ERDC/CERL SR-05-3, U.S. Army Corps of Engineers, 2005.

Nature of the Accelerated Corrosion

Most of the corrosion on pilings in the Duluth-Superior harbor is confined to the first 1.5 meters below the waterline and decreases in magnitude from 1.5 to 3 meters below the surface. In addition, extensive zebra mussel colonization occurs on the steel pilings below 3 meters to the bottom of the pile, where little or no corrosion is observed. The corroding steel pilings have a rusty appearance characterized by orange, blister-like, raised tubercles on the surface. Corrosion tubercles are hollow mounds of corrosion products and deposits that cap localized regions of metal loss. These tubercles vary in diameter from a few millimeters to several centimeters and, when removed, reveal large and often deep pits (6 to 10 millimeters) in the steel, which is sometimes perforated.

Three lines of evidence indicate that the rate of steel corrosion is faster than normally expected in the Duluth-Superior harbor. First, the panel of experts indicated that the pit depths in steel pilings within this harbor are deeper than the average pit depths for comparable corroding materials in freshwater. Second, in 2006, Bushman & Associates, Inc., an independent consulting firm hired by the U.S. Army Corps of Engineers, measured instantaneous corrosion rates of 153 to 165 micrometers per year ($\mu\text{m}/\text{yr}$) at sites that appeared most affected by corrosion. These instantaneous corrosion rates were

considerably higher (~4 to 13 times) than normal (13 to 38 $\mu\text{m}/\text{yr}$ according to Bushman & Associates), suggesting that these high rates could only be explained by some accelerating factor, such as microbiologically influenced corrosion (Table 2). Upon closer inspection, these data also revealed a gradient of corrosion from the entry to the Duluth-Superior

harbor at Lake Superior toward the inner part of the harbor, where the most extensive corrosion has been seen. These corrosion rates also varied with seasonal temperature changes, which is consistent with biological and chemical processes. Finally, Chad Scott, from AMI Consulting Engineers, noticed that orange corrosion tubercles rapidly appeared on unprotected steel sheet-pilings that were replaced at the Superior entry to the harbor during June and July 2006. By September, corrosion pits were already apparent below the corrosion tubercles on these new steel sheet-pilings.

The pattern of instantaneous corrosion rates was similar to that of differences in water chemistry within the Duluth-Superior harbor in 2006 (Table 2). Sulfate concentrations were 5 to 8 times higher and the instantaneous corrosion rates were 3 times greater at areas in the inner harbor compared to the entries to the harbor where the sulfate concentrations and instantaneous corrosion rates were both lower. The sulfate concentrations and instantaneous corrosion rates were also higher (2 and up to 4 times, respectively) in the inner harbor compared to the St. Louis River at the head of the harbor. Similarly, the chloride concentrations were twice as high in the inner harbor than at the entries to the harbor or in the St. Louis River. These results indicated that local water quality was at least related to the corrosion and



Orange corrosion tubercles below the waterline on a steel piling at the Midwest Energy dock in the Duluth-Superior harbor.

Photograph by R.E. Hicks

may directly or indirectly influence the corrosion of steel in the harbor. The instantaneous corrosion rates measured in 2006 tended to be greater at sites with high sulfate concentrations, suggesting that sulfate-reducing bacteria might be involved in the corrosion process.

A scanning electron microscope examination of corroded sheet steel removed from a dock in the harbor during December 2005 revealed a complex community of microorganisms attached to the surface of the corroding steel, composed of bacteria, filamentous algae, and diatoms, a type of single-celled algae. There was also extensive coverage of bacteria-sized cells in pits under the rusty tubercles. Microbiologically influenced corrosion is a general term for corrosion resulting from the presence and activities of microorganisms. Microbiologically mediated reactions can alter both rates and types of electrochemical reactions, and microorganisms can cause such things as pitting, crevice corrosion, anaerobic conditions in biofilms, and increased galvanic corrosion (see the workshop report by Marsh et al., 2005).

The visual appearance of the Duluth-Superior harbor corrosion is consistent with the appearance of corrosion caused by iron-oxidizing bacteria and similar to corrosion of steel structures recently observed at other harbors in Lake Superior. Soils, bedrock, and groundwater in the vicinity of this harbor are rich

Table 2. Estimated Instantaneous Corrosion Rates and Water Quality in the Duluth-Superior Harbor in 2006

Site	Location	Corrosion Rate ¹ (µm/yr)		Sulfate ² (mg/L)	Chloride ² (mg/L)
		Sept	Nov		
Duluth Entry	Entry	53	23	4–6	<10
Superior Entry	Entry	—	46	6–16	10–11
DECC	Outer Harbor	—	—	12	<10
Cutler Magner	Outer Harbor	117	43	19	14
DSPA Berth 4	Outer Harbor	99	53	21	14
Midwest Energy	Inner Harbor	155	58	32	21
Hallett Dock 5	Inner Harbor	163	64	30	21
Oliver Bridge	St. Louis River	132	15	14	11

¹ Bushman & Associates, Inc., 2006. Linear polarization resistant corrosion rate. Final Report [average corrosion rate with mild steel electrodes].

² September 19–24, 2006; Trace Analytical Laboratories, Inc., Muskegon, Michigan.

in iron, and neutral pH iron-oxidizing bacteria can be found in seeps on the hillside overlooking the Duluth-Superior harbor. Microbiologically influenced corrosion is rarely caused by a single microbial group, however, but is more often caused by consortia of microbes including iron-oxidizing and sulfate-reducing bacteria. The corrosion seen in the Duluth-Superior harbor is also similar to accelerated low-water corrosion reported during the past decade

on marine steel-pilings in the United Kingdom and Baltic Sea, which has been thought to be accelerated by the action of sulfate-reducing bacteria.²

Research Methodology and Analysis Results

This section briefly describes our methodology and the results of our analysis.

Collection of Samples. We collected samples from the surfaces of steel pilings in the Duluth-Superior harbor in August and September 2006 to examine microscopically, to isolate iron-oxidizing bacteria, and to extract DNA from biofilms to compare bacterial communities on these steel surfaces and identify their members. We chose to compare two sites in the inner harbor, where steel corrosion was severe, to a less affected site at the Duluth entry to the harbor. A commercial diver collected these biofilm samples from corroded structures approximately 1 meter below the waterline at Hallett Dock 5 (August 1 and September 14) and the Midwest Energy dock (August 15) in the harbor and at the Duluth entry (September 15), using a syringe-brush sampler (Figure 1).

Examination of Samples for the Presence of Microbial Biofilms. The first goal of our research was to examine

² J.B. Christie. *Concentration Corrosion of Berths and Jetties, the Threat to our Maritime Transport Infrastructure*. Aberdeen Harbour Board Report, Aberdeen, U.K., 2001; and M. Graff and O. Seifert. "ALWC on a Jetty: A Case History from Discovery to Repair." Second International Conference on Accelerated Low Water Corrosion, June 21–22, 2005, Liverpool, England.

Photograph courtesy of Gene Clark, Wisconsin Sea Grant Program



Severe corrosion that has perforated the sheet steel at the DM&IR ore docks near Hallett Dock 5, exposed during low water levels in 2007.

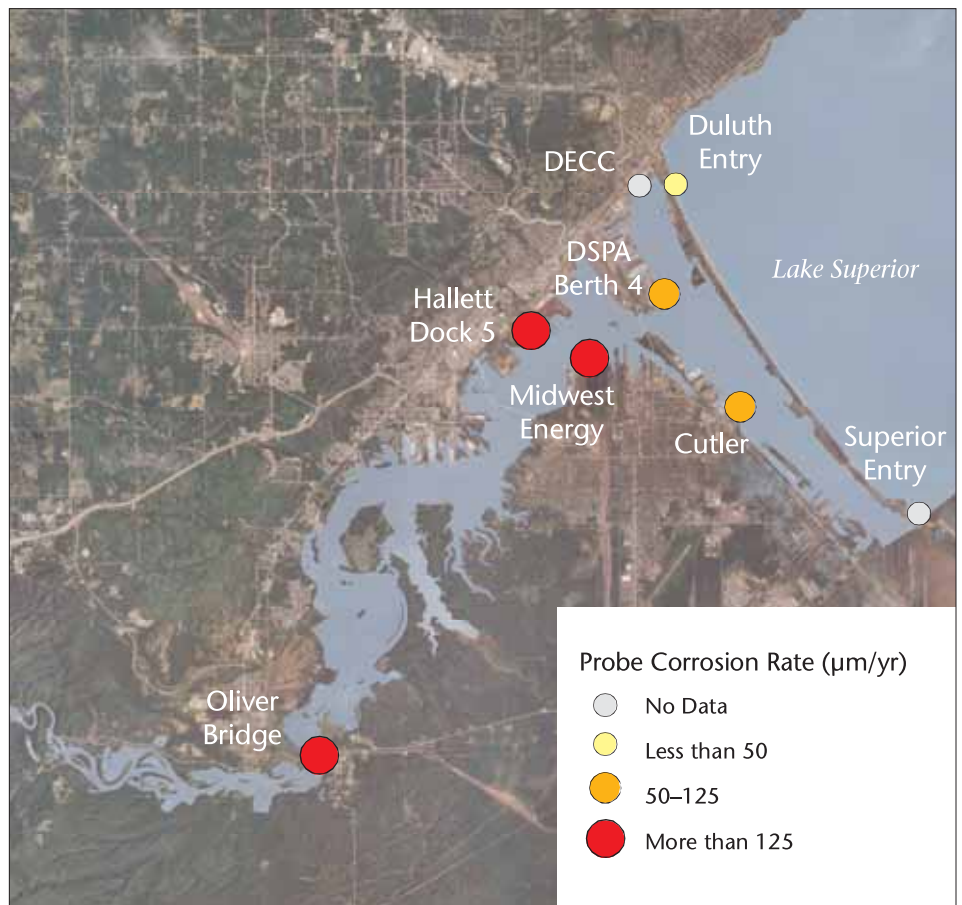
corroded areas on steel pilings to verify the presence of microbial biofilms and evaluate the biological complexity of these microbial communities. We stained one portion of the samples with a fluorescent dye (DAPI) and examined the stained samples using epifluorescence microscopy. Samples scraped from the corroded steel surfaces at two inner harbor sites, the Hallett Dock 5 and Midwest Energy docks, demonstrated that complex microbial biofilms composed of filamentous algae, diatoms, and various bacteria covered the steel surfaces and corrosion tubercles. These results supported the earlier scanning electron microscope evaluation of corroded steel removed from the harbor in late 2005. Our collaborator at the Naval Research Laboratory, Brenda Little, examined samples collected in 2006 with an electron microscope, which confirmed the presence of bacteria on surfaces and even possibly embedded in the orange tubercles covering the corrosion pits.

Examination of Samples for the Presence of Iron-Oxidizing Bacteria.

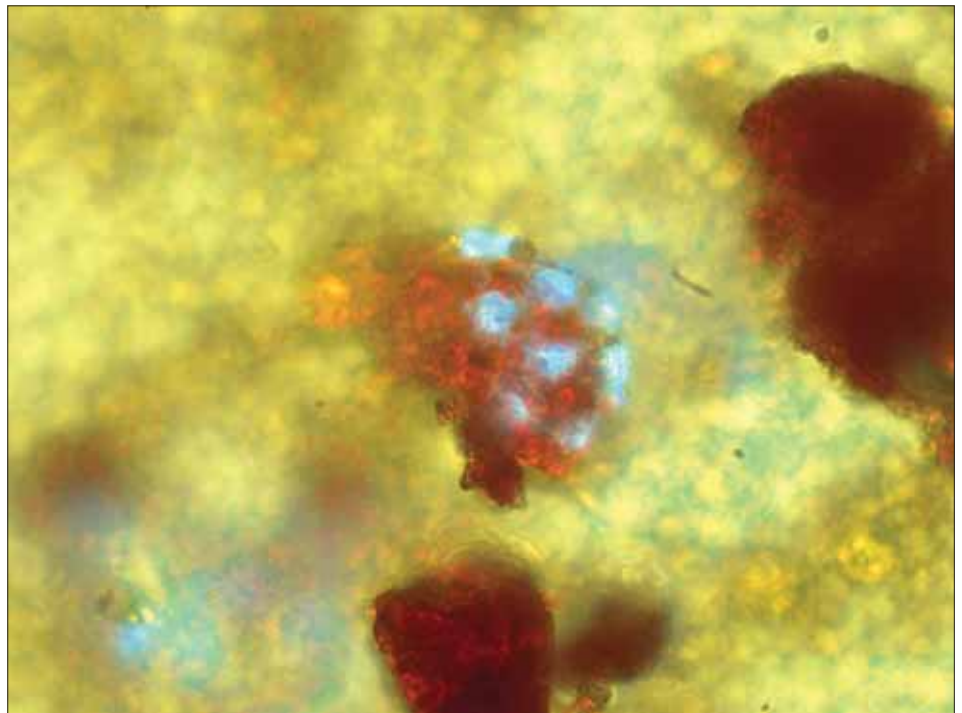
Our second goal was to isolate and identify iron-oxidizing bacteria that might be present in the samples recovered from steel structures at the two inner harbor sites, as well as the Duluth Entry that is less affected by corrosion. Using another portion of the samples collected, we enriched and isolated iron-oxidizing bacteria by an iron sulfide gradient-tube culturing technique. After 14 to 21 days, we removed samples from individual bands of the microbial growth that had formed in these gradient tubes and then extracted, amplified, and sequenced the DNA for one gene (16S rRNA) in the sample's bacteria. We then compared this bacterial DNA sequence information with the sequences of known bacteria from a public database to help identify the closest bacterial relative.

We isolated an iron-oxidizing bacterium, which we found to be most similar (96% similarity) to *Sideroxydans lithotrophicus* by the partial 16S rRNA gene sequence, from corroded areas of the Hallett Dock 5 and the Midwest Energy dock sites. To date, we have not isolated this bacterium from the site at the entry to the Duluth-Superior harbor that is less affected by corrosion. We verified the presence of this bacterium in the microbial biofilms from the corroded sites by comparing its DNA fingerprint with the DNA fingerprints of bacterial communities collected from

Figure 1. Map of the Duluth-Superior Harbor



Note: Hallett Dock 5, Midwest Energy, and Duluth Entry were sampled during August and September 2006.



Photomicrograph by R.E. Hicks

Microorganisms (stained blue) on an orange particle of corrosion material. The corrosion material was collected during August 2006 from the surface of corroded steel sheet-piling at Hallett Dock 5 in the Duluth-Superior harbor.

corroding structures in the inner harbor. *S. lithotrophicus* is a microaerophilic

γ -Proteobacterium that oxidizes iron (converting Fe^{2+} to Fe^{3+}). Iron-oxidizing

bacteria have been demonstrated to cause corrosion of steel in other environments,³ so isolating a bacterium similar to *S. lithotrophicus* from these corroding steel structures was certainly intriguing. However, microbiologically influenced corrosion is rarely caused by a single microbial group, but is instead more often caused by consortia of microbes (including iron-oxidizing and sulfate-reducing bacteria).

Comparisons of Microbial Biofilms from Different Sampling Sites. Our third goal was to determine if microbial communities attached to corroding steel were different than communities attached to steel at the less-corroded Duluth entry site. We used total DNA extracted directly from microbial biofilms for a community DNA fingerprinting analysis called terminal restriction fragment length polymorphism analysis (T-RFLP), and for developing bacterial clones whose DNA could be sequenced to help identify bacterial members of these microbial communities.

We used T-RFLP analysis to compare bacterial biofilm communities collected from several sites. This analysis indicated that bacterial communities on corroding steel-pilings at sites in the most affected part of the Duluth-Superior harbor were different from bacterial communities on steel sheet-piling at the Duluth entry, a less affected site (Table 3). At Hallett Dock 5, the composition of bacterial communities associated with corrosion tubercles was even different from bacterial communities on adjacent areas of the steel piling where corrosion tubercles were not present (data not shown).

We amplified DNA from the bacterial 16S rRNA gene in four microbial community samples from the Hallett Dock 5 dock and two samples from the Midwest Energy dock to create a small bacterial clone library and then to identify the major bacterial groups associated with corroded steel-piling materials in the Duluth-Superior harbor during late summer. We partially sequenced small DNA fragments from these bacterial clones and then compared their sequences to 16S rRNA gene sequences in a public database to identify their closest bacterial relatives. This analysis demonstrated that the

Table 3. Percent Similarity of Bacterial Communities on Steel Structures at Corroded Sites in the Inner Part of the Duluth-Superior Harbor (MWE, HD5) and the Entry to the Harbor, an Area Less Affected by Corrosion

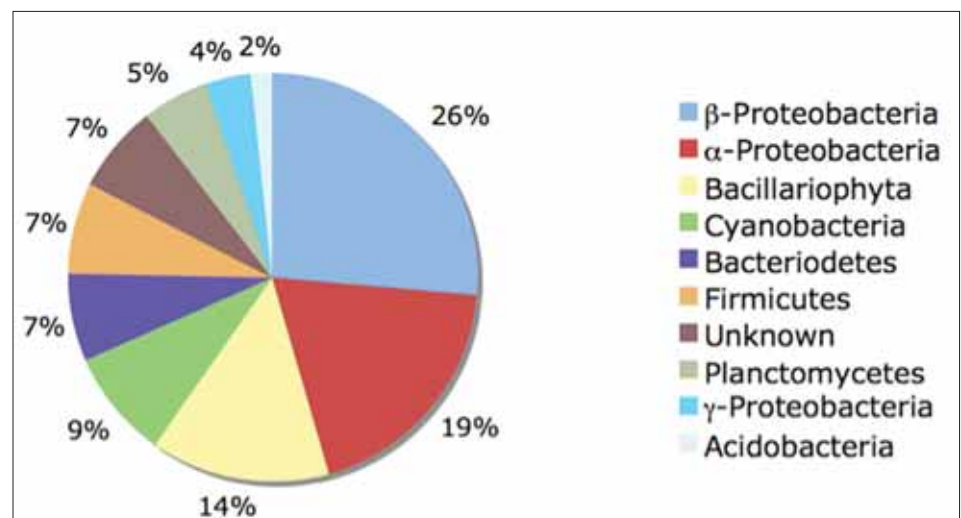
Site	Duluth Entry	Midwest Energy	Hallett Dock 5 (Aug)	Hallett Dock 5 (Sept)
Duluth Entry	71	2	2	2
Midwest Energy		98	23	23
Hallett Dock 5 (Aug)			86	44
Hallett Dock 5 (Sept)				67

Note: Similarities are based on community DNA fingerprints (T-RFLP) developed from samples collected in 2006. Values along the diagonal represent the minimum similarity between replicate samples from the same site.

three most common types of bacteria associated with the corroded steel surfaces were from three bacterial phyla: β -Proteobacteria, α -Proteobacteria, and Cyanobacteria (Figure 2). Bacterial DNA from the β -Proteobacteria, a phylum that includes several iron-oxidizing bacteria, was mostly commonly found in the microbial biofilms. One 16S rRNA clone from the β -Proteobacteria group was most similar to *Rhodospirillum rubrum*. This iron-reducing bacterium grows well at the near-freezing temperatures that are seasonally encountered in this harbor. The DNA sequences from other clones were most similar to *S. lithotrophicus*, the bacterium that was most similar to the iron-oxidizing bacterium we isolated from the corroding steel surfaces and cultured in the laboratory. To date, we have not isolated any clones from the δ -Proteobacteria, a bacterial phylum dominated by sulfur- and sulfate-reducing bacteria.

Our data indicated that corroding steel structures in the Duluth-Superior harbor are covered by complex microbial biofilms containing bacteria of the type responsible for corrosion of steel in other environments. Although these data lead us to suspect that microbiologically influenced corrosion may be responsible for the accelerated corrosion seen in the Duluth-Superior harbor, they do not provide conclusive evidence that *S. lithotrophicus* or any other bacterium isolated or found in the clone library so far are responsible for this corrosion. All the data collected to this point, however, are consistent with the hypotheses that corrosion in the Duluth-Superior harbor is directly or indirectly accelerated by local differences in water quality or the action of microorganisms.

Figure 2. Proportions of Different Bacterial Phyla in Biofilm Samples Collected from Two Inner Harbor Sites in the Duluth-Superior Harbor



Note: Samples were collected in 2006 from Hallett Dock 5 (August 1, September 14) and Midwest Energy (August 15). Bacillariophyta are diatoms, a type of single-cell algae, rather than bacteria.

³ D.R. Starosvetsky, J. Yahalom Armon, and J. Starosvetsky. "Pitting Corrosion of Carbon Steel Caused by Iron Bacteria." *International Biodeterioration and Biodegradation* 47 (2001):79-87.

Related Findings and Future Directions

This section discusses additional findings and suggests directions for future research.

Geographic Extent of the Problem.

This corrosion problem was initially identified in the Duluth-Superior harbor, and its worst effects seem to be confined to the inner part of the harbor. However, similar corrosion was later discovered at the Oliver Bridge where the St. Louis River empties into the harbor. Recent observations of steel corrosion in other ports by port authority and Sea Grant extension professionals have indicated moderate to severe corrosion in some of the busiest harbors in Lake Superior, including Two Harbors, Minnesota; Thunder Bay, Ontario; and Ontonagon and Houghton, Michigan. Steel structures with the most severe corrosion were often found in harbors with highly colored water typical of inputs from streams and rivers entering Lake Superior, whereas steel structures in harbors directly connected to Lake Superior such as the harbor at Silver Bay, Minnesota, usually showed little or less severe corrosion. Given all the existing data, the question of whether biological or chemical differences exist between Lake Superior and harbor waters that are directly or indirectly responsible for this type of corrosion remains.

Understanding the Cause of this Corrosion Problem and Beyond.

Although our research reported here could not prove a microbial cause for this corrosion, it has led to new questions, additional research support, and unanticipated research directions. We are examining microbiological aspects of this corrosion in greater detail through additional sampling in the harbor, studying test coupons placed in the harbor, and evaluating the effects of several biological and water quality treatments in the laboratory with new funding from the Minnesota Sea Grant Program, the Great Lakes Maritime Research Institute, and the U.S. Army Corps of Engineers. Examining the data collected so far, we believe a risk assessment tool can be developed to predict the probability of similar corrosion occurring at other ports and to help assess the geographic extent of this type of corrosion in other parts of Lake Superior and the Great Lakes.

As part of another project funded by the Great Lakes Protection Fund, we are developing a method to quantify the abundance of iron-oxidizing bacteria and evaluating whether ballast water exchange from commercial ships may

transfer bacteria, such as iron-oxidizing bacteria, that may be harmful to structures in other ports. Most recently, we are collaborating with other researchers to evaluate the biocatalytic capabilities of the iron-oxidizing bacterium that we isolated from the Duluth-Superior harbor with funding from the University of Minnesota Initiative for Renewable Energy and the Environment.

Public Policy Implications

Shipping through the Duluth-Superior harbor, the largest port by total cargo volume in the Great Lakes, contributes more than \$200 million annually to Minnesota's economy. Solving the accelerated corrosion problem has important implications for the economic vitality of the many companies whose 15 major cargo terminals ship ore, coal, and grain from this port. Currently, responses to this problem have been limited to repairing corroded areas, localized protection of corroded spots, application of protective coatings, or replacement of entire structures. Except for replacing entire structures, these practices are temporary solutions. For example, the best protective coatings may only prevent or reduce corrosion for 5 to 10 years in the Duluth-Superior harbor, where ice scouring is common. Corrosion similar to that seen on unprotected steel surfaces rapidly appears on coated sheet pilings after they are scratched or abraded. Thus, it is important to understand the mechanisms and agents responsible for this accelerated corrosion to find better solutions. Until then, companies and governments might consider revising the economic forecasts they use to decide when to repair or replace their docks, bulkheads, and piers because the useful lifetime of these steel structures in the Duluth-Superior harbor may be less than expected in freshwater.

The corrosion issue is attracting not only local attention but also regional, national, and international attention. Other ports and businesses in the Great Lakes started to report similar steel corrosion problems once accelerated corrosion was discovered, reported, and investigated in the Duluth-Superior harbor. As the frequency of these reports has increased, businesses and governments in other regions have become concerned that their structures and facilities may be experiencing similar accelerated corrosion or will likely face it in the future.

A more thorough understanding of this accelerated corrosion process in

Minnesota will be invaluable to other port authorities in the Great Lakes, individual companies that own docks and slips, the U.S. Army Corps of Engineers, and engineering and construction firms hired to assess, repair, protect, or replace steel structures in ports. More funding from private, state, and federal sources would be useful, not only to verify the extent of the corrosion problem beyond the Duluth-Superior harbor and identify the cause, but also to test mitigation efforts like protective and antifouling coatings. If better ways to control or eliminate this problem cannot be found, then financial assistance to maritime businesses, port authorities, marina operators, and local governments may soon become necessary as more docks, piers, and channel markers require replacement or face failure. Ultimately, understanding the cause of this accelerated corrosion should be helpful in guiding and testing mitigation practices, which could lead to improved control and remediation efforts.

Randall E. Hicks is professor of biology at the University of Minnesota at Duluth (UMD) and director of the UMD Center for Freshwater Research and Policy. His research focuses on the ecology of aquatic microorganisms and their roles in nutrient cycling, biogeochemistry, and processes such as corrosion, and the survival, transport, and sources of potentially harmful microbes in aquatic ecosystems.

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