Modeling the Corrosive Loss of Port Infrastructure in the Duluth-Superior Harbor and the North Shore of Lake Superior

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Dedication

This thesis is dedicated to my family and friends who have been supportive in all of my life choices, especially my education. Without all of your advice and encouragement this would not have been possible.

Abstract

Corrosion of steel infrastructure in the Duluth-Superior Harbor (DSH) is a concern for those who own and maintain structures that are critical for maritime transportation. Long-term corrosion rates of steel structures in the DSH were 2 to 4 times faster than is typical for other freshwater habitats, ranging from 0.06 to 0.14 mm/yr. The highest rates of steel corrosion were found at moderately to severely corroded sites and were within the lower range for corrosion of steel in seawater. It is important to know the potential roles that water quality and microorganisms play in the corrosion process to better understand why steel structures in the DSH are corroding faster than expected and to develop methods to prevent or mitigate this problem. Dissolved oxygen increased and chloride and sulfate concentrations decreased in the late 20^{th} century in the DSH after the Western Lake Superior Sanitary District became operational. In 2010, only alkalinity, chloride, and conductivity were positively related to long-term steel corrosion rates in the DSH and interestingly, dissolved oxygen was inversely related to it. The Larson-Skold Index, which measures the corrosivity of water towards steel, decreased or remained constant at three sites between 1972 and 1996. The Larson-Skold Index was usually below the threshold for concern in 2010-2011, indicating that changes in water chemistry alone may not be responsible for the severe corrosion of steel in this harbor. *Gallionella*, a genus of iron-oxidizing bacteria, was more abundant within corrosion tubercles on severely corroded steel structures in the DSH where more than 10^9 *Gallionella* 16S rRNA copies/dry g of tubercle were observed, representing 2% to 34% of the total prokaryotic

cells recovered from these tubercles. *Gallionella* bacteria were less abundant (~10^7 copies/dry g) on steel structures at sites along the north shore of Lake Superior. DNA from *Gallionella* was not detected in the water surrounding corroding steel structures in the DSH or in harbors on the north shore of Lake Superior, indicating that these bacteria were enriched on corroding steel. Sulfate-reducing bacteria (SRB) were also more abundant within tubercles at severely corroded sites but at least 2 orders of magnitude less abundant than *Gallionella* bacteria, accounting for less than 1% of prokaryotic cells within these corrosion tubercles. Considered alone, neither the abundance of *Gallionella* or SRB was related to long-term steel corrosion rates in the DSH. A multiple linear regression model was developed using water quality parameters and bacterial abundances to predict steel corrosion rates. The model used alkalinity, sulfate concentration, and $\log_{10}$ transformed SRB abundance to predict the long-term steel corrosion rate. It overestimated the long-term corrosion rate of a steel structure in one harbor along the north shore of Lake Superior and slightly underestimated the corrosion rate at a second harbor. It is clear that the corrosion of steel structures is accelerated in the DSH compared to other freshwater environments and water chemistry is not likely the sole cause of this corrosion. Rather, a combination of chemical and microbiological factors appears to influence the corrosion of steel structures in this harbor.

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Sulfate-reducing bacteria	SRB
Iron-oxidizing bacteria	FeOB
Oliver Bridge	OB
Burlington Northern Railroad Bridge	BNRR
Bascule Bridge	BB
Dissimilatory sulfite reductase	DSR
Larson-Skold Index	LSI

Chapter 1

Duluth-Superior Harbor Corrosion and Corrosion Modeling Overview

The economy of the Laurentian Great Lakes region is heavily dependent on the transportation of commodities by the shipping industry. With the opening of the St. Lawrence Seaway system in 1959, the trade and economies of many port cities in the Great Lakes expanded, partly due to the ability of ocean vessels to transport goods to and from Europe (NOAA 2004). An estimated 322.1 million tons of cargo pass through the Great Lakes every year from four primary cargoes: iron ore, coal, stone aggregates, and grain (Martin Associates 2011). Along with bulk transportation of these materials, the local economies of 16 port cities have generated nearly 227,000 jobs both directly and indirectly related to the shipping industry (Martin Associates 2011). Shipping and rail may play an even more crucial role in the transport of these goods in the Great Lakes region in the future due to the increasing price of fuels and an increasing concern for environmental impacts from carbon and other greenhouse emissions. It is projected that trucking and air transport may be the preferred transport methods in years to come because these tend to be more time-sensitive modes of transport. However, these methods also consume the most energy and have a greater impact on carbon emissions (Winebrake *et al.* 2008). The economic benefits of shipping by transporting more product per load can potentially save $1.2 to 3.6 billion in transportation costs over the next cheapest transport method (Martin Associates 2001). Shipping on the Laurentian Great Lakes has been an integral part of the economy of not only the Great Lakes states,

but to the entire world, and any potential disruption to the movement of cargo could impact local, regional and global economies.

Steel infrastructure including docks, bulkheads, piers, and pilings is a critical component of maritime transportation, specifically for the loading and unloading of materials. This infrastructure is ultimately important for the success of the economies of port cities that contain these structures. Structural integrity of port infrastructure is critical for maritime commerce. If the service life of these structures is compromised, obvious negative economic impacts will occur, not only with regard to the cost of replacing deteriorating structures, but also the potential loss of business while structures are fixed. The ability to accurately assess rates and possible risk of corrosion are of great importance to businesses and governments who maintain this infrastructure. Inherently, there are challenges in assessing corrosion risk because of the variety of parameters that interact to cause increased rates of corrosion.

Located on the western arm of Lake Superior in the port cities of Duluth, Minnesota and Superior, Wisconsin, the Duluth-Superior Harbor (DSH) has a unique problem for a freshwater environment. Beginning in the 1970s, the rate of corrosion seemed to be more aggressive in the DSH and has become a major issue for carbon steel structures in this port (Ray *et al.* 2009). A recent report suggested that accelerated corrosive loss of steel could be 2 to 12 times greater in the DSH than in other similar environments (Bushman and Associates 2006). This same report suggested that the expected rate of corrosion in a similar freshwater environment would be 0.5 to 1.5 mils/year (0.01 to 0.04 mm/yr). Average corrosion rates of steel in seawater are between

0.1 to 0.3 mm/yr (Wiener and Salas, 2005) and several sites in the DSH may have long-term corrosion rates within the lower end of this range. A 16-year study comparing carbon steel corrosion in freshwater and seawater showed freshwater rates faster initially at 0.195 mm/yr and declined to 0.044 mm/yr after 16 years. Seawater corrosion was initially 0.149 mm/yr and declined to a rate of 0.073 mm/yr after 16 years, which is 1.7 times faster than in the freshwater environment (Dismuke *et al.* 1981). Allowing corrosion to continue unabated has created a situation where steel that was expected to last 50 years or more will need to be replaced much sooner (Mitman 2006). Extensive pitting on the surface of steel structures in the DSH has been observed after only one decade (Mitman 2006), which is a concern because of the expense involved with replacing this steel. It is estimated that the 20.8 km (13 miles) of steel present in the DSH will need to be replaced at a cost greater than $200 million (Marsh *et al*. 2005, Mitman 2006, Hicks 2008, Hicks 2009). The cause of this severe corrosion is still unknown, but studies evaluating microbiologically influenced corrosion (MIC) and water chemistry are critical for understanding this problem.

Observations of *in situ* steel structures indicate that the most severe corrosion typically occurs in a specific range from the water surface to 1.5 meters below the water surface in the DSH. Corrosion appears to decrease below 1.5 meters, and below 3 meters depth zebra mussels tend to colonize and cover the steel and very little corrosion is generally observed (Hicks 2008, Mitman 2006, Ray *et al.* 2009). The corrosion in DSH has a characteristic appearance and is dominated by the formation of rust-orange blisters or tubercles attached to the steel surface, under which deep pits are present (Ray *et al.*

2009, Hicks 2007, Hicks 2008, Bostrom 2010). The formation of the tubercles and the pits underneath are typical of a combination of both MIC and water chemistry (Baylis 1926, Simard *et al.* 2001, Starosvetsky *et al.* 2001, Beech 2003, Montemor *et al.* 2003, Beech and Sunner 2004, Wiener and Salas 2005). Tubercles and corrosion scales are formed partially due to the deposition of varying forms of ferric hydroxide and oxyhydroxides on the steel surface through electrochemical, cathodic and anodic reactions that cause the oxidation and dissolution of iron from the steel surface (Baylis 1926, Hamilton 1985, Sarin *et al.* 2001).

Corrosion or rusting is caused by oxidation of iron by oxygen and water. This type of generalized corrosion can lead to the formation of non-passive scales or films formed by multiple species of ferric hydroxides and oxyhydroxides (Huang and Zhang, 2005). These iron species are insoluble in water and form corrosion scales over the steel surface. This reaction typically occurs due to the coupling of the oxidation of iron, an anodic reaction, and the reduction of oxygen near the bare metal surface, a cathodic reaction (Lee and Newman 2003). Graedel and Frankenthal (1990) described a series of mechanisms that potentially lead to the corrosion of iron and steel that has been exposed to atmospheric and aqueous conditions. They suggested that in the initial stages of corrosion, zero valent iron (Fe^{o}) is oxidized to ferrous iron (Fe^{2+}) through the reduction of water and dissolved oxygen. After Fe^{2+} is formed, it can be precipitated from solution onto the steel as up to twelve different forms of iron oxides and iron hydroxides or rust, and the final corrosion products will contain ferric iron (Fe^{3+}). Ultimately, the rate of

corrosion is determined by how quickly electrons can flow from the anode to the cathode (Hamilton 2003).

Along with the chemical oxidation of iron, MIC can also be a prominent factor in the dissolution of iron and deposition of corrosion products. Two main groups of microorganisms, iron-oxidizing bacteria (FeOB) and sulfate-reducing bacteria (SRB) have been extensively studied and determined to influence corrosion on steel surfaces. Iron-oxidizing bacteria such as *Gallionella* spp. can be involved with the formation of tubercles (Hamilton 1985, Emerson and Moyer 2002). Ferric hydroxide is often deposited by iron-oxidizing species such as *Gallionella* spp., *Leptothrix* spp., and *Sideroxydans* spp. (Emerson and Moyer 2002, Emerson *et al.* 2010). In the case of *Gallionella,* the ferric hydroxide can attach to the twisting stalks that protrude from their cell surface (Hamilton 1985, Ray *et al.* 2009, Ray *et al.* 2010). Freshwater FeOB typically belong to the *Betaproteobacteria,* are chemolithoautotrophic, microaerophilic, utilize iron as their energy source, and can grow in neutral pH (Emerson *et al.* 2010). Neutral pH and oxygenic conditions are typical characteristics of the Duluth-Superior Harbor. The amount of energy these microbes gain from the oxidation of Fe^0 to Fe^{2+} is very little (about 29 kJ/mol), but they can obtain approximately double this energy if Fe^{2+} can further be oxidized to Fe^{3+} to form and precipitate iron as oxyhydroxides (Emerson *et al.* 2010). In the DSH, DNA from bacteria related to *Gallionella* and *Sideroxydans lithotrophicus* has been cloned and sequenced only from sites such as Hallett Dock 5 and Midwest Energy Resources (Hicks 2009), where corrosion appears to be the most severe. *Sideroxydans* and *Gallionella* species belong to the *Betaproteobacteria* and are closely

related phylogenetically forming the order *Gallionellales* (Emerson *et al.* 2010). The tubercles are usually covered in carbohydrate biofilms produced by a consortium of FeOB, SRB, and other microorganisms (Hamilton 1985). The formation of these biofilms plays an important role by creating a microenvironment with an oxygen gradient that allows different microorganisms to inhabit these biofilms (Hamilton 1985, Lee and Characklis 1993) on steel surfaces. While oxygen gradients can be established within the biofilm, local concentrations of chemicals can also change from the outside environment (Lee and Newman 2003), which can also influence the composition of microorganisms within these biofilms.

In the anaerobic zone under these tubercles, SRB are present and can affect the dissolution of iron from the steel surfaces. Sulfate-reducing bacteria are a group of heterotrophic microorganisms, most commonly belonging to the *Deltaproteobacteria* (Kondo *et al.* 2008), that use sulfate as their terminal electron acceptor (Gibson 1990) and the enzyme dissimilatory sulfite reductase (DSR), which catalyzes the six-electron reduction of sulfite to hydrogen sulfide, the final step in the dissimilatory sulfate reduction pathway (Kondo *et al.* 2004, Kondo *et al.* 2008). Sulfate reduction produces hydrogen sulfide and ultimately iron-sulfide (FeS). FeS is an important corrosion product that assists in developing an electrochemical cell that can cause pitting of steel surfaces (Hamilton 1985). The development of an electrochemical cell with bare steel acting as the anode and the FeS acting as the cathode can remove electrons from the steel resulting in the pitting of the steel surface (Potekhina *et al.* 1999, Hamilton 2003). Cathodic depolarization can then occur due to the removal of hydrogen from the cathode

through hydrogenase activity of SRB. Electrons are then removed from the metal surface via FeS (Potekhina *et al.* 1999) and can lead to pit growth.

The DSR gene (*dsr*A), which is only present in SRB, can be quantified to estimate abundances of these microbes in corrosion tubercles (Kondo *et al.* 2008, Kondo *et al.* 2004). Microbial metabolic processes are known to influence corrosion by changing the chemistry adjacent to the metal surface, and thus water quality may be just as influential as the presence of microorganisms on these corroding areas. One goal of this study was to estimate the abundances of both FeOB and SRB in corrosion tubercles and adjacent biofilms using quantitative PCR (qPCR) assays. If there were significant correlations between the abundances of these microorganisms and the rate of steel corrosion in the DSH, then these parameters might be included in a model to predict the rate or risk of corrosion. The variety of microorganisms on steel surfaces in the DSH is thought to be influenced by the water chemistry surrounding that steel (Bostrom 2010).

Water quality is an important factor in the dissolution of iron from steel in both marine and freshwater environments. Ions such as chloride, sulfate, and dissolved oxygen have been implicated in aggressive corrosive action on steel surfaces (Huang and Zhang 2005, Montemor *et al.* 2003, Simard *et al.* 2001, Larson and Skold 1958). Chloride can cause voids in corrosion films and scales, which initially provide some protection against generalized corrosion (Sarin *et al.* 2004) and lead to pitting of the steel through the development of FeCl complexes that break down causing localized acidification (Montemor *et al.* 2003, Simard *et al.* 2001). Sulfate reduces the effectiveness of corrosion scales made of iron oxyhydroxides, which are known to limit

the corrosion reaction, by replacing this film with one that is less protective (Al-Tayyib *et al.* 1988). Not only does the sulfate concentration affect the scales produced by the general corrosion reaction, it also supports the metabolism of SRB (Liu *et al.* 2009, Gibson 1990, Hamilton 1985). As mentioned earlier, SRB are heterotrophic bacteria and convert sulfate to sulfide (S^{2-}) under anoxic conditions. These sulfides can then form FeS, which acts as a cathode in the development of the electrochemical cell that ultimately leads to pitting of the steel surface (Potekhina *et al.* 1999).

Calcium carbonate can deposit within corrosion layers and inhibit corrosive action on steel (Melchers 2006, Larson and Skold 1958). This layer eventually leads to a reduction in the availability of oxygen and therefore the corrosion rate. Melchers (2006) discussed the importance of pH and water hardness on corrosion in freshwater systems. Soft water tends to have greater carbonate solubility decreasing the deposition of carbonates on steel surfaces and potentially allowing increased corrosion. Melchers (2006) also explained the importance of SRB in freshwater corrosion. A system supersaturated with $CaCO_3$ typically limits the availability of sulfate for SRB metabolism. In an analysis of a current marine corrosion model, it was determined that anaerobic corrosion has a larger effect on long term exposure and may not depend on the number of SRB, but rather on the availability of nutrients for these microorganisms and how these nutrients or ions interact with the steel surface. Overall, it is believed that water temperature, pH, hardness, and an understanding of basic nutrient levels is important for research into fresh and brackish water corrosion (Melchers 2006).

The Larson-Skold Index (LSI) can be used to evaluate the corrosivity of the water on the steel structures in the DSH. The model predicts a low risk of water being corrosive to mild steel when the Larson-Skold Index (LSI) is between 0 to 0.8, a moderate risk when the LSI is between 0.8 and 1.2, and high risk when the LSI is greater than 1.2 (Larson and Skold 1958). In this study, the index developed by Larson and Skold (1958) was used to predict whether the corrosive effects of chloride (Cl^-) and sulfate (SO_4^{2-}) and the inhibitory effects of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) might influence the corrosion of steel at several sites in the DSH.

Past studies attempting to model corrosion rates have focused mainly on marine ecosystems and have proven difficult because of great statistical uncertainty within the measurements (Melchers 2003). There have been very few studies on corroding structural steel in freshwater and modeling corrosion in freshwater ecosystems has been discussed little (Melchers 2006). The study described here attempts to address the importance of both water chemistry and microbiology on the corrosion of steel in a freshwater environment.

Chapter 2

Evaluation and Application of Historical Water Quality Measurements in the Duluth-Superior Harbor to Corrosion of Port Infrastructure

Introduction

The Duluth-Superior Harbor (DSH), located on the western arm of Lake Superior, has experienced rates of steel corrosion that are much faster than expected. The ongoing deterioration of port infrastructure is of economic concern as corrosion continues unabated. The DSH is the largest shipping port on the Great Lakes and major cargoes include taconite, coal, grain, and stone aggregates (Martin Associates 2001, Martin Associates 2011), which contribute significantly to the economy of this port city. The Duluth Seaway Port Authority (DSPA), which manages operations in this harbor estimated that on an annual basis over $2 billion of cargo is shipped through the DSH, supports over 2,000 jobs within the harbor, and has an overall $210 million annual local economic impact. It is clear that any disruption to the daily operations of this port would have significant negative economic consequences. Therefore, it is critical to understand how different factors, including water chemistry, are contributing to the corrosion of port infrastructure.

The corrosion of steel in the United States affects multiple sectors including infrastructure, utilities, transportation, and manufacturing. Among all of these sectors corrosion has been estimated to cost $275.5 billion per year in direct costs or approximately 3.14% of the United States entire GDP (Furbeth and Schutze 2009). Deteriorating steel infrastructure including docks, piers, and pilings is of local concern

because of the estimated $200 to 250 million (Hicks 2009, Larsen 2008) it will cost to replace the 13 miles (20 km) of steel that are currently affected in this harbor (Marsh *et al*. 2005). Corrosion in the DSH is typically characterized by varying sized orange blisters (called tubercles) that develop on the surface of steel structures. These tubercles are found in a zone from the water line to 3 m below the water surface (Ray *et al.* 2009), however, the presence of corrosion pits tends to diminish 1.5 m below the water surface (Hicks 2009). The tubercles may be partially formed due to water chemistry (Larson and Skold 1958) and the presence of iron-oxidizing bacteria (Emerson *et al.* 2010, Emerson and Moyer 2002, Hamilton 1985, Ray *et al.* 2010). Iron-oxidizing bacteria (FeOB), such as *Gallionella* can precipitate ferric oxyhydroxides that attach to twisting stalks which protrude from the bacterial cells and can partially form the hard shell of corrosion tubercles (Emerson *et al.* 2010, Emerson and Moyer 2002). Iron-oxidizing bacteria have been found within tubercles at the DSH (Hicks 2009, Ray *et al*. 2010) and the consumption of oxygen in their metabolism decreases the concentration of oxygen and results in more favorable growth conditions for sulfate-reducing bacteria (SRB) that can actively corrode metal surfaces (Emerson *et al.* 2010). The steel area under the tubercles in the DSH are deeply pitted and the cause is hypothesized to be the water chemistry, the presence of iron-oxidizing and sulfate-reducing bacteria (Hamilton 1985), copper galvanization (Ray *et al*. 2009, Ray *et al*. 2010), or possibly a combination of these factors.

Multiple causes have been investigated, but none to date have been determined as the sole cause of steel corrosion in the DSH. Factors such as stray electrical currents,

metallurgy of the steel, temperature, zebra mussel colonization, and ballast water discharge have been studied and ruled out as potential causes of this corrosion (Marsh *et al*. 2005). There are many studies investigating the impact of water chemistry in other environments on the corrosion of steel structures (Montemor *et al.* 2003, Sarin *et al.* 2004, Sarin *et al.* 2001, Simard *et al.* 2001, Wiener and Salas 2005). The DSH is an interesting case because it is a freshwater environment and only a few other ports in the Great Lakes have observed and reported similar corrosion. One anecdotal observation is that harbors containing tannin stained water (indicative of high humic acids) may have more extensive corrosion than harbors in direct contact with Lake Superior (Hicks 2009). Systems with high dissolved organic carbon and high humic acids, such as those with riverine inputs like the DSH and Thunder Bay, Ontario, are examples. In freshwater ecosystems, corrosion rates can range from 0.01 to 0.04 mm/yr (Bushman and Associates 2006) and typical corrosion rates in seawater are an order of magnitude higher (between 0.1 to 0.3 mm/yr; Weiner and Salas, 2005). Several sites in the DSH appear to have long-term corrosion rates that are in the lower range of what is typical for seawater. The fact that steel structures in the DSH are corroding at rates more typically observed in seawater is disconcerting and points to the need to investigate historic changes in water quality to identify factors that might accelerate rates of corrosion.

There are many factors related to water quality that are important in the dissolution of iron from steel infrastructure in both marine and freshwater environments. Chloride (Larson and Skold 1958, Simard *et al.* 2001, Montemor *et al*. 2003), sulfate (Larson and Skold 1958, Al-Tayyib *et al.* 1988, Simard *et al.* 2001), and dissolved

oxygen (Huang and Zhang 2005, Sarin *et al.* 2004) have been implicated in aggressive corrosive action on steel surfaces. Water chemistry has long been thought to be the cause of corrosion seen in domestic drinking water systems (Rao *et al*. 2000) and steel in marine ecosystems (Melchers 1999, Melchers and Jeffrey 2005). Chloride can cause voids in corrosion films and scales, which initially provide some protection against generalized corrosion (Sarin *et al*. 2004). Chloride is responsible for the displacement of water in protective biofilms, and can eventually lead to localized acidification by the formation and breakdown of iron-chloride complexes. These complexes can ultimately cause pitting of the steel structures (Simard *et al*. 2001, Montemor *et al*. 2003). Sulfate (SO_4^{2-}) reduces the effectiveness of protective corrosion scales made of iron oxyhydroxides by replacing this scale with one that is less protective (Al-Tayyib *et al*. 1988). This change may in turn accelerate corrosive action on the steel. Sulfate is also essential for the metabolism of SRB, known also to cause pitting of steel structures (Gibson 1990, Hamilton 1985, Liu *et al*. 2009). SRB utilize sulfate as a terminal electron acceptor and can convert sulfite into sulfide (S^{2-}) (Kondo *et al.* 2008) ultimately forming iron sulfide (FeS), which develops an electrochemical cell that leads to pitting of the steel surface (Liu *et al*. 2009; Potekhina *et al*. 1999). Due to acidic and potentially anoxic conditions at the steel surface, an anode can develop and the production of FeS may act as a cathode creating an electrochemical cell (Potekhina *et al*. 1999). Cathodic depolarization can ensue due to the removal of hydrogen from the cathode through hydrogenase activity of SRB. Electrons can then be removed from the metal surface via FeS (Potekhina *et al*. 1999), and lead to pit growth. Finally, alkalinity, measured in the

form of calcium carbonate ($CaCO_3$) may act to inhibit corrosion. The development of a carbonate film over the steel surface may be an important component limiting the rate of corrosion (Larson and Skold 1958) and affecting the density of corrosion products (Melchers 2006).

Larson and Skold (1958) determined that the presence of chloride and sulfate caused mild steel to corrode at an accelerated rate, while the presence of bicarbonates inhibited corrosion of mild steel. Utilizing the Larson-Skold Index (LSI) of corrosivity, it is possible to predict where the highest risk of corrosion may occur based on these water chemistry parameters. The Larson-Skold Index demonstrates the relationship between water quality, the development of corrosion scales, and corrosion rate. It is a ratio of the corrosive effects of chloride (Cl^-) and sulfate (SO_4^{2-}) to the inhibitory effects of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), measured as alkalinity (typically reported as mg/L of $CaCO_3$), on the corrosion of mild steel (Larson and Skold 1958).

The concentrations of the water chemistry parameters in the LSI may be used to predict the corrosivity of water on mild steel in the DSH. The Western Lake Superior Sanitary District (WLSSD), a local wastewater treatment plant, went online in 1978. WLSSD collected water samples from multiple sites in the DSH and upstream in the St. Louis River until the mid-1990s. By analyzing historical water chemistry measurements like alkalinity, chloride, sulfate, and dissolved oxygen, significant trends may be recognized. Water quality has never been analyzed in relation to corrosion at the DSH and may be important for understanding why steel infrastructure here is corroding faster than in other freshwater systems. In this study, the Larson-Skold Index was calculated

for three sites in the DSH over at least a decade to provide insight into whether changes in water chemistry were responsible for the severe corrosion of steel seen in this harbor.

Methods

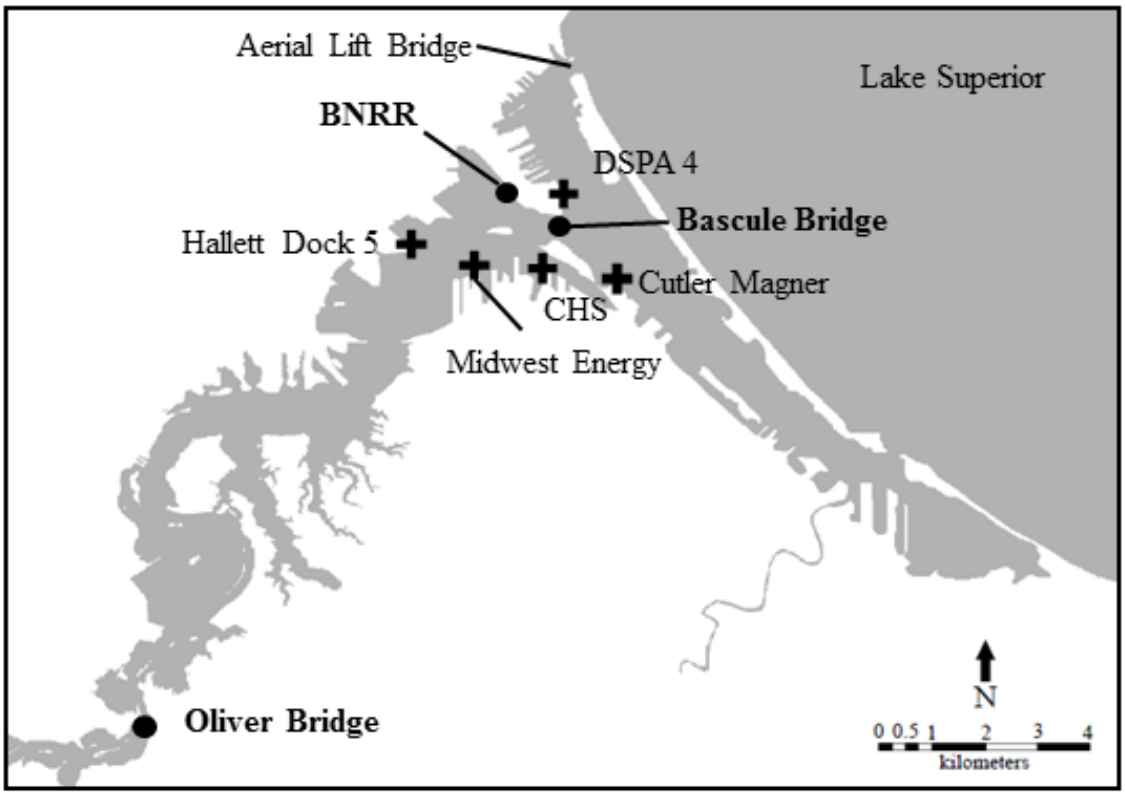
Sample Locations

Water quality data were collected by the Western Lake Superior Sanitary District (WLSSD) in the Duluth-Superior Harbor and upstream in the St. Louis River from the 1970s to the 1990s. Multiple sample locations created the historical data set and these sites spanned from the outer harbor, inner harbor, and several miles upstream in the St. Louis River. In this study, water quality data from two sites were analyzed in the Duluth-Superior Harbor (DSH) and one further upstream in the St. Louis River (Fig. 1).

Data from site SL-135 (Oliver Bridge), located at 46^{o} 65.673′ N 092^{o} 20.225′ W, approximately 13.5 river miles from the Aerial Lift Bridge, were evaluated. Oliver Bridge (OB) is upstream of the Duluth-Superior Harbor in the St. Louis River and is a moderately corroded site. Site SL-27 (Burlington Northern Railroad Bridge) is 2.7 miles from the Aerial Lift Bridge at 46^{o} 75.6217′ N, 92^{o} 11.2178′ W. The Burlington Northern Railroad Bridge (BNRR) was located in the inner harbor of the DSH, across from WLSSD, but has been recently demolished. Site SL-23 (Bascule Bridge Fishing Pier) is 2.3 miles upstream of the Aerial Lift Bridge at 46^{o} 75.0215′ N, 92^{o} 10.0323′ W. Bascule Bridge (BB) is located in the transition zone between the inner and outer harbor.

Ten sites in the Duluth-Superior Harbor (near Duluth, MN and Superior, WI) and Lake Superior, where steel structures ranged from slightly to severely corroded, were selected for study in 2010 and 2011 (Fig. 2). The Superior Entry (46^{o} 71.014′ N, 092^{o}

Figure 1. Map showing the Duluth-Superior Harbor and locations of Oliver Bridge, Burlington Northern Railroad Bridge, and Bascule Bridge sampling sites (filled circles) analyzed in this study. Sites with ”+” symbols are locations where long-term corrosion rates were compared to the historic water quality.


Aerial Lift Bridge
Lake Superior
BNRR
DSPA 4
Bascule Bridge
Hallett Dock 5
Cutler Magner
CHS
Midwest Energy
Oliver Bridge
N
0 0.5 1 2 3 4
kilometers

00.661′ W) and the lake side of the Duluth Entry (46° 77.987′ N, 092° 08.829′ W) represented sites known to have lower corrosion rates. Moderately corroded sites included White Box Dock (formerly owned by Cargill; 46° 76.948′ N, 092° 10.529′ W), the Army Corps of Engineers dock (46° 77.519′ N, 092° 09.234′ W), the Duluth Seaway Port Authority Berth 4 (46° 75.724′ N, 092° 09.571′ W), Graymont (formerly known as Cutler Magner; 46° 73.332′ N, 092° 07.468′ W), Cenex Harvest States dock (46° 74.288′ N, 092° 10.116′ W), and the Oliver Bridge (46° 65.673′ N, 092° 20.225′ W). Two sites sampled were known to be more severely corroded; the Midwest Energy Resources Company dock (46° 74.232′ N, 092° 11.546′ W) and Hallett Dock 5 (46° 74.563′ N, 092° 13.223′ W). Steel structures at all of these sites are constructed of the same type of A328 sheet or piling steel.

In 2011, six of the ten original sample sites from 2010 were sampled again in the Duluth-Superior Harbor. Four sites, Superior Entry, Duluth Entry (lake side), DSPA Berth 4, and Cenex Harvest States were not sampled in 2011 but one new site at the harbor-side of the Duluth Entry (46° 46.674′ N, 092° 05.607′ W) was added for sampling in 2011. This site was moderately corroded compared to the Duluth Entry lake-side area sampled in 2010. Other steel structures along the north shore of Lake Superior were also sampled in 2011 to gain a better understanding of the geographic extent to corrosion of steel infrastructure. Samples were taken from steel docks and structures (Fig. 9) at three locations at the Knife River Marina (46° 56.773′ N, 091° 46.923′ W), Two Harbors, MN (47° 01.032′ N, 091° 40.391′ W), and Silver Bay, MN (47° 17.030′ N, 091° 15.668′ W). Only water was sampled from Taconite Harbor, MN (47° 52.24′ N, 90° 92.88′ W).

Water Quality Measurements

Multiple water quality parameters were measured by WLSSD at sites in the DSH from the 1970s to the 1990s. Long-term changes in dissolved oxygen, chloride, sulfate, and alkalinity were evaluated in this study. Measurements of these dissolved chemicals were made following procedures from Clesceri *et al.* (1998). Alkalinity was measured using the titration procedure SM2320-B following the method by Pohland and Bloodgood (1963). Chloride was measured using the mercuric nitrate method SM4500-Cl C (Marks and Glass 1942), dissolved oxygen using the Winkler titration method SM 4500-O A (Winkler 1888), and sulfate using SM4500-SO_4, following the turbidimetric method by Sheen *et al.* (1935). In 2006, 2010, and 2011 water chemistry measurements were performed by Trace Analytical Laboratories, Inc. (Muskegon, MI) using standard methods. Alkalinity was measured using titration method SM 2320 (Pohland and Bloodgood 1963) and chloride and sulfate using ion chromatography (EPA 300.0; Pfaff 1993).

Historic Water Quality Analysis

Historic trends in dissolved oxygen, chloride, sulfate, alkalinity, and Larson-Skold Index were plotted over time at each of the three sample locations using Microsoft Excel™. Basic linear regression analysis was performed to obtain slopes and p-values of each parameter over their respective time periods using the data analysis tool in Microsoft Excel™ (Redmond, WA).

The Larson-Skold Index (LSI) of corrosivity was calculated using water quality data at each of the three sites examined. The LSI is a ratio of the water quality parameters

known to cause corrosion, including chloride and sulfate, to the ions bicarbonate and carbonate thought to inhibit corrosion and measured as alkalinity (expressed as $CaCO_3$) all expressed in milliequivalents (meq). The formula used followed that of Larson and Skold (1958):

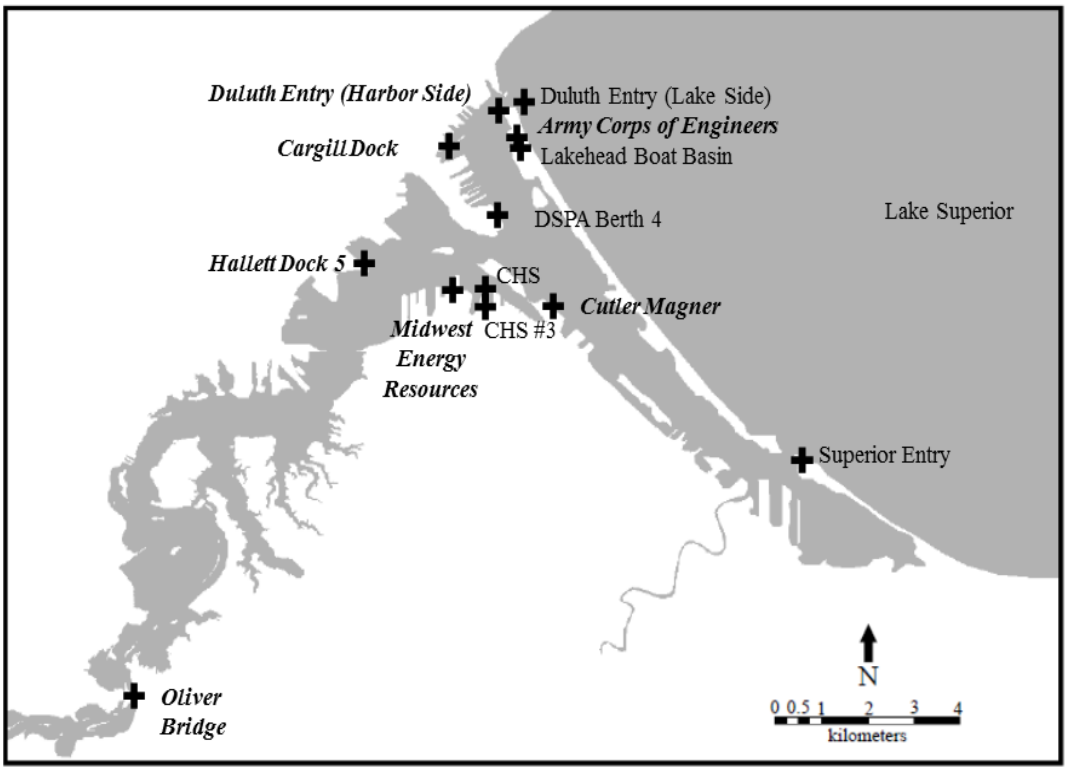
$$(1)\ (\text{meq } Cl^- + \text{meq } SO_4^{2-}) / (\text{meq } CaCO_3)$$

The meq of Cl^- was determined by dividing the concentration in mg/L by its molecular weight of 35.45 g/mol. The meq of SO_4^{2-} was determined by dividing the measured dissolved concentration (mg/L) by its equivalent weight of 48.03 g/mol and the meq of bicarbonate and carbonate was determined by dividing alkalinity (mg/L) by its equivalent weight of 50 g/mol.

Long-term Corrosion Rates

Long-term corrosion rates were estimated for corroded steel structures made of the same type of A328 sheet steel in the DSH (Chad Scott, pers. comm.). Corrosion pit depths and diameters were measured at each site by a hardhat diver using a manual pit depth gauge. The surface of the steel was first cleaned using a wire brush where corrosion pits were measured. The point on the pit gauge arm was then placed into the corrosion pit and the bottom of the gauge is pushed flush against the surface of the steel. The pit gauge arm points to the scale (in inches) on the side of the pit gauge (ASTM 2005). Fifteen total pit depths and diameters were taken at each site at the water line (n=5), three feet below the water line (n=5), and at six feet below the water line (n=5). Pit diameters were measured using a ruler on the manual pit depth gauge for the same corrosion pits where pit depths were measured.

Figure 2. Map of locations in the Duluth-Superior Harbor where samples were taken in August 2010 and July 2011. Bold, italicized locations were sampled in both 2010 and 2011.


Duluth Entry (Harbor Side)
Duluth Entry (Lake Side)
Army Corps of Engineers
Lakehead Boat Basin
Cargill Dock
DSPA Berth 4
Lake Superior
Hallett Dock 5
CHS
Cutler Magner
Midwest Energy Resources
CHS #3
Superior Entry
Oliver Bridge
N
0 0.5 1 2 3 4
kilometers

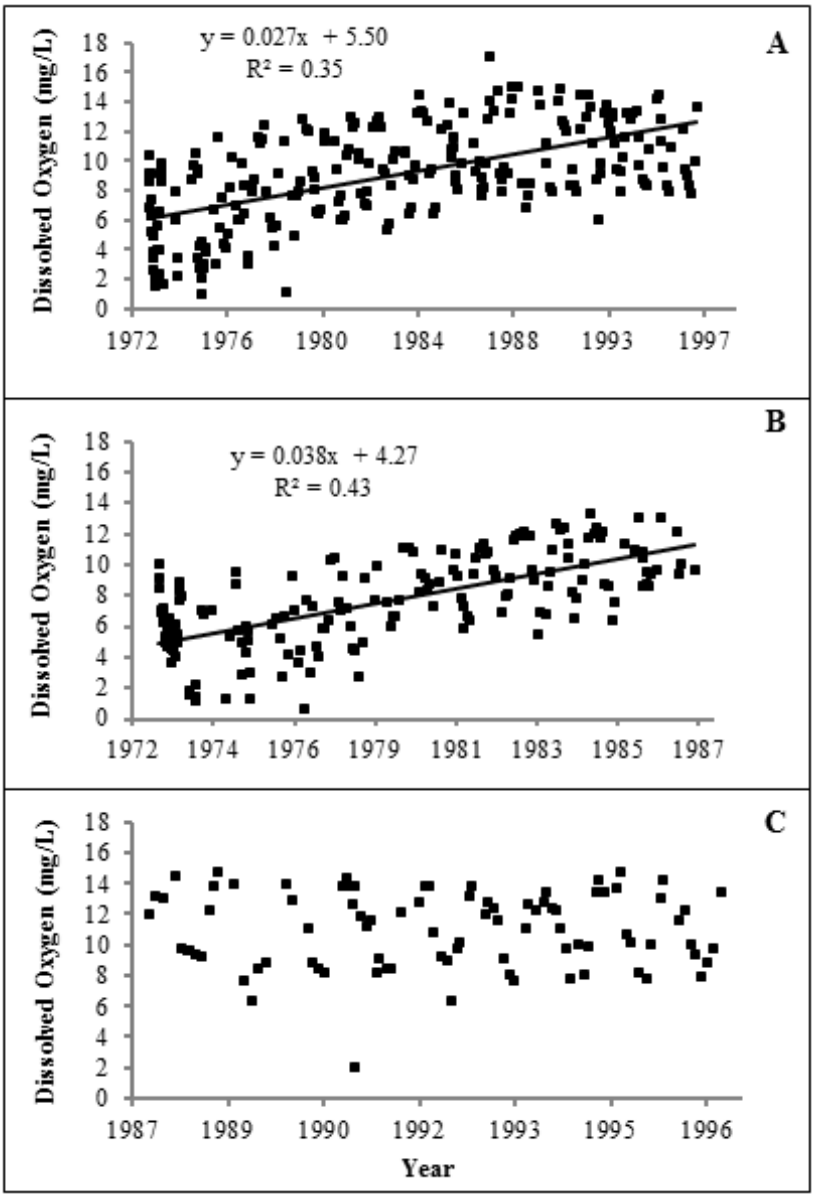
All pit depths and diameters were converted from inches to millimeters after collection. The long-term corrosion rate of the steel structure sampled was estimated by dividing the average corrosion pit depth by the in-service age of the steel structure. Service age of steel was determined from original installation plans, United States Army Corps of Engineers documentation, and the word of private dock owners from non-public records (Chad Scott, pers. comm.). The long-term corrosion rates were compared with average concentrations of historic water quality measurements to determine if any significant relationships existed.

Results

Historic Changes in Water Quality

Historic changes in water chemistry were evaluated at three sites in the DSH; the Oliver Bridge (OB), Burlington Northern Rail Road Bridge (BNRR), and Bascule Bridge Fishing Pier (BB). Dissolved oxygen concentrations (DO) increased significantly ($p < 0.05$) at the OB and BNRR sites. At OB, the average yearly DO steadily increased from approximately 5.0 mg/L in 1972 to 10.0 to 12.0 mg/L in 1996 (Fig. 3; panel A). DO was lower during the summer months and greater during the winter, reflecting the dependence of DO concentration on water temperatures. A seasonal analysis indicated average yearly DO increased ($p<0.05$) during all seasons over this period. At the BNRR, average yearly dissolved oxygen increased significantly ($p<0.05$) between 1973 to 1987 from around 5.0 mg/L to 11.0 mg/L (Fig. 3; panel B). Average DO at the BNRR also showed a

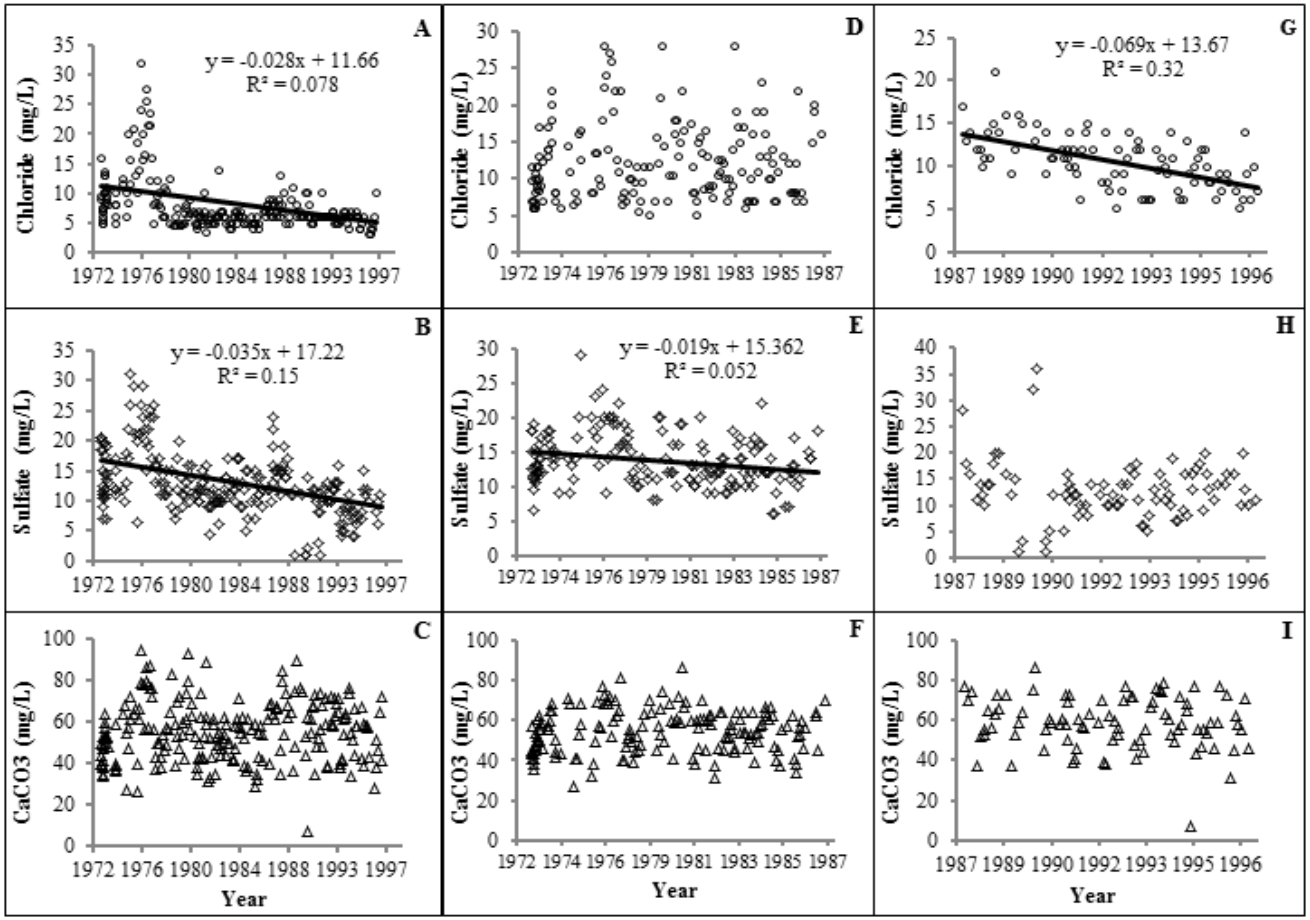
Figure 3. Historic dissolved oxygen concentration (mg/L) at Oliver Bridge (panel A), Burlington Northern Railroad Bridge (panel B), and Bascule Bridge (panel C) in the Duluth-Superior Harbor. Trend lines indicate a significant ($p<0.05$) increase in dissolved oxygen.


A
y = 0.027x + 5.50
R² = 0.35
Dissolved Oxygen (mg/L)
0 2 4 6 8 10 12 14 16 18
1972 1976 1980 1984 1988 1993 1997
B
y = 0.038x + 4.27
R² = 0.43
Dissolved Oxygen (mg/L)
0 2 4 6 8 10 12 14 16 18
1972 1974 1976 1979 1981 1983 1985 1987
C
Dissolved Oxygen (mg/L)
0 2 4 6 8 10 12 14 16 18
1987 1989 1990 1992 1993 1995 1996
Year

significant increase ($p<0.05$) over all four seasons at this site. Dissolved oxygen at the Bascule Bridge Fishing Pier (BB) remained constant from 1987 to 1996, averaging 10.9 mg/L (Fig. 3; panel C) and also remained unchanged during all four seasons. The greatest average DO concentration occurred during the winter months at 13.5 mg/L. The lowest average DO concentration at BB was during the summer months, averaging 8.6 mg/L.

Three dissolved ions found in water, chloride, sulfate, and carbonate (measured as alkalinity), are of particular interest because chloride and sulfate are corrosive to steel while carbonate provides some protection from corrosion. At the OB, chloride concentrations were higher in the 1970s, peaking at 32.0 mg/L in 1976, but have remained constant since the early 1980s with an average of 8.3 mg/L (Fig. 4; panel A). Seasonal analysis indicated yearly average chloride concentrations declined significantly ($p<0.05$) in all seasons, except in summer. More recently, chloride concentrations at this site were similar to those in the 1980s, ranging from 7.4 to 9.4 mg/L in 2011 and 2010, respectively. Much like chloride, dissolved sulfate at the OB peaked in the mid-1970s at 31.0 mg/L (Fig. 4; panel B), and a seasonal analysis showed a significant decline ($p=0.003$) in sulfate concentration from around 16.0 mg/L to 8.0 mg/L (1973 to 1996) during the spring months. Sulfate also declined significantly ($p=0.001$) from 14.0 mg/L to 9.0 mg/L during this same time period during the summer months. Significant declines have occurred since the 1970's to 10.0 mg/L in 1996. In September 2006, sulfate was 14.0 mg/L at the OB. However, concentrations of 49.0 and 10 mg/L were

Figure 4. Long-term changes in water quality at three sites in the Duluth-Superior Harbor. Panels A-C indicate chloride, sulfate, and alkalinity concentrations measured at the Oliver Bridge, panels D-F are concentrations measured at Burlington Northern Railroad, and G-I from Bascule Bridge. Trend lines indicate a significant ($p < 0.05$) decrease in water quality values over their respective time periods. Open circles (o) are chloride measurements, open diamonds (◊) sulfate, and open triangles (Δ) alkalinity as ($CaCO_3$).


A
y = -0.028x + 11.66
R² = 0.078
Chloride (mg/L)
1972 1976 1980 1984 1988 1993 1997
B
y = -0.035x + 17.22
R² = 0.15
Sulfate (mg/L)
1972 1976 1980 1984 1988 1993 1997
C
CaCO3 (mg/L)
1972 1976 1980 1984 1988 1993 1997
Year
D
Chloride (mg/L)
1972 1974 1976 1979 1981 1983 1985 1987
E
y = -0.019x + 15.362
R² = 0.052
Sulfate (mg/L)
1972 1974 1976 1979 1981 1983 1985 1987
F
CaCO3 (mg/L)
1972 1974 1976 1979 1981 1983 1985 1987
Year
G
y = -0.069x + 13.67
R² = 0.32
Chloride (mg/L)
1987 1989 1990 1992 1993 1995 1996
H
Sulfate (mg/L)
1987 1989 1990 1992 1993 1995 1996
I
CaCO3 (mg/L)
1987 1989 1990 1992 1993 1995 1996
Year

measured in 2010 and 2011, indicating variability of sulfate concentration at this site in the most upper part of the DSH. Alkalinity, measured as calcium carbonate ($CaCO_3^{2-}$) remained constant since the early 1970s at the OB with no significant change from the long-term average of 55.5 mg/L (Fig. 4; panel C).

There was no change ($p>0.05$) in chloride or alkalinity concentrations (Fig. 4; panels D and F) from 1973 to 1987 (15 years) at the Burlington Northern Rail Road bridge (BNRR), which is 0.3 miles upstream from the BB and closer to WLSSD. Alkalinity expressed as $CaCO_3$ averaged 54.4 mg/L, average chloride was 12.2 mg/L and the average sulfate concentration was 13.8 mg/L. Sulfate declined ($p<0.05$) slightly from 15.0 mg/L to 12 mg/L. Seasonally, only the yearly average sulfate declined significantly in the winter months ($p=0.003$) from 17.5 mg/L to 7.0 mg/L from 1973 to 1987 at BNRR.

Similarly, data for the Bascule Bridge Fishing Pier (BB) spanned 10 years from 1987 to 1996 and indicated no significant change in sulfate or alkalinity analyzed during this period (Fig. 4; panels H and I). Chloride at BB declined ($p<0.05$) from 15.0 mg/L to 10 mg/L with a long-term average of 10.5 mg/L (Fig. 4; panel G). A seasonal analysis indicated a significant average yearly decline in chloride during the autumn (12.0 mg/L to 6.0 mg/L; $p=0.001$) and winter months (13.0 mg/L to 10.0 mg/L; $p=0.002$) from 1987 to 1996. Sulfate remained constant averaging 12.8 mg/L and the mean alkalinity was 58.8 mg $CaCO_3$/L.

The Larson-Skold Index of water corrosivity relies on chloride, sulfate, and alkalinity concentrations, and was calculated for each of these three sites to evaluate the effect of water chemistry on steel corrosion. From 1972 to 1997, the LSI decreased

($p<0.05$) at the Oliver Bridge from a value of 0.6 to 0.3 (Fig. 5, panel A). Prior to WLSSD coming online in 1978, the average LSI was 0.66 and remained unchanged ($p>0.05$) from 1972 through 1978. After WLSSD coming on line (1979 to 1997), the average LSI was 0.39 and declined significantly ($p<0.05$). It is unlikely that WLSSD's activities influenced the OB site because OB is located approximately 10 miles upstream of the WLSSD discharge site. The LSI at BB also declined significantly ($p<0.05$) from 0.6 to 0.4 (Fig. 5, panel C) from 1987 to 1996. Whereas, this index remained unchanged with a value of 0.6 at the BNRR site (Fig. 5, panel B). Regression analysis showed that before and after WLSSD operation, this average remained at 0.6. In all cases, the average LSI remained well below the 0.8 threshold considered intermediate corrosion risk. It is important to note that among these three sites and of the 478 Larson-Skold calculations, there were only 37 instances (7.7% of the time) during this 25-year period when the Larson-Skold Index was above the 0.8 threshold considered an intermediate risk for corrosion.

The LSI was above the 1.2 threshold only three times and only at the OB from 1972 to 1997, which indicates a potentially high risk for corrosion on the day of measurement. In 2006, the LSI remained below the intermediate risk threshold at all sites except at the DSPA Berth 1 site where the LSI was 0.91 (Fig. 6). The Larson-Skold index in 2010 and 2011 at all sites in the DSH showed that the corrosivity of water was well below the intermediate corrosion threshold of 0.8 (Fig. 6). The only exception was at the Oliver Bridge site in 2010, and this was due to a high sulfate concentration (49 mg/L) on the day of sampling at that site. The Lake Superior north shore sites, had the

Figure 5. Larson-Skold Index of corrosivity estimated at Oliver Bridge (panel A), Burlington Northern Railroad (panel B), and Bascule Bridge (panel C) from the 1970's to the 1990's. The gray box indicates values above the 0.8 threshold considered an intermediate risk for corrosion according to this index. Trend lines indicate significant ($p < 0.05$) declines in the corrosivity of water at two sites.

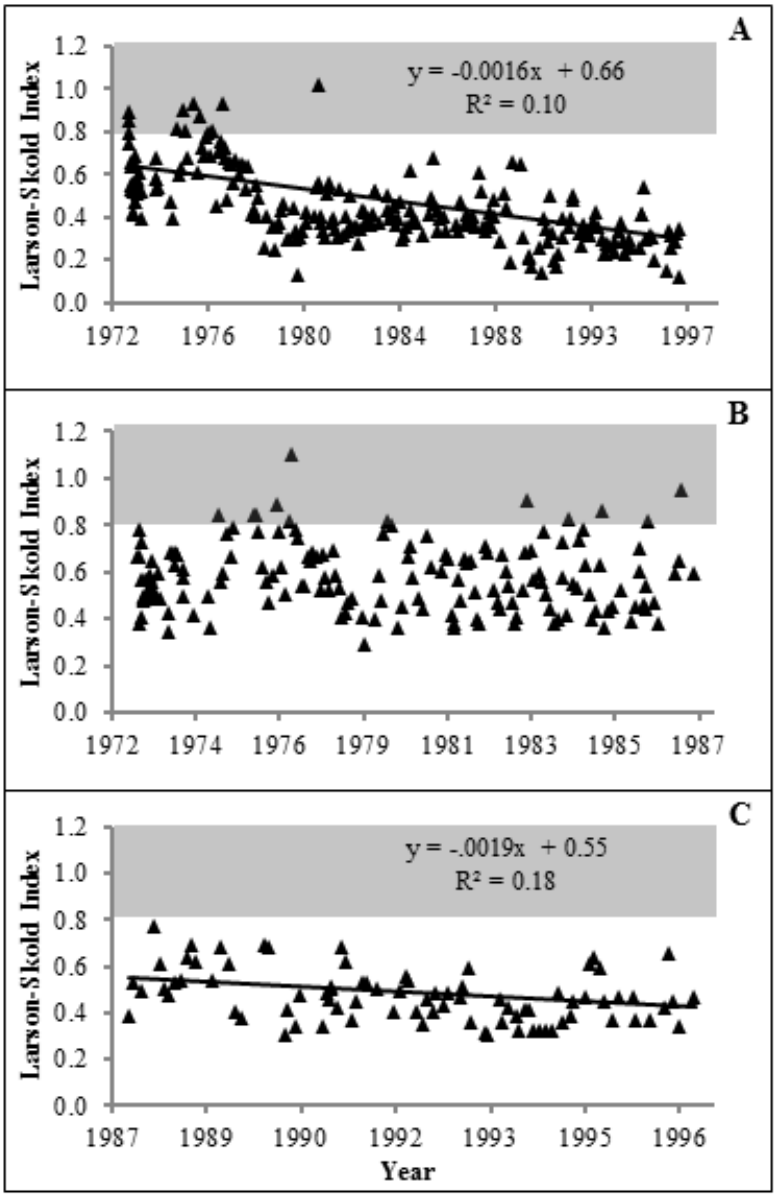
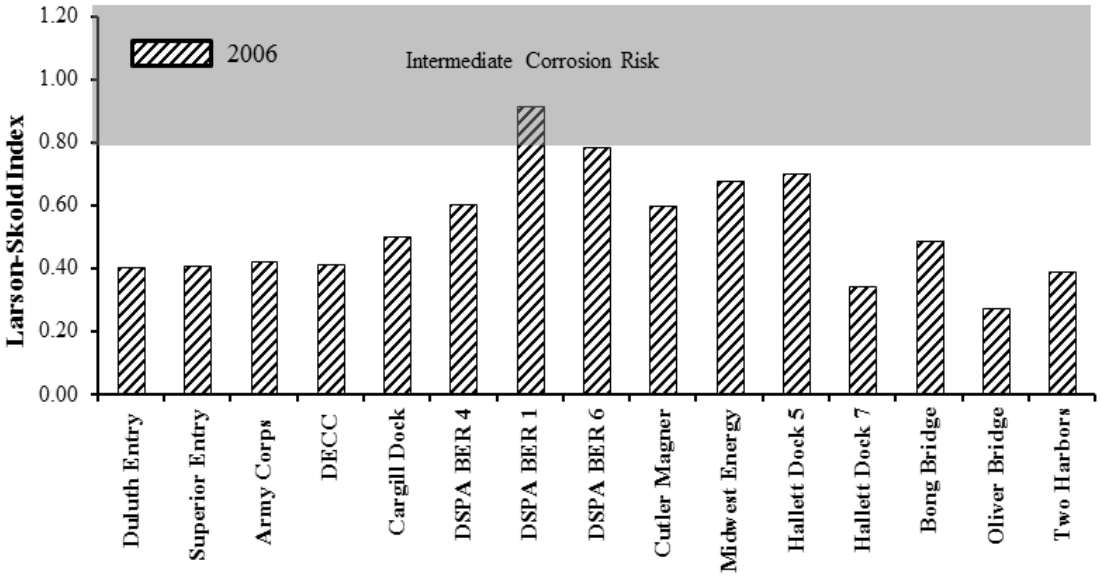

A
y = -0.0016x + 0.66
R² = 0.10
Larson-Skold Index
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1972 1976 1980 1984 1988 1993 1997
B
Larson-Skold Index
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1972 1974 1976 1979 1981 1983 1985 1987
C
y = -.0019x + 0.55
R² = 0.18
Larson-Skold Index
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1987 1989 1990 1992 1993 1995 1996
Year

Figure 6. Comparison of the Larson-Skold Index at 14 sites in the Duluth-Superior Harbor in 2006 and 11 sites in the Duluth-Superior Harbor and the north shore of Lake Superior sampled during 2010 and 2011. Columns with diagonal black lines are Larson-Skold Values from 2006. Black columns represent estimates made in 2010 and gray columns represent 2011 estimates. Site locations are the same as shown in Fig. 2.


1.20
1.00
0.80
0.60
0.40
0.20
0.00
Larson-Skold Index
2006
Intermediate Corrosion Risk
Duluth Entry
Superior Entry
Army Corps
DECC
Cargill Dock
DSPA BER 4
DSPA BER 1
DSPA BER 6
Cutler Magner
Midwest Energy
Hallett Dock 5
Hallett Dock 7
Borg Bridge
Oliver Bridge
Two Harbors

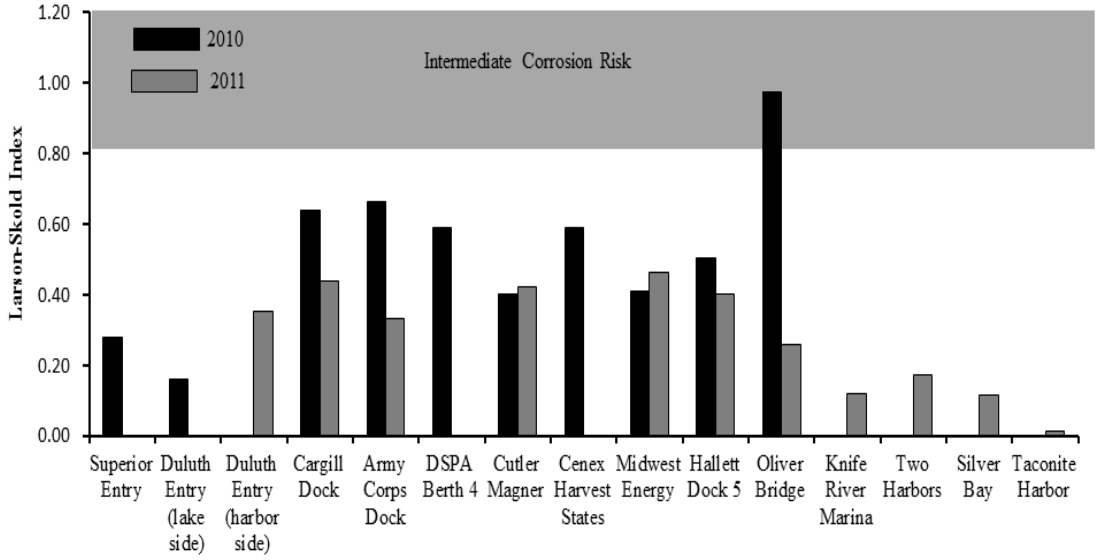

1.20
1.00
0.80
0.60
0.40
0.20
0.00
Larson-Skold Index
2010
2011
Intermediate Corrosion Risk
Superior Entry
Duluth Entry (lake side)
Duluth Entry (harbor side)
Cargill Dock
Army Corps Dock
DSPA Berth 4
Cutler Magner
Cenex Harvest States
Midwest Energy
Hallett Dock 5
Oliver Bridge
Knife River Marina
Two Harbors
Silver Bay
Taconite Harbor

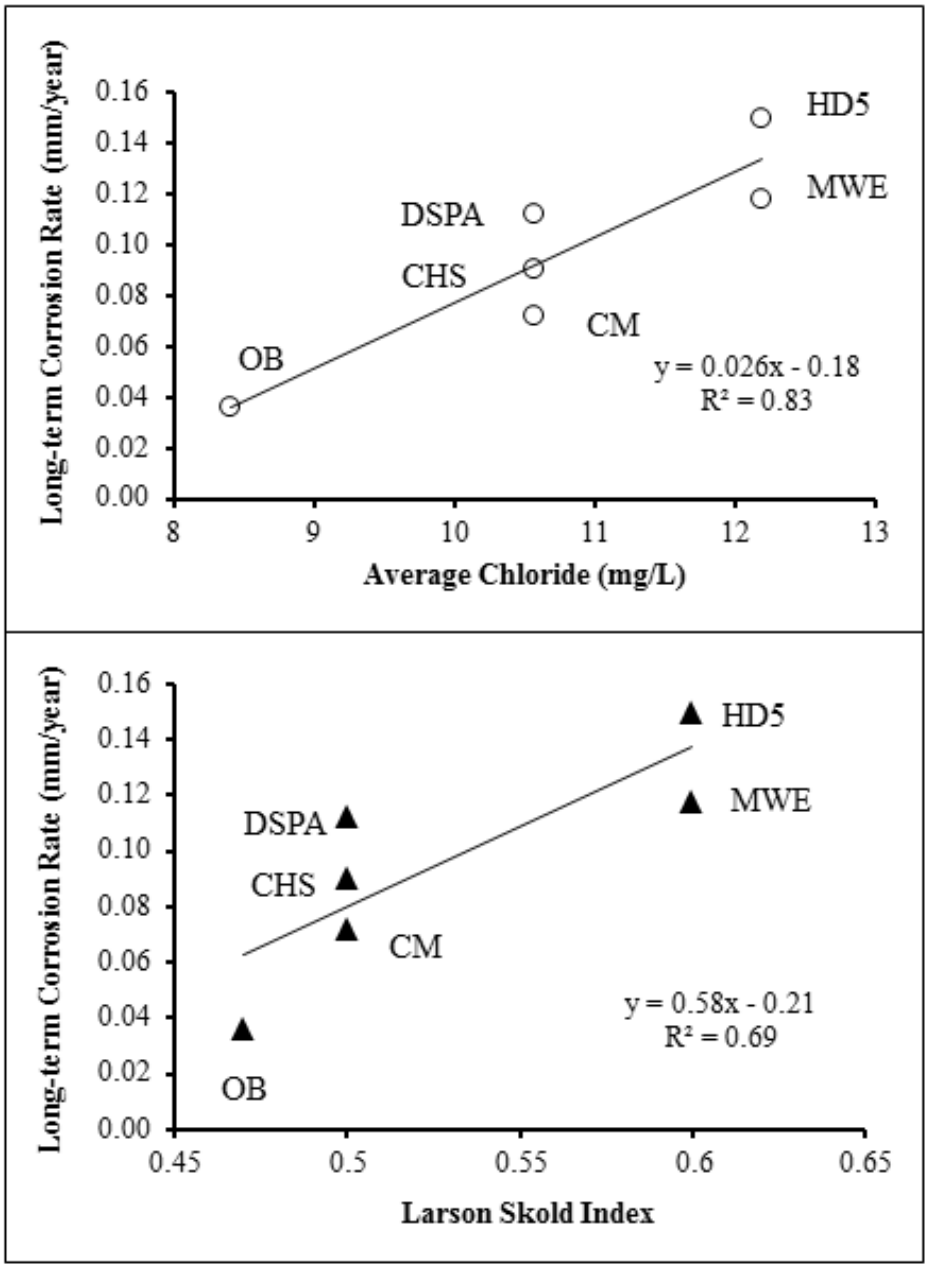
Table 1. Estimates of the long-term corrosion rates at multiple locations in the Duluth-Superior Harbor and on the north shore of Lake Superior. Average long-term corrosion rates were determined by dividing the average pit depth by the total years the steel structure was in service. Site locations are the same as shown in Fig. 2. Sample locations with the same superscript letters indicate long-term corrosion rates were statistically different ($p<0.05$) at those sites. * 2010 Oliver Bridge corrosion rate was significantly slower ($p<0.05$) than all sites, except for the Duluth and Superior Entries. SD = standard deviation; ND = not determined.

Sample Location	Average Pit Depth (mm)		Average Pit Diameter (mm)		Year Steel Installed	Average Corrosion Rate (mm/yr ± SD)	
	2010	2011	2010	2011		2010	2011
St. Louis River							
Oliver Bridge	3.41	ND	13.61	ND	1916	0.036 ± 0.017[d,*]	ND
Inner Harbor							
Hallett Dock 5	3.28	3.28	12.28	10.16	1988	0.149 ± 0.043[c]	0.143 ± 0.049[e,f]
Midwest Energy	4.23	3.60	12.91	12.91	1974	0.118 ± 0.032[b]	0.097 ± 0.050
Cenex Harvest States	4.23	ND	11.85	ND	1963	0.090 ± 0.021[c]	ND
Outer Harbor							
Cutler Magner	3.60	3.18	11.91	9.31	1960	0.072 ± 0.016[b,c]	0.062 ± 0.026[e]
DSPA Berth 4	5.93	ND	16.72	ND	1957	0.112 ± 0.026[a]	ND
Army Corps	3.44	3.18	12.70	9.31	1968	0.082 ± 0.065[c]	0.074 ± 0.031
Cargill	3.81	3.07	15.56	8.04	1977	0.115 ± 0.051	0.090 ± 0.041
Duluth Entry (harbor-side)	ND	2.96	ND	7.62	1987	ND	0.123 ± 0.049
Lake Superior							
Duluth Entry (lake)	1.38	ND	5.29	ND	1987	0.060 ± 0.020[a,b,c]	ND
Superior Entry	6.24	ND	25.46	ND	1909	0.062 ± 0.019[a,b,c]	ND
Knife River	ND	3.92	ND	7.62	1974	ND	0.106 ± 0.051
Two Harbors	ND	2.54	ND	5.40	ND	ND	ND
Silver Bay	ND	3.39	ND	9.74	1952	ND	0.057 ± 0.014[f]

Figure 7. Long-term corrosion rates of steel (mm/yr) in the DSH compared to the service age (years) of that steel in 2010 and 2011. Open diamonds (◊) denote site locations within the inner and outer harbor, open circles (O) represent sites at the Duluth and Superior entries exposed to Lake Superior, and the open square (□) is the Oliver Bridge site in the St. Louis River. The horizontal dashed line indicates the demarcation between rates at the inner and outer harbor sites (above line) and rates at the Lake Superior and St. Louis River sites (below the line).


0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
Long-term Corrosion Rate (mm/yr)
y = -0.0009x + 0.13
R² = 0.45
0
20
40
60
80
100
120
Service Age of Steel (Years)

Figure 8. Relationships between the average chloride concentration (mg/L) and the Larson-Skold Index at Oliver Bridge, Burlington Northern Railroad Bridge, and Bascule Bridge and long-term corrosion rates (mm/yr as of 2010) of steel at locations in the DSH in close proximity to these sites. The Oliver Bridge chloride concentration and LSI were compared to the Oliver Bridge long-term corrosion rate, while chloride and LSI values at the Burlington Northern Railroad Bridge were compared to corrosion rates at sites HD5 and MWE, and Bascule Bridge values were compared to corrosion rates at sites DSPA, CHS, and CM. OB = Oliver Bridge; HD5 = Hallett Dock 5; MWE = Midwest Energy Resources; DSPA = Duluth Seaway Port Authority Berth 4; CHS = Cenex Harvest States; CM = Cutler Magner.


Long-term Corrosion Rate (mm/year)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
8
9
10
11
12
13
Average Chloride (mg/L)
HD5
MWE
DSPA
CHS
CM
OB
y = 0.026x - 0.18
R² = 0.83
Long-term Corrosion Rate (mm/year)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.45
0.5
0.55
0.6
0.65
Larson Skold Index
HD5
MWE
DSPA
CHS
CM
OB
y = 0.58x - 0.21
R² = 0.69

lowest LSI of all sites ranging from 0.01 at Taconite Harbor to 0.17 at Two Harbors. The Knife River Marina and Silver Bay, both had a very low LSI of 0.12.

Analysis of water quality from the early 1970s to the late 1990s in the DSH indicated dissolved oxygen increased during this period at two sites, but there were few major changes in water quality parameters associated with corrosion. In fact, the corrosivity of the water, as indicated by the Larson-Skold Index, remained unchanged at one site (BNRR) and appeared to decrease from the 1970s to the 1990s at the upper most part of the DSH (OB and BB).

Long-term corrosion rates of steel structures varied among sites in the DSH during both 2010 and 2011 (Table 1). Corrosion rates were lower at the entries to the DSH ranging from 0.060 mm/yr to 0.062 mm/year and in the St. Louis River at Oliver Bridge where a corrosion rate of 0.036 mm/yr was measured. Long-term rates of corrosion in the DSH were greater in the inner and outer harbor ranging from 0.062 to 0.149 mm/yr in 2010 and 2011 (Table 1). Though not statistically significant, the 2011 measurements were lower at all sites where rates were measured in 2010 and 2011. Steel in the inner and outer part of the DSH had higher corrosion rates (0.062 to 0.149 mm/yr) than steel at sites exposed to Lake Superior and the St. Louis River (0.036 to 0.062 mm/yr; Fig. 7). The average corrosion rate of steel in the inner and outer parts of the DSH (0.097 mm/yr) was significantly higher ($p=0.03$) than for steel structures at sites exposed to Lake Superior and the St. Louis River (0.052 mm/yr).

Long-term corrosion rates (Table 1) of steel structures estimated in 2010 were compared to long-term averages of water chemistry at the three sites (OB, BNRR, and

BB). Only sites sampled in 2010 in closest proximity to these three locations were used in this analysis. The long-term corrosion rate estimated at OB was compared to water quality from that site. The BNRR water quality measurements were compared to long-term corrosion rates estimated at Midwest Energy Resources and Hallett Dock 5 because all three areas were inner harbor sites. Water chemistry measured at the BB site was compared to the corrosion rates estimated at Cenex Harvest States, Cutler Magner, and the Duluth Seaway Port Authority Berth 4 (DSPA), which were all near the transition zone between the inner and outer parts of the DSH. There were significant ($p < 0.05$) positive relationships between the long-term steel corrosion rate and both chloride concentration and the Larson-Skold Index (Fig. 8); as the concentration of chloride or LSI increased so did the corrosion rate.

Discussion

For the first time, long-term corrosion rates (mm/yr) were determined for steel structures in the DSH where severe corrosion has been observed (Table 1) and then these rates were compared to historic water quality data. Long-term steel corrosion rates were higher ($p<0.05$) at sites in the DSH (0.062 to 0.149 mm/yr) than at a site in the St. Louis River (0.036 mm/yr) or at sites exposed to Lake Superior water (0.057 to 0.062 mm/yr; Fig. 7). Within the DSH, steel corrosion rates decreased with the age of the steel structure (Fig. 7). This trend indicates that either the corrosion rate of steel structures in this harbor has increased in recent years, or that the steel corrosion in this harbor is initially fast and then slows as steel structures age. Comparing water chemistry

parameters with corrosion rates over a long time scale (years to decades) may improve our understanding of corrosion of steel infrastructure in the DSH.

Dissolved oxygen increased at two of three long-term sites in the Duluth-Superior harbor (Fig. 3). However, even with this increase, dissolved oxygen may play a diminishing role in the corrosion process after the initial formation of corrosion products such as lepidicrocite (Huang and Zhang 2005). After the development of corrosion scale and as DO decreases inside the scale, the black precipitate magnetite becomes the dominant corrosion product under the corrosion scale (Huang and Zhang 2005). This is relevant because the tubercle anatomy seen in the DSH typically consists of a brownish-orange outer shell made of goethite and lepidocrocite and products containing magnetite under this surface layer (Ray *et al.* 2010). This change indicates that the inner part of the tubercle becomes and stays anoxic, and any increase in dissolved oxygen may not be directly involved with pitting of the steel surface that occurs under the tubercle.

Whitman *et al.* (1924) described a situation in which the protective films on steel in natural waters could be destroyed. They suggested that in situations where water becomes sufficiently acidic, the film becomes neutralized and can be destroyed at the metal surface, thus reducing the protectiveness of that film. The destruction of these films due to pH changes are not a concern in the DSH because pH ranged from neutral to slightly alkaline (pH 6.79 to 8.04). Whitman *et al.* (1924) also proposed oxygen diffusion from the surrounding water matrix to the metal surface is the most influential parameter affecting corrosion. However, the anatomy of the tubercles seen in the DSH (Ray *et al.* 2010) showed that the tubercle is anoxic and DO may not be penetrating to the

metal surface. The impact of dissolved oxygen is thought to be negligible after the corrosion scale has formed because the water surrounding the scale is not acidic enough to reduce protectiveness. Melchers (2006) suggested that after corrosion scales form, the potential for DO to have a direct influence on metal corrosion lessens.

While the acidity of the harbor may not be of concern in terms of the protective films being destroyed, water freezing in the DSH during winter may play an important role through ice scouring, especially in the spring when the ice pack begins to break up. Ice scouring of tubercles caused by the movement of ice across the steel surface would allow bare steel to once again be exposed to dissolved oxygen once the protective passive film is removed (Ray *et al.* 2009). Because DO is influenced by water temperature, the near freezing water may be saturated with oxygen causing even greater corrosive action.

Dissolved ions are known to cause corrosion of steel surfaces and chloride ions in particular seem to be related to long-term corrosion rates in the DSH (Fig. 8). When chloride concentrations at OB, BNRR, and BB were compared to the long-term corrosion rates determined at locations in close proximity to these sites, chloride was strongly related ($p=0.01$) to long-term corrosion rates (Fig. 8). The Larson-Skold Index might be expected to have a similar relationship with long-term corrosion rates because chloride concentration is one aspect of the LSI. In fact, the Larson-Skold Index at the OB, BNRR, and BB sites were positively related ($p=0.04$) to estimates of the long-term corrosion rate at nearby sites (Fig. 8) Thus, higher chloride concentrations may be at least partly responsible for the higher corrosion rates observed at sites in the DSH.

The Larson-Skold Index predicts the corrosivity of water towards mild steel such as steel used to construct many structures in the DSH. This index indicated a decrease ($p<0.05$) in the corrosivity of water from the 1970's to the 1990's in the St. Louis River (OB site) and the inner part of the DSH (BB site; Fig. 5). The LSI decreased by approximately 50% at each of these sites over one to two decades and remained below the intermediate corrosivity threshold of 0.8. The LSI remained unchanged ($p>0.05$) at another site in the harbor (BNRR) over 16 year period (Fig. 5), and was well below the threshold considered to be moderate risk for corrosion. LSI values calculated from water quality data collected in 2010 and 2011 (Fig. 6) indicated that recent water quality was also not particularly corrosive towards steel. Thus, water chemistry may not be solely responsible for the severe corrosion seen in the DSH, although water quality measurements may change substantially on a daily basis due to several processes like the Lake Superior seiche, discharge from the WLSSD wastewater treatment plant, storm events, and seasonal patterns in the flow of the St. Louis River. Although the LSI has decreased in the DSH since the 1970's and values observed in this harbor were usually below a threshold indicating a moderate risk of corrosion, the LSI index and chloride concentration in the DSH were related to long-term estimates of steel corrosion rates in this harbor (Fig. 8).

Conclusion

Dissolved oxygen increased (Fig. 3) and chloride and sulfate concentrations (Fig. 4) decreased in the late 20th century in the Duluth-Superior Harbor after the Western

Lake Superior Sanitary District became fully operational in 1978. Although these water quality parameters appeared to improve in the DSH, long-term corrosion rates estimated for steel surfaces at many places in this harbor were higher than rates in Lake Superior the St. Louis River and typical of other freshwater environments. While dissolved oxygen increased in concentration in waters of the DSH after 1978, it may not play a large role after tubercles have already formed on steel surfaces. Tubercles are thought to provide protection against corrosive elements such as chloride, sulfate, and dissolved oxygen by reducing their passivity to the steel surface (Melchers 1999, Melchers 2010). Even though chloride concentration and the LSI were related to long-term corrosion rates in the DSH (Fig. 8), the Larson-Skold Index decreased since the 1970's at several sites in this harbor (Fig. 5). This trend indicates that water chemistry alone may not be the sole cause of corrosion observed in the DSH and that other factors such as microbiologically influenced corrosion may play an important role in severe corrosion of steel seen in this harbor.

Chapter 3

Microbiological and Water Chemistry Analyses for Modeling Corrosion Rates of Steel Infrastructure in the Duluth-Superior Harbor

Introduction

While water quality may be an influential factor in the dissolution of iron from steel infrastructure in both marine and freshwater environments, water chemistry may not be the sole cause of the severe corrosion observed in the Duluth-Superior Harbor (DSH). Bostrom (2010) determined through laboratory microcosm experiments that water chemistry may ultimately influence the composition of microbial groups within the biofilms of corroded steel structures in this harbor. Microbiologically influenced corrosion (MIC) can also be an important factor in the dissolution of iron and deposition of corrosion products in the DSH in addition to the chemical oxidation of iron.

The corrosion of steel infrastructure in the DSH has a rusty appearance and raised, hard deposits called tubercles that are characteristic of MIC. Typically, tubercles like these are mostly ferric hydroxide but also contain a variety of organic and inorganic compounds that indicate the presence of iron-oxidizing bacteria (Hamilton 1985). The tubercles are often covered in carbohydrate slimes or biofilms produced by iron-oxidizing bacteria (FeOB), sulfate-reducing bacteria (SRB), and a consortium of other microorganisms (Hamilton 1985). Iron-oxidizing species such as *Gallionella sp.* and *Leptothrix sp.* are responsible for the deposition of such ferric oxides (Emerson and Moyer 2002). Bacteria like these growing in biofilms create a gradient of decreasing oxygen from outside to the inside of the biofilm. The oxic to anoxic conditions that develop are important in determining the types of microorganisms that can be found

within the biofilm (Hamilton 1985, Lee and Characklis 1993). While oxygen gradients can be established within biofilms, local concentrations of chemicals are also influenced by diffusion through the corrosion scale (Lee and Newman 2003), which also affects the composition of microorganisms within the biofilm.

Microbial metabolic processes are known to influence corrosion by changing the chemistry on and near the metal surface. Two main groups of microorganisms, iron-oxidizing bacteria and sulfate-reducing bacteria, have been extensively studied and determined to influence the corrosion of steel surfaces. Freshwater FeOB typically belong to the *Betaproteobacteria*, are chemolithoautotrophic, microaerophilic, utilize iron as an energy source, and grow at neutral pH (Emerson *et al.* 2010). Neutral pH and oxygenic conditions are typical characteristics of the Duluth-Superior Harbor. FeOB such as *Gallionella* spp. can be involved with the formation of tubercles (Hamilton 1985, Emerson and Moyer 2002). Ferric hydroxide is often deposited by FeOB genera such as *Gallionella* spp., *Leptothrix* spp., and *Sideroxydans* spp. (Emerson and Moyer 2002, Emerson *et al.* 2010). Ferric hydroxide has been shown to attach to the twisting stalks that protrude from the cell surface of *Gallionella* species (Hamilton 1985, Ray *et al.* 2009, Ray *et al.* 2010). These bacteria gain very little energy from the oxidation of Fe^{2+} (about 29 kJ/mol), but can obtain approximately double this energy if Fe^{2+} can further be oxidized to Fe^{3+} to form and precipitate iron as an oxyhydroxides (Emerson *et al.* 2010). In the DSH, DNA from bacteria related to *Gallionella* and *Sideroxydans lithotrophicus* were cloned and sequenced from only sites such as Hallett Dock 5 and Midwest Energy Resources (Hicks 2009), where corrosion is known to be the most severe. In this study, a

qPCR assay was utilized which amplified a portion of the 16S rRNA gene, specific to *Gallionella* spp. to estimate their abundance (Li *et al.* 2010) within the corrosion tubercles.

In the anaerobic zone under tubercles, the metabolic activity of SRB can also affect the dissolution of iron from steel surfaces. Sulfate-reducing bacteria are a group of heterotrophic microorganisms, most commonly belonging to the *Deltaproteobacteria* (Kondo *et al.* 2008). SRB use sulfate as a terminal electron acceptor (Gibson 1990) and have an enzyme called dissimilatory sulfite reductase (DSR) to catalyze the reaction reducing sulfite to sulfide (Kondo *et al.* 2004, Kondo *et al.* 2008).

The classic theory of corrosion, electrons are transported from the metal surface into the sulfate reduction pathway of SRB through the activity of hydrogenase enzymes and the production of hydrogen intermediates that carry these electrons (Beech 2003, Beech and Sunner 2004). An electrochemical cell forms where bare steel under the tubercle acts as the anode (site of oxidation), and FeS in adjacent areas acts as the cathode (site of reduction). This coupling can remove electrons from the steel surface and move them to FeS, and as a result, causes the pitting of the steel surface (Potekhina *et al.* 1999, Hamilton 2003). Hydrogenase enzymes and iron-sulfide (FeS) are still regarded as the causative agents of corrosion by SRB. Hydrogenase is responsible for the oxidation of $H_2 \rightarrow 2H^+ + 2e^-$ (Beech 2003) while the production of sulfide is important because it ultimately forms iron-sulfide (FeS). FeS is an important corrosion product that assists in the development of a galvanic cell that can cause pitting of steel surfaces (Hamilton 1985, Beech 2003, Beech and Sunner 2004). The abundance of SRB in

corrosion tubercles can be estimated by measuring the abundance of the *dsr*A gene they contain using quantitative PCR (Kondo *et al.* 2004, Schippers and Neretin 2006, Kondo *et al.* 2008).

Multiple factors working together can either accelerate or inhibit corrosive action on steel in marine and freshwater systems. Wiener and Salas (2005) indicated that average corrosion rates in marine environments are 0.1 to 0.3 mm/year. Typical rates of corrosion in freshwater are about an order of magnitude lower between 0.01 to 0.04 mm/year (Bushman and Associates 2006). Corrosion of steel in the DSH is well above the rates estimated for freshwater ecosystems and multiple locations in the DSH are corroding in the lower range typical of marine ecosystems. Modeling the potential rates of corrosion a port may experience using water chemistry and microbiological analyses is important for local governments and businesses as it would allow them to properly mitigate the damage to and extend the life of their steel structures. Past studies attempting to model corrosion rates have focused mainly on marine ecosystems and have proven difficult because of great statistical uncertainty within aqueous measurements (Melchers 1999, Melchers 2003) and the lack of availability of long-term data. There have been very few observations of corroding infrastructure in freshwater and modeling corrosion in freshwater environments has been largely overlooked (Melchers 2006).

My hypothesis is that a combination of chemical and microbiological factors contributes to the acceleration of corrosion in the Duluth-Superior Harbor. Thus, the influence of water chemistry and the presence of specific microbial groups on the corrosion of steel in a freshwater environment will be examined in this chapter.

Abundances of both FeOB and SRB were measured in corrosion tubercles using quantitative PCR (qPCR) to better understand their relationship to corrosion in the DSH. Microbial abundances and water quality parameters were evaluated and then used to develop a multiple regression model that predicts steel corrosion rates seen in the DSH and along the north shore of Lake Superior.

Methods

Sample Site Locations

Eleven sites in the Duluth-Superior Harbor (near Duluth, MN and Superior, WI) and the north shore of Lake Superior, where steel structures ranged from low to severely corroded, were selected for study in 2010 and 2011 (Fig. 2). The Superior Entry (46^{o} 71.014′ N, 092^{o} 00.661′ W) and lake side of the Duluth Entry (46^{o} 77.987′ N, 092^{o} 08.829′ W), represented sites known to have lower corrosion rates. Moderately corroded sites included White Box Dock (formerly owned by Cargill; 46^{o} 76.948′ N, 092^{o} 10.529′ W), the Army Corps of Engineers dock (46^{o} 77.519′ N, 092^{o} 09.234′ W), the Duluth Seaway Port Authority Berth 4 (46^{o} 75.724′ N, 092^{o} 09.571′ W), Graymont (formerly known as Cutler Magner; 46^{o} 73.332′ N, 092^{o} 07.468′ W), Cenex Harvest States dock (46^{o} 74.288′ N, 092^{o} 10.116′ W), and the Oliver Bridge (46^{o} 65.673′ N, 092^{o} 20.225′ W). Two sites sampled were known to be more severely corroded; the Midwest Energy Resources Company dock (46^{o} 74.232′ N, 092^{o} 11.546′ W) and Hallett Dock 5 (46^{o} 74.563′ N, 092^{o} 13.223′ W). Two additional sites where water chemistry and pit depth measurements were taken in 2006 were also analyzed. The Lakehead Boat Basin (46^{o}

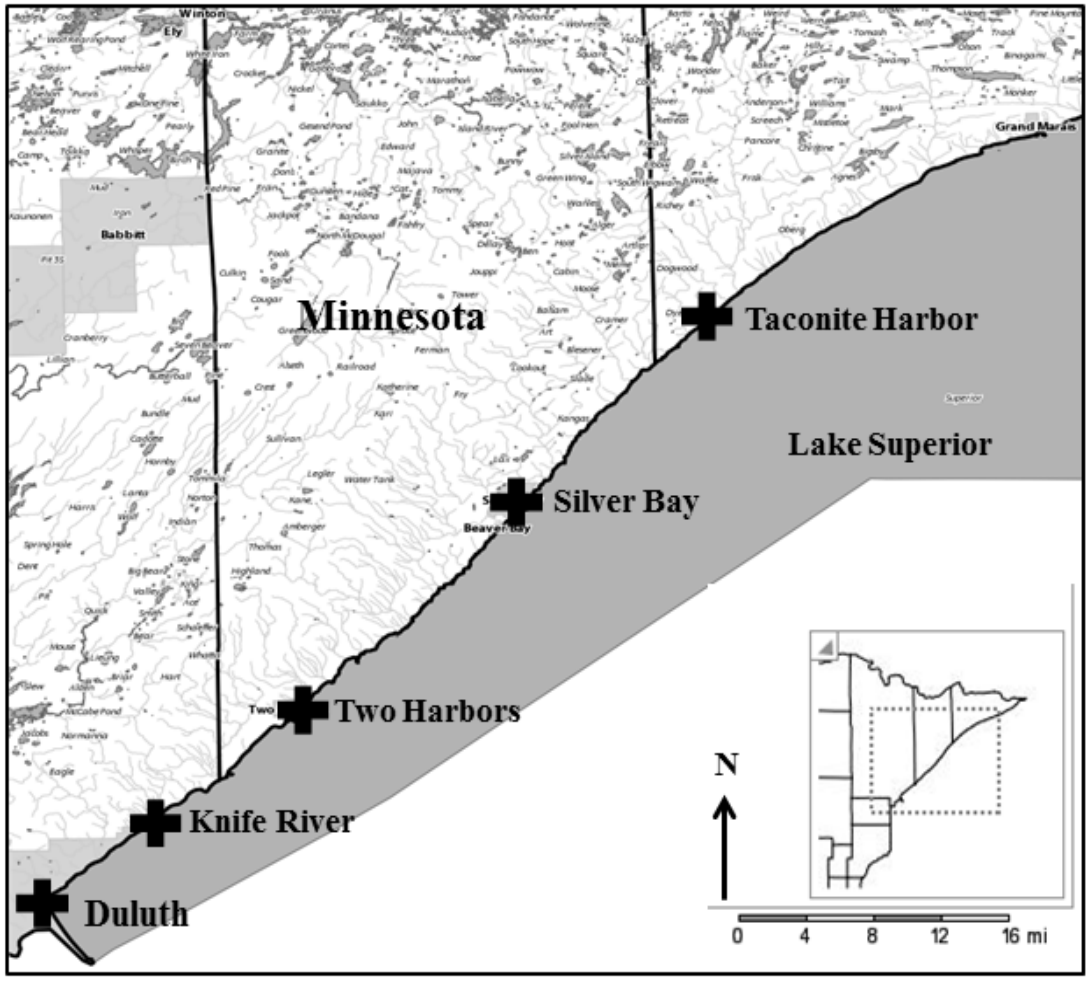
46.457′ N, 092° 05.563′ W) and Cenex Harvest States #3 (46° 44.406′ N, 092° 06.151′ W) were sampled on August 9 and August 8, respectively. Steel structures at all of these sites are constructed of the same type of A328 sheet or piling steel.

In 2011, six of the ten original sample sites from 2010 were sampled again in the Duluth-Superior Harbor. Four sites, Superior Entry, Duluth Entry lake-side, DSPA Berth 4, and Cenex Harvest States were not sampled in 2011 but one new site at the harbor-side of the Duluth Entry (46° 46.674′ N, 092° 05.607′ W) was added for sampling in 2011. This site was moderately corroded compared to the Duluth Entry lake-side area sampled in 2010. Other steel structures along the north shore of Lake Superior were also sampled in 2011 to gain a better understanding of the geographic extent to corrosion of steel infrastructure. Samples were taken from steel docks and structures (Fig. 9) at three locations at the Knife River Marina (46° 56.773′ N, 091° 46.923′ W), Two Harbors, MN (47° 01.032′N, 091° 40.391′W), and Silver Bay, MN (47° 17.030′ N, 091° 15.668′ W). Only water was sampled from Taconite Harbor, MN (47° 52.24′ N, 90° 92.88′ W).

Sampling

Water, corrosion tubercles, and biofilm adjacent to tubercles were collected at these sample sites in the DSH and Lake Superior on August 9-10, 2010 and July 26-27, 2011. All samples were collected by hardhat divers (AMI Consulting Engineers, P.A.; Superior, WI) from sheet steel and pilings at these sites. Dissolved oxygen, conductivity, and water temperature measurements were made using a Yellow Springs Instruments 85 probe at all sample sites (YSI, Yellow Springs Ohio). A YSI 63 probe was used to make

Figure 9. Map of locations along the north shore of Lake Superior where samples were taken in July 2011.


Minnesota
Taconite Harbor
Lake Superior
Silver Bay
Two Harbors
Knife River
Duluth
Grand Marais
Babbitt
Ely
N
0 4 8 12 16 mi

pH measurements and to verify conductivity and temperature measurements. Water for chemical analyses was collected at each site in triplicate using 1 L Nalgene bottles that had been prewashed, rinsed with 10% HCl, and rinsed with sterile Milli-Q water. Water was collected approximately 1 m from the steel surfaces, 1 to 2 m below the water line and prior to tubercle and biofilm sampling at all sites. Collected water was stored on ice in the field and at 4^{o}C in the laboratory before being sent to Trace Analytical Laboratories Inc. (Muskegon, MI) for water quality analyses. Larger volumes of water were obtained in 20 L carboys from each site in 2010 and 2011 to collect microbial cells. Water samples were filtered through one Duropore membrane filter (142 mm diameter, 0.22 µm pore size; Millipore Corp.) to collect microbial cells for subsequent extraction of bacterial DNA for qPCR analyses.

Corrosion tubercles and biofilm adjacent to the tubercles were collected by a professional diver on steel surfaces 1 to 2 m below the water line where corrosion was observed to be the most severe. Sterile 60-ml syringes modified by attaching brushes to the syringe plungers were used to scrape off tubercles or biofilm adjacent to corrosion tubercles (Ksoll *et al.* 2007). Sample material was then drawn into the body of the syringe, capped with a silicone stopper and brought to the surface, where the samples were then transferred to Whirlpak® bags, sealed, and placed on ice for transport to the laboratory. A small portion of tubercle and biofilm samples (0.025 to 0.035 g each) were preserved in 1.9 ml of nuclease free water and 100 µl 37% formaldehyde (2% final concentration) for counting bacterial cells and stored at 4^{o}C for less than two weeks prior to these microscopic counts.

Dry weights of replicate (n=3) portions of tubercle and biofilm (0.5 to 1.0 g) from each sample site were also measured. Aluminum weigh dishes were pre-weighed, wet weights of replicate tubercle and biofilm samples were collected, and then all samples were placed in a 150^{o}F drying oven for two days. Dry weights of each sample were then measured on a Mettler-Toldedo Excellence XS analytical balance (Columbus, OH). Wet to dry ratios were then calculated for determining prokaryotic cell abundances per dry gram of sample. The remaining samples were frozen (-20^{o}C) at the laboratory for extracting microbial DNA.

Corrosion pit depths and diameters were measured at each site at the water line (n=5), 1 m below the water line (n=5), and at 2 m below the water line (n=5) by the diver using a manual pit depth gauge. To measure corrosion pit depths, the needle of the pit depth gauge was placed in the center of a corrosion pit and the gauge was pushed flush with the steel surface to measure the pit depth in inches (ASTM 2005). Pit diameters were measured on the same corrosion pits where pit depths were measured using a ruler on the manual pit depth gauge. The long-term corrosion rate of the steel structure sampled at these sites was estimated by dividing the average corrosion pit depth by the in-service age of the steel structure. Service age of steel was determined from original installation plans, United States Army Corps of Engineers documentation, and the word of private dock owners from non-public records (Chad Scott, pers. comm.). Pit depths and steel corrosion rates were also estimated during 2006 at two additional sites in the DSH using the same methods; Lakehead Boat Basin and Cenex Harvest States site 3.

Water Quality Analyses

Most water chemistry measurements were performed by Trace Analytical Laboratories, Inc. (Muskegon, MI). Alkalinity was measured using titration method SM 2320 (Pohland and Bloodgood 1963) and chloride and sulfate using ion chromatography (EPA 300.0; Pfaff 1993). Dissolved copper concentration was measured by inductively coupled plasma-atomic emission spectrophotometry (EPA 200.7; Martin *et al.* 1994). Water used for the dissolved copper analysis was pre-filtered using a 0.45 µm-pore PVDF Millipore filter to remove large particulate matter and was then acidified with nitric acid to pH 2.0. Dissolved organic carbon (DOC) was analyzed using the procedure of Burdige and Homstead (1994) using a Shimadzu TOC-Vcsh/TN Analyzer at the Large Lakes Observatory at the University of Minnesota Duluth. Water samples (20 ml) were acidified to pH 2 with 6M HCl in glass vials that were pre-combusted to remove inorganic carbon.

Prokaryotic Cell Counts

Total prokaryotic cell abundance was counted using a DAPI staining method developed by Porter and Feig (1980). Replicate subsamples (n=3) of tubercle and biofilm samples preserved in formaldehyde (2% final concentration) were stained with DAPI (10 µM final concentration) for 5 min and then filtered onto black polycarbonate filters (Poretics, 25 mm dia., 0.22 µm pore) prior to counting prokaryotic cells with a Nikon Eclipse 80i epifluorescence microscope. Fluorescent prokaryotic cells were counted at a total magnification of 1000x using UV excitation. Cells in ten fields of view were

counted on each of the three replicate filters from each site and then these counts were converted to prokaryotic cells per dry gram.

DNA extraction

DNA from tubercles, biofilm, and filtered water was extracted using PowerSoil® DNA isolation kits from MoBio Laboratories, Inc (Carlsbad, CA). Prior to the corrosion tubercle and adjacent biofilm samples being frozen, 0.25 to 0.35 g of material from each sample was used to extract total DNA. Two separate extracts of each sample were made and then these extracts were combined and concentrated on one silica spin filter supplied with the MoBio kits. This combined sample was then eluted in 50 µl of TE buffer to obtain a final DNA concentration sufficient for qPCR analyses (greater than 2 ng/µl). For water samples, one-eighth of the Duropore (142 mm diameter, 0.2 µm pore) membrane filter was extracted using the same PowerSoil® DNA isolation kit. These filter portions were cut into small strips before being placed in the PowerSoil® extraction tubes. Total DNA was quantified (ng/µl) using a Thermo Scientific (Wilmington, DE) NanoDrop 3300 full spectrum fluorospectrometer. DNA samples were fluorescently stained using Quant-iT™ PicoGreen® dsDNA reagent from Invitrogen™ Molecular Probes, Inc (Eugene, OR). Extraction efficiencies were calculated in triplicate using autoclaved corrosion tubercle material amended with DNA from *E. coli* cells. Approximately 500 ng of *E. coli* DNA was extracted through the PowerSoil® DNA isolation kit and re-measured on the NanoDrop fluorospectrometer.

Quantitative PCR

Two quantitative PCR assays were used to estimate the abundance of *Gallionella* spp. and sulfate-reducing bacteria. All PCR primers and probes for these assays (Table 2) were synthesized by Integrated DNA Technologies (Coralville, IA).

Iron-oxidizing bacteria (*Gallionella* spp.) qPCR. The primers, probe, and qPCR method developed by Li et al. (2010) were used to estimate the abundance of *Gallionella* spp. in DNA from tubercles, adjacent biofilms, and water samples. QPCR was performed in a reaction volume of 25 µl consisting of 12.5 µl of Brilliant II Master Mix (Agilent Technologies), 0.5 µl of 10 µM solutions of the appropriate forward and reverse primers (Table 2), 1.0 µl of a 3 µM solution of the Gal1p probe, 2.0 µl of 10 mg/ml bovine serum albumin, 0.5 µl of ROX reference dye, 3.0 µl of nuclease-free water and 5.0 µl of DNA template (10 ng total). The 5′ end of the Gal1p probe was fluorescently labeled with 6-carboxyfluorescein (FAM) and the 3′ end with the quencher 6-carboxytetramethylrhodamine (TAMARA). Amplification was performed on a Rotor-Gene 3000 (Corbett Life Sciences) qPCR thermal cycler following the protocol of Li *et al.* (2010): 10 min at 95^{o}C followed by 40 cycles of 95^{o}C for 30 sec and 58^{o}C for 40 sec. A 16S RNA gene clone isolated from the Duluth-Superior Harbor (HD5-Clone 113) containing PCR fragment with a maximum sequence identity of 97% to a *Gallionella* species was cultured and the 16S rRNA gene fragment (141 bp) was reamplified as an authentic standard to construct standard curves. A standard curve ranging from 200 pg to 2 ag (131 to 1.31 x 10^{9} copies of the 16S rRNA gene) of HD5-Clone113 DNA that was

Table 2. PCR primers and probes used for quantitative PCR analyses to estimate abundances of iron-oxidizing and sulfate-reducing bacteria.

Primer/ Probe	**Sequence (5′→3′)**	**Specificity**	**Final Conc. (nM)**	**Reference**
GAL1f	CGA AAG TTA CGC TAA TAC CGC ATA	*Gallionella*	200	Li *et al.*, 2010
GAL1r	CTC AGA CCA GCT ACG GAT CGT	*Gallionella*	200	Li *et al.*, 2010
GAL1p	CCT CTC GCT TTC GGA GTG GCC G	*Gallionella*	200	Li *et al.*, 2010
DSR1F+	ACS CAC TGG AAG CAC GGC GG	SRB	400	Kondo *et al.*, 2004
DSR-R	GTG GMR CCG TGC AKR TTG G	SRB	400	Kondo *et al.*, 2004

amplified with the Gal1F/Gal1R primer set. All qPCR was performed in triplicate for each sample.

Sulfate-reducing bacteria qPCR. A modified procedure from Schippers and Neretin (2006) and Kondo *et al.* (2008) was used to estimate the abundance of sulfate-reducing bacteria by quantifying copies of the *dsr*A gene. Quantitative PCR was performed in a 25 µl reaction volume consisting of 12.5 µl Brilliant II SYBR Green Master Mix (Agilent Technologies), 1.0 µl of 10 µM forward and reverse primers (Table 2), 2.0 µl of 10 mg/ml bovine serum albumin, and 3.0 µl nuclease-free water, 0.5 µl of ROX reference dye, and 5.0 µl of DNA template (10 ng total) on a Rotor-Gene 3000 (Corbett Life Science) qPCR thermal cycler. A standard curve was developed using *Desulfovibrio vulgaris* subsp. *vulgaris* genomic DNA (ATCC 29579D-5) amplified with the DSR1F+ and DSR-R primer set. The standard curve ranged from 2 pg to 2 ag (8 to 8 x 10^9 copies of the *dsr*A gene) of this genomic DNA. The cycling conditions used in this SYBR green qPCR method were: 10 min at 95^{o}C initial denaturation and enzyme activation, 40 cycles of 15 sec at 95^{o}C, 60^{o}C for 60 sec and an additional data acquisition step of 15 sec at 85^{o}C. Finally, a melt-curve analysis was performed with a melt ramp from 72-95^{o}C to detect primer dimers and other non-specific binding. The additional step at 85^{o}C reduced baseline noise in the melt curve analysis and allowed for more accurate data acquisition around our expected product size of 221 bp. The qPCR analyses were performed in triplicate on each sample.

Statistical Analyses

Linear regression was used to evaluate relationships between water quality parameters, bacterial abundances and long-term corrosion rates estimated from corrosion pit depths. A multiple linear regression model was constructed to predict corrosion rates and used water chemistry and bacterial abundance measurements from the DSH to estimate regression parameters. A forward selection as described by Montgomery *et al.* (2006) was applied to each parameter, where only parameters that were significant at a $p<0.05$ level were selected to remain in the model. Forward selection enters the variable that is most correlated with corrosion rate first, then continues this process with the other variables. This selection process recalculates the significance of each variable based on the partial F-statistic, thus building the model based on the variables that have already been included. The forward selection process ends once a parameter is no longer significant. A final model with statistical significance ($p<0.05$) was found to predict long-term corrosion rates. The model included SRB abundance that was $\log_{10}$ transformed to normalize variance. The model was parameterized with data collected from the DSH in 2010 and 2011 and then applied to data collected during 2011 at three harbors on the north shore of Lake Superior. All simple linear and multiple linear regressions were made using the JMP™ version 9.0 statistical software package from SAS Institute, Inc (Cary, NC).

Results

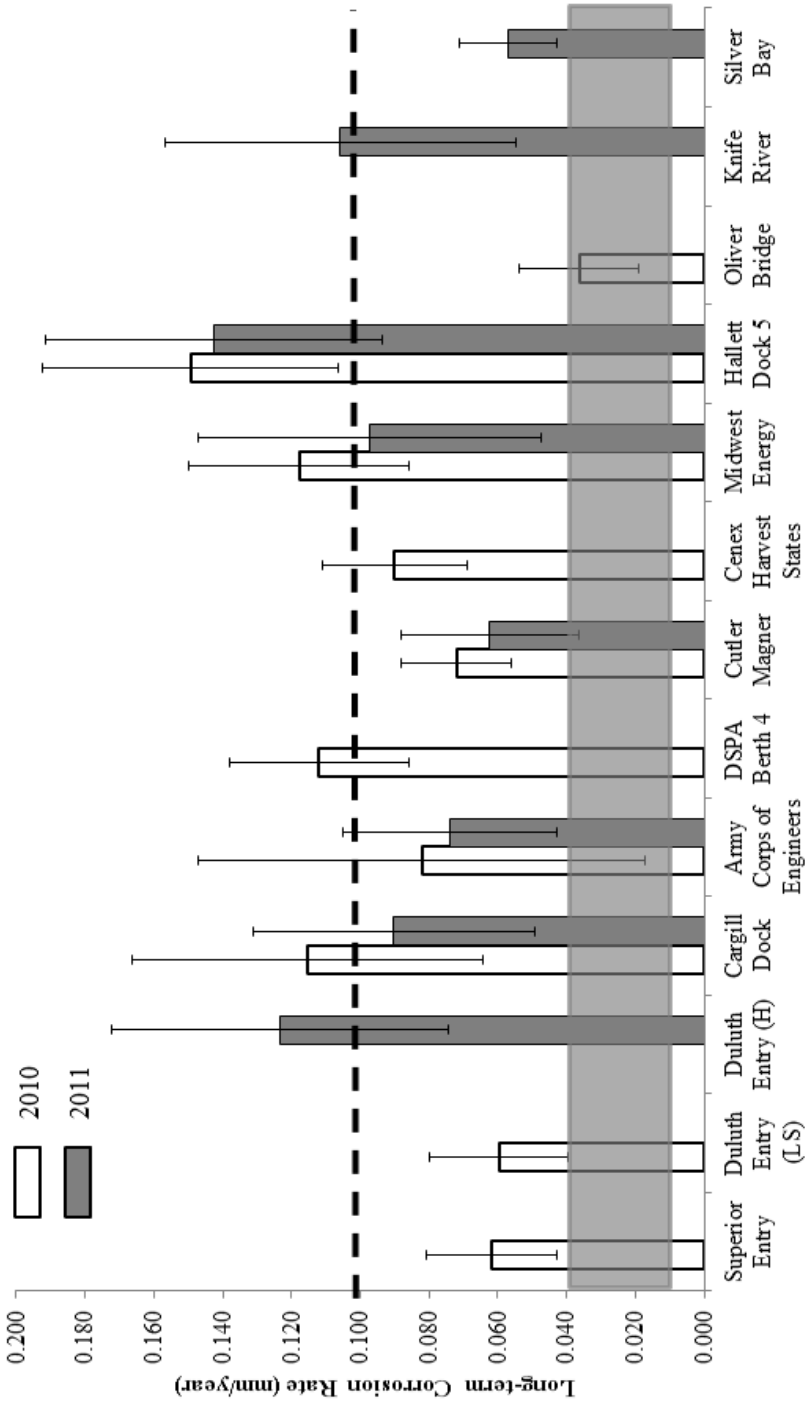
Long-term Corrosion Rate Estimates in the DSH

Corrosion rates on steel estimated in 2006, 2010, and 2011 represent long-term corrosion that occurred over 30 to 100 years (see Chapter 2, Table 1; Appendix Table 9). Two of the sites sampled in 2006, Lakehead Boat Basin and Cenex Harvest States site 3 (CHS 3), had steel that was three and four years old, respectively, and steel corrosion rates higher (0.369 mm/yr, Lakehead Boat Basin; 0.227 mm/yr; CHS 3) than at sites with older steel structures (Fig. 10). In 2006, 2010, and 2011 corrosion rates varied among sites in the Duluth-Superior Harbor and the north shore of Lake Superior (Figs. 10 and 11). Steel corrosion rates were similar ($p>0.05$) between years at sites where measurements were made in both 2010 and 2011. The lowest *in situ* corrosion rates were observed at the head (Oliver Bridge) and mouth of the harbor (Duluth and Superior entries) in 2010 and 2011 (Chapter 2, Table 1). Similarly, corrosion rates were lowest at Oliver Bridge and the Superior Entry in 2006 (Fig. 10). The highest corrosion rate of 0.149 mm/yr was measured at Hallett Dock 5 where corrosion is the most severe. The corrosion rate at Hallett Dock 5 is significantly greater ($p<0.05$) than all other sites except for the Duluth Entry harbor- side, DSPA Berth 4, Midwest Energy Resources, and the Knife River (Chapter 2, Table 1). Corrosion rates of steel structures at the north shore sites, ranging from 0.057 to 0.106 mm/yr, were similar ($p>0.05$) to those estimated in the DSH, (Chapter 2, Table 1). It is important to note that while these rates were comparable to those observed in the DSH, pitting appeared less extensive on steel structures at the north shore sites. In the DSH, corrosion pits were overlapping underneath corrosion

Figure 10. Long-term steel corrosion rates in the Duluth-Superior Harbor estimated in 2006. The dashed line represents the lower limit of the steel corrosion rate observed in seawater (0.1 mm/yr). Error bars represent the standard deviation in average pit depth measurements that were used to calculate long-term corrosion rates.

Corrosion Rate (mm/year)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
Duluth Entry 1
Duluth Entry 2
Duluth Entry 3
Duluth Entry 4
Duluth Entry 5
Duluth Entry 6
Duluth Entry 7
Duluth Entry 8
Duluth Entry 9
Duluth Entry 10
Superior Entry 1
Superior Entry 2
Superior Entry 7
Superior Entry 8
Superior Entry 9
Superior Entry 10
DBCC
Cargill 1
Cargill 2
Cargill 3
Army Corps 1
Army Corps 2
DSPA Berth 1
DSPA Berth 4
DSPA Berth 6
Lakehead 1
Lakehead 2
Community Sailing
Cutler Magner
CHS 1
CHS 2
CHS 3
MWE 1
MWE 2
Erie Pier 1
Erie Pier 2
Hallett Dock 5
Bong Bridge Range
Spirit Lake Marina
Oliver Bridge
CN Two Harbors
Entry (Lake Exposed)
Outer Harbor
Inner Harbor

Figure 11. Long-term steel corrosion rates in the Duluth-Superior Harbor and along the north shore of Lake Superior estimated in 2010 and 2011. The dashed line represents the lower limit of the steel corrosion rate observed in seawater (0.1mm/yr) and the shaded area represents the typical range of the rate of steel corrosion in freshwater environments (0.01 to 0.04 mm/yr). Error bars represent the standard deviation of long-term corrosion rates (n=15).


Long-term Corrosion Rate (mm/year)
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
2010
2011
Superior Entry
Duluth Entry (LS)
Duluth Entry (H)
Cargill Dock
Army Corps of Engineers
DSPA Berth 4
Cutler Magner
Cenex Harvest States
Midwest Energy
Hallett Dock 5
Oliver Bridge
Knife River
Silver Bay

tubercles and the pit diameters were generally much larger than those found at sites along the north shore of Lake Superior (Chapter 2, Table 1).

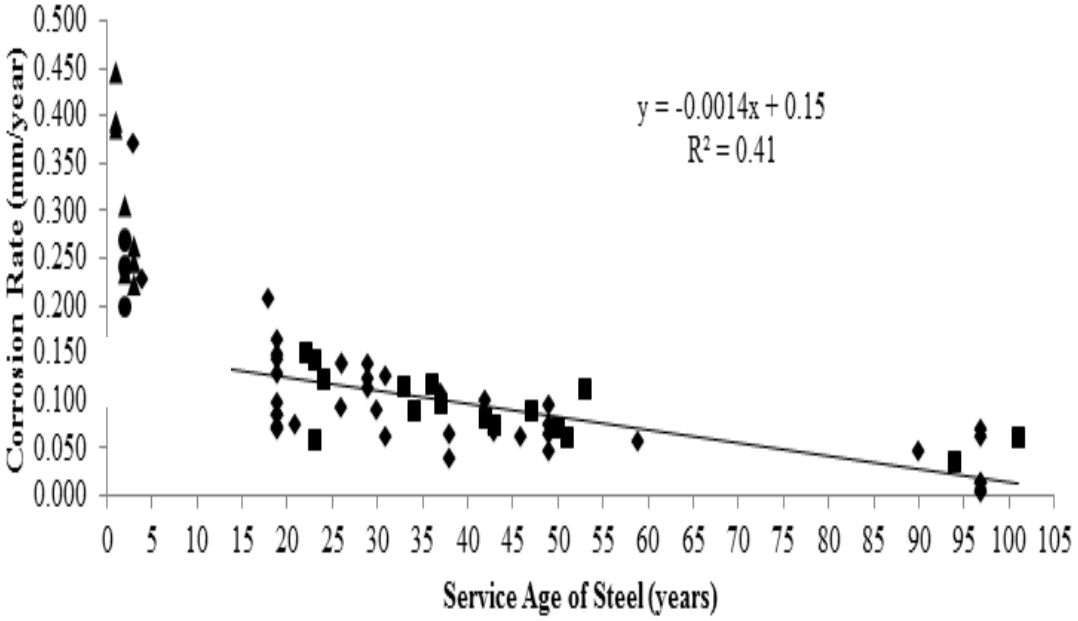
The smallest average pit diameter in the DSH was at the Duluth Entry lake-side location (5.3 mm), a location known to be the less corroded. At sites on the north shore of Lake Superior, corrosion tubercles tended to be much larger and more rigid than those in the DSH. The pitting included a few deep pits under these tubercles, but the pits were much smaller in diameter (5.4 to 9.7 mm; Chapter 2, Table 1). There was some variability in the corrosion rates of steel in the DSH and the north shore, but almost all long-term corrosion rates that were estimated in 2006, 2010, and 2011 were above rates that are considered normal for freshwater environments (0.01 to 0.04 mm/yr; (Figs. 10 and 11).

The corrosion rates of experimental steel coupons exposed in the DSH for one or two years, (Ray et al, 2009, 2010) were two to three times faster than corrosion rates of *in situ* steel structures that were 30 to 100 years old (Table 3). Corrosion rates were compared using pit depth data from steel coupons examined in 2009 and 2010 (Ray *et al.* 2009, 2010), and from *in situ* steel structures studied in 2006, 2010, and 2011 to determine how corrosion rates change over the service life of steel structures in the DSH, (Table 3, Fig. 12). This analysis indicated corrosion rates of steel were greater ($p<0.05$) over the first four years of service life and declined with age (Fig. 12).

Table 3. Comparison of corrosion rates (mm/yr) of steel structures at various sites in the Duluth-Superior Habor in 2006, 2010, and 2011, experimental steel coupons placed at the same locations, and steel coupons in unaltered Duluth-Superior Harbor water from a lab microcosm experiment. Numbers in parentheses are the number of years the steel was exposed to water. Superscript numbers refer to the studies that provided corrosion pit and steel age data needed to estimate the corrosion rates. [1]Ray *et al.* 2009, [2]Ray *et al.* 2010, [3]Bostrom 2010. ND = not determined.

Site Location	*In situ* Steel Structures			Steel Coupon Studies	
	Corrosion Rate (mm/yr)			Corrosion Rate (mm/yr)	
	2006	2010	2011	*In situ*	Microcosm
Oliver Bridge	0.045 (90)	0.036 (94)	ND	0.199 (2)[1] 0.466 (1)[2] 0.235 (2)[2]	ND
Midwest Energy	0.094 (31)	0.118 (35)	0.097 (36)	0.241 (2)[1] 0.394 (1)[2] 0.306 (2)[2]	ND
Cutler Magner	0.062 (46)	0.072 (50)	0.062 (51)	0.269 (2)[1]	ND
DSPA Berth 4	0.094 (49)	0.112 (53)	ND	0.387 (1)[2]	ND
Harbor Water					0.471 (1)[3]

Figure 12. Comparison of corrosion rates (mm/yr) for *in situ* steel structures and experimental steel coupons (from Ray et al. 2009) versus the service life of the structures or exposure time of the coupons (yr) in the Duluth-Superior Harbor. The regression line ($p<0.05$) shows the decline in the long-term corrosion rate when only corrosion rates of *in situ* steel structures were considered. Diamonds = 2006 *in situ* steel corrosion rates; circles = experimental steel coupon corrosion rates (Ray *et al.* 2009); triangles = experimental steel coupon corrosion rates (Ray *et al.* 2010); squares = 2010 and 2011 *in situ* steel corrosion rates.


y = -0.0014x + 0.15
R² = 0.41
Corrosion Rate (mm/year)
Service Age of Steel (years)
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105

Relationship Between Long-term Corrosion Rates and Water Quality in the DSH During 2010 and 2011

Several water quality parameters were measured (see Appendix Tables 7 and 8) at sites throughout the DSH (Fig. 2) during August 2010 and July 2011 to evaluate gradients and relate these measurements to long-term rates of corrosion. Dissolved oxygen increased from the head of the harbor (8.4 mg/L at Hallett Dock 5) to the Duluth and Superior entries, where DO concentrations were 11.2 and 11.3 mg/L, respectively. Interestingly, the long-term estimates of steel corrosion were inversely related ($p=0.04$) to the dissolved oxygen concentration in 2010 (Table 4). The corrosion rates were typically higher at sites with lower DO concentrations (see Appendix).

The dissolved chloride concentration was similar throughout the harbor with a median of 12.0 mg/L and average of 10.2 mg/L, but was positively related ($p=0.02$) to the long-term rate of corrosion at these sites in 2010 (Table 4). Sulfate concentration was more variable among sites and there was no significant relationship between sulfate and the long-term steel corrosion rate in 2010 and 2011 (Table 4). The highest sulfate concentration was found at the Oliver Bridge (49.0 mg/L) in August 2010 and the lowest at the Duluth (3.6 mg/L) and Superior (7.4 mg/L) entries to the DSH. The higher concentration at the OB may have been due to a rain event the night prior to sampling. The sulfate concentration at other sites ranged from 14.0 to 35.0 mg/L in 2010 and 2011. There was an indication of a slight alkalinity gradient in the harbor in 2010 and 2011, with higher alkalinity in the inner harbor and lower concentrations near the harbor entrances.

Table 4. Linear regression analyses comparing the long-term corrosion rates estimated for steel structures in the Duluth-Superior Harbor (y) and measures of water chemistry or the Larson-Skold Index (x) made in 2010. Only dissolved oxygen, chloride, alkalinity and conductivity were significantly ($p<0.05$) related to the corrosion rates of steel structures in this harbor.

Water Chemistry Parameter	Regression Equation	P-value
Dissolved Oxygen	$y = -0.0151x + 0.2306$	0.04
Chloride	$y = 0.0055x + 0.0382$	0.02
Sulfate	$y = 0.0008x + 0.0735$	0.23
Alkalinity	$y = 0.0014x – 0.0103$	0.01
Larson-Skold Index	$y = 0.0372x + 0.0751$	0.40
pH	$y = -0.0155x + 0.2113$	0.29
Conductivity	$y = 0.0004x + 0.0052$	0.04
Dissolved Copper	$y = 3.7851x + 0.0803$	0.43
Dissolved Organic Carbon	$y = 0.0016x + 0.0683$	0.08

The highest alkalinity measurements were typically found at sites noted to be the most severely corroded such as Midwest Energy Resources Company (73 to 91 mg/L) and Hallett Dock 5 (70 to 95 mg/L). In 2010, alkalinity was positively related ($p=0.005$) to the long-term corrosion rate at these sites in the DSH (Table 4).

The Larson-Skold Index (LSI; Chapter 2, Fig. 6) indicated low water corrosivity at all sites in the DSH in 2010 and 2011, except at the OB in August 2010. There was no relationship ($p>0.05$) between the LSI calculated at sites in the DSH during 2010 and the estimated long-term steel corrosion rate (Table 4).

The water pH was in the neutral (7.71) to slightly alkaline (8.17) range at all DSH sites in August 2010 and was not related ($p>0.05$) to the long-term corrosion rate of steel (Table 4). In both 2010 and 2011, water conductivity was typically higher at sites such as Midwest Energy Resources (215-239 µS/cm), Hallett Dock 5 (191-240 µS/cm), and Cenex Harvest States (248 µS/cm) where extensive corrosion has been observed than at sites like the Duluth Entry (101 µS/cm) where less corrosion has been observed. In 2010, water conductivity was positively related ($p=0.04$) to the long-term steel corrosion rate (Table 4). Dissolved copper in water ranged from 0.8 to 8.3 µg/L within the DSH when measurements were made in August 2010 and July 2011. Dissolved copper was not related ($p<0.05$) to estimates of the long-term corrosion rate (Table 4). Dissolved organic carbon (DOC) exhibited a strongly decreasing gradient from the head of the harbor at OB (~19 mg/L) to the entries of the DSH (2 to 6 mg/L; see Appendix). DOC was not related ($p<0.05$) to long-term corrosion rates in the DSH (Table 4).

Prokaryotic, Iron-oxidizing and Sulfate-Reducing Bacterial Abundances within Corrosion Tubercles

Total prokaryotic cell abundances in the Duluth-Superior Harbor varied between sites ranging from 313 x 10^7 to 1,080 x 10^7 cells/dry g in 2010 and 2011 (Table 5). The greatest prokaryotic cell abundances were at Hallett Dock 5 and Midwest Energy Resources in 2011, where 1,010 and 1,080 x 10^7 cells/dry g were counted, respectively (Table 5). The corroded structures on the north shore of Lake Superior had total prokaryotic cell counts that ranged from 130 to 201 x 10^7 cells/dry g. These cell abundances were lower than all sites located in the DSH.

DNA from iron-oxidizing (*Gallionella* spp.) and sulfate-reducing bacteria was found within corrosion tubercles on corroded steel structures in the DSH. The amount of *Gallionella* spp. DNA in corrosion tubercles varied between sites in the DSH and from year-to-year when estimates made in August 2010 and July 2011 were compared (Table 5). Steel structures at Hallett Dock 5 and Midwest Energy Resources (324 to 1,120 x 10^7 16S rRNA gene copies/dry g), where corrosion has been observed to be the most severe, had the highest amounts of *Gallionella* spp. DNA in corrosion tubercles. DNA from *Gallionella* spp. was not detected on the steel surface at the Lake Superior side of the Duluth Entry in August 2010 where no corrosion tubercles developed. *Gallionella* spp. was less abundant (2.38 to 3.07 x 10^7 16S rRNA copies/dry g) on steel structures along the north shore of Lake Superior in July 2011 ($p<0.05$) than at all sites in the DSH.

Table 5. Prokaryotic cell, *Gallionella* spp. (FeOB), and sulfate-reducing bacterial (SRB) abundances within corrosion tubercles on corroding steel structures at various sites in the Duluth-Superior Harbor and along the north shore of Lake Superior during August 2010 and July 2011. *Gallionella* and sulfate-reducing bacterial abundances were estimated by quantitative PCR measurements of *Gallionella*-specific 16S rRNA and *dsr*A gene copies, respectively, per dry gram of tubercle material. nd = not determined.

	2010			2011		
Location	Prokaryotes (10^7 cells/g)	FeOB (10^7 copies/g)	SRB	Prokaryotes (10^7 cells/g)	FeOB (10^7 copies/g)	SRB
St. Louis River						
Oliver Bridge	636	43	0.5	782	58	3.1
Inner Harbor						
Hallet Dock 5	700	122	2.2	1,010	99	1.9
Midwest Energy Resources	448	44	0.02	1,080	324	0.8
Cenex Harvest States	495	169	0.8	nd	nd	nd
Outer Harbor						
Cutler Magner	318	82	0.02	616	43	0.2
DSPA Berth 4	432	16	0.7	nd	nd	nd
Army Corps	724	206	1.1	822	143	25
Cargill	378	127	0.6	578	22	3.8
Duluth Entry (harbor side)	nd	nd	nd	628	32	57
Lake Superior						
Duluth Entry (lake side)	nd	0	0	nd	nd	nd
Superior Entry	313	193	0.02	nd	nd	nd
Knife River Marina	nd	nd	nd	148	2.4	2.1
Two Harbors	nd	nd	nd	201	3.1	3.7
Silver Bay	nd	nd	nd	130	2.6	2.3

DNA from *Gallionella* spp. was not detected in the water surrounding corroding steel structures in the DSH or along the north shore of Lake Superior, indicating that *Gallionella* bacteria were enriched on corroding steel. If each *Gallionella* cell is assumed to contain only one copy of 16S rRNA gene, then *Gallionella* bacteria would account for 2% to 34% of all prokaryotic cells within corrosion tubercles (Table 5). The abundance of *Gallionella* bacteria was unrelated ($p=0.85$) to the long-term corrosion rate of steel at sites in the DSH.

DNA from sulfate-reducing bacteria was also detected within corrosion tubercles on corroding steel structures in the DSH and the north shore of Lake Superior during 2010 and 2011 but was less common than DNA from *Gallionella* spp. Copies of the dsrA gene found in SRB was about 2 orders of magnitude less abundant than the *Gallionella* spp. 16S rRNA gene within corrosion tubercles (Table 5). Like *Gallionella*, the abundance of SRB also varied between 2010 and 2011 where measurements were made in both years. SRB were often found in greatest abundance (1.91 to 2.15 x 10^7 *dsr*A gene copies/dry g) at Hallett Dock 5, a severely corroded site. In 2011, however, corroding steel at the harbor side of the Duluth Entry, which is moderately corroded, had the greatest number of *dsr*A gene copies (Table 3; 57 x 10^7 *dsr*A gene copies/dry g). Much fewer SRB were found on steel structures at the Lake Superior side of the Duluth and Superior Entries (0 to 0.2 x 10^5 *dsr*A gene copies/dry g) where corrosion is less severe (Table 5). SRB gene copies accounted for less than 1% of the total prokaryotic cell counts in corrosion tubercles on steel structures at most locations in the DSH (Table 5). The abundance of SRB estimated in 2010 and 2011 was not related ($p<0.05$) to the

long-term corrosion rates estimated in the DSH when simple linear regression was applied.

Corrosion Risk Assessment Tool

A multiple regression model was developed to predict long-term steel corrosion rates using data collected in the DSH during 2010 and 2011 (Fig. 13). This model was parameterized with water quality data and microbiological abundance measurements made in the DSH and then applied to steel structures at sites along the north shore of Lake Superior where similar measurements were made. The model used alkalinity (mg/L), sulfate (mg/L) and $\log_{10}$ transformed SRB abundance to predict the long-term steel corrosion rate ($p=0.012$). SRB abundance was $\log_{10}$ transformed to normalize variance in the measurements. The adjusted R^2 explained 51% of the variability ($R^2_{ADJ} = 0.51$) in the long-term corrosion rate (Fig. 13, Table 6). The equation for the model was:

Predicted Corrosion Rate (mm/year) = ((0.0021*Alkalinity (mg/L)) + (-0.0014* Sulfate (mg/L)) + (0.0150* Log_{10} SRB (*dsr*A gene copies/dry g)) – 0.1364)

The model was used to predict long-term corrosion rates at three sites along the north shore of Lake Superior. The model predicted corrosion rates of 0.067 ± 0.015 mm/yr at the Knife River, 0.084 ± 0.012 mm/yr at Silver Bay, and 0.066 ± 0.016 mm/yr at Two

Figure 13. Long-term corrosion rate predicted using a multiple linear regression model parameterized with data collected in the Duluth-Superior Harbor during 2010 and 2011. This model used sulfate-reducing bacterial abundance, water alkalinity, and sulfate concentration as parameters to predict the long-term steel corrosion rate. The dashed lines surrounding the regression line represent the 95% confidence intervals.

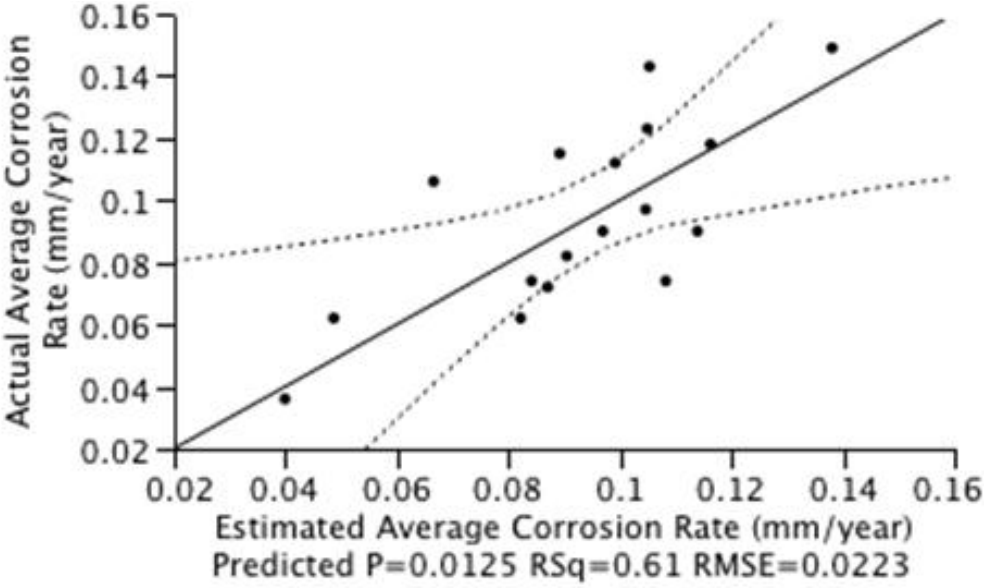

Actual Average Corrosion Rate (mm/year)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16
Estimated Average Corrosion Rate (mm/year)
Predicted P=0.0125 RSq=0.61 RMSE=0.0223

Table 6. Comparison of long-term corrosion rates to corrosion rates predicted by the multiple regression model. The standard deviation (SD) of actual corrosion rate measurements and 95% confidence interval (CI) of predicted corrosion rates estimated by the model are shown. ND indicates that a long-term corrosion rate could not be determined at the Two Harbors site because the age of the steel structure was unknown.

Location	Actual Corrosion Rate (mm/year ± SD)	Model Predicted Corrosion Rate (mm/year ± 95% CI)
Knife River	0.106 ± 0.051	0.067 ± 0.015
Silver Bay	0.057 ± 0.014	0.084 ± 0.012
Two Harbors	ND	0.066 ± 0.016

Harbors (Table 6). The predicted corrosion rate at Silver Bay (0.084 mm/yr) overestimated the measured corrosion rate at this site (0.057 mm/yr) while the predicted corrosion rate for the Knife River marina (0.067 mm/yr) underestimated the measured corrosion rate at that site (0.106 mm/yr; Table 6). No comparison could be made at Two Harbors, Minnesota because the exact age of the steel structure was unknown and thus a long-term steel corrosion rate could not be estimated but the model predicted a steel corrosion rate (0.066 ± 0.016 mm/yr), which was similar to the corrosion rate predicted for the steel structure at the Knife River marina.

Discussion

It is critical to know the potential roles that water quality and microorganisms play in the corrosion process to better understand why steel structures in the Duluth-Superior Harbor are corroding faster than expected, and to develop methods to prevent or mitigate this problem. This study examined water chemistry and the abundance of specific microbial groups, related these parameters to long-term corrosion rates, and developed a multiple regression model that predicted long-term corrosion rates. The regression model relating water quality and microbiological parameters to the corrosion rate of steel structures in the DSH did not accurately predict measured corrosion rates at two sites along the north shore of Lake Superior. It underestimated the corrosion rate at the Knife River marina and overestimated the corrosion rate of a steel structure at Silver Bay. MN, Therefore, it should be more fully developed before being used by dock owners and governments to predict long-term corrosion rates of their steel structures in the DSH or the western part of Lake Superior.

Long-term corrosion rates of steel structures measured in the DSH were higher than is typical for other freshwater habitats. Normal rates of corrosion in freshwater environments are reported to range from 0.01 to 0.04 mm/yr (Bushman and Associates 2006). Long-term corrosion rates ranged from 0.058 mm/yr on the Lake Superior side of the Duluth entry to the harbor to 0.143 mm/yr at Hallett Dock 5 in the inner part of the Duluth-Superior Harbor (Fig. 11; Chapter 2, Table 1). Thus, long-term steel corrosion rates in this harbor were 1.5 to 3.6 times greater than in other freshwater environments. The Duluth entry is less severely corroded than locations such as Hallett Dock 5 where thick steel can be completely perforated below the water line and has caused concern about the structural integrity of steel structures.

The highest rates of steel corrosion in the DSH were found at moderately to severely corroded sites such as Hallett Dock 5 (0.143 mm/yr), the harbor side of Duluth Entry (0.123 mm/yr), Duluth Seaway Port Authority berth 4 (0.110 mm/yr), and Midwest Energy Resources (0.106 mm/yr) (Fig. 11). The corrosion rates at these sites were within the lower part of the range of corrosion rate of steel in seawater (0.1 to 0.3 mm/yr; Wiener and Salas 2005).

Corrosion rates of steel structures in the DSH that have been in service the longest tend to have slower rates than steel coupons that have been exposed to this harbor water for a shorter time period (one to four years) (Fig. 12, Table 3). Three studies on steel coupons of the same type of steel most often used in the DSH, showed initial rates of corrosion were up to three times faster than the long-term corrosion rates estimated in this study (Ray *et al.* 2009, Ray *et al.* 2010). Bostrom (2010) determined that similar steel

coupons had a corrosion rate of 0.471 mm/yr during a one-year laboratory microcosm experiment when they were immersed in harbor water collected from the Great Lakes Aquarium in Duluth, MN.

A study reported by Dismuke *et al.* (1981) showed that corrosion rates during the first four years in freshwater and seawater were similar (0.101 to 0.195 mm/yr) and declined after 16 years to a rate of 0.073 mm/yr in seawater and 0.044 mm/yr in the freshwater system. This trend of the corrosion rate decreasing with the length of exposure was also observed for steel in the Duluth-Superior Harbor (Fig. 12). Yet, the long-term corrosion rates of some steel structures in the DSH after 30 to 100 years of exposure to harbor water were more than 3 three times higher than the long-term corrosion rate of steel in freshwater determined by Dismuke et al. (1981). This difference supports the contention that steel corrosion rates may be accelerated in the DSH compared to other freshwater environments. There is concern about the longevity of steel structures that are critical for maritime transportation and ultimately the economy of the Duluth-Superior metropolitan area because of the corrosion rates detected in the DSH, which can be similar to rates observed in marine systems.

An aqueous system such as the DSH is chemically complex and the corrosion of steel is potentially influenced by many different ions or compounds. Therefore, it may be difficult to pinpoint a single cause of the enhanced corrosion rates in the DSH. Interestingly, dissolved oxygen was inversely related to the long-term corrosion rate in 2010 (Table 4), indicating areas with higher corrosion rates had lower DO concentrations. However, this may be an artifact of the inability of DO to diffuse to the corroding steel

surface after the development of corrosion scales and tubercles. Dissolved oxygen has been implicated in the aggressive corrosive action on steel and the formation of various corrosion products in aqueous systems (Huang and Zhang 2005). Initially, oxygen plays a critical role in the dissolution of iron from the surface of steel (Graedel and Frankenthal 1990, Sarin *et al.* 2004, Huang and Zhang 2005). As corrosion products begin to form and microbial biofilms develop, however, the diffusion of oxygen to metal surfaces decreases (Melchers and Wells 2006, Melchers 2006) and other factors begin to have more influence on the corrosion rate. If corrosion products are removed from the surface through impact or abrasion (water current, wave action, or ice scour), then oxygen may once again play a critical role (Ray *et al.* 2009, Melchers 2006).

Under well-developed corrosion structures like corrosion tubercles, nutrients can control corrosion by developing corrosive chemicals or supporting the metabolic needs of bacteria (Melchers 1999, Melchers 2006). In aerobic freshwater environments, steel corrosion tends to be associated with water hardness, pH, and various nutrient levels. However, none of these parameters, except nutrient levels, seem to be significant in the anaerobic corrosion process (Melchers 2006). In the short-term, freshwater corrosion seems to be controlled by dissolved oxygen, alkalinity, hardness, and pH. However, in the long-term, anaerobic corrosion accelerated by the metabolic activity of bacteria like SRB seems to be the dominant process occurring in freshwater (Melchers 2006, Melchers 2007).

In 2010, only alkalinity, chloride, and conductivity were positively related ($p<0.05$) to the long-term steel corrosion rate estimates in the DSH (Table 4). When

2010 and 2011 water quality data were considered together, there was no significant relationship between any water chemistry parameter and the estimated long-term corrosion rate, except for alkalinity ($p=0.04$). Considering that the concentration of chemical ions can vary on a daily basis, individual measurements on a particular day might not be expected to be related to steel corrosion over large time scales. Melchers (1999) described the statistical uncertainty of such short-term measurements. So, it may be more informative to look for relationships between long-term corrosion rates and the average or maximum concentration of chemicals in long-term data sets. When long-term data is limited, it may be difficult to assess the influence of aqueous chemistry on steel corrosion.

Until recently, the abundances of prokaryotic cells, iron-oxidizing bacteria like *Gallionella,* and sulfate-reducing bacteria have never been measured within corrosion tubercles on steel structures in the DSH. These types of bacteria have been implicated as agents influencing the corrosion of steel in many other studies. Iron-oxidizing bacteria such as *Gallionella* spp. can be involved in the formation of tubercles (Hamilton 1985, Emerson and Moyer 2002, Ray *et al*. 2010). Ferric hydroxide is often deposited by iron-oxidizing species such as *Gallionella* spp., *Leptothrix* spp., and *Sideroxydans* spp. (Emerson and Moyer 2002, Emerson *et al.* 2010). In the case of *Gallionella,* the ferric hydroxide can attach to the twisting stalks that protrude from the cell surface (Hamilton 1985, Ray *et al.* 2009, Ray *et al.* 2010). The metabolic activities of these types of bacteria can also influence the pitting of steel structures (Hamilton 1985, Beech 2003, Beech and Sunner 2004, Melchers 2010).

Previous studies have found bacterial cells similar in morphology to *Gallionella* species within corrosion tubercles in the DSH (Ray *et al*. 2009, Ray *et al.* 2010). Bacterial DNA most similar to iron-oxidizing bacteria like *Gallionella* spp., and *Sideroxydans lithotrophicus* was found in the 16S rRNA gene clone libraries constructed from microbial DNA extracted from corrosion tubercles in the DSH (Hicks 2009, Hicks et al. unpublished data). Also, a bacterium tentatively identified as *S. lithotrophicus* was isolated from corrosion tubercles in the DSH and cultivated (Hicks 2009).

In this study, *Gallionella* was more abundant within corrosion tubercles on severely corroded steel structures at Hallett Dock 5 and Midwest Energy Resources where more than 10^9 *Gallionella* 16S rRNA copies/dry g of tubercles were observed than on steel structures at sites along the north shore of Lake Superior (~10^7 Gallionella copies/dry g; Table 5). Overall, *Gallionella* spp. abundance represented 2% to 34% of the total prokaryotic cells counted in tubercle samples from most steel structures in the DSH (Table 5). DNA from *Gallionella* spp. was not detected in the adjacent water surrounding corroded steel surfaces within the DSH, indicating that corrosion tubercles on steel surfaces are enriched with *Gallionella*.

Wang *et al.* (2011) found up to 10^5 *Gallionella* 16S rRNA copies/dry g in sediments of freshwater marshes using the same primer set used in this study, and these abundances tended to be greater in sediment where Fe^{3+} was most concentrated. Bostrom (2010) reported total FeOB abundance ranged from 4 to 60 x 10^4 cells/cm^{-2} on steel coupons placed at multiple sites in the DSH using a culture-based method (Emerson and Moyer 1997).

DNA from sulfate-reducing bacteria was detected within corrosion tubercles on corroding steel structures in the DSH and harbors located along the north shore of Lake Superior (Table 5). SRB were most abundant at sites known to be more severely corroded, such as Hallett Dock 5 and less abundant at sites exposed to Lake Superior water such as the lakeward sides of the Duluth and Superior entries (Table 5). SRB were at least 2 orders of magnitude less abundant than *Gallionella* bacteria and accounted for less than 1% of prokaryotic cells within corrosion tubercles in the DSH (Table 5). Similarly, Bostrom (2010) found that SRB were about one order of magnitude less abundant than FeOB on corroding steel coupons when the same qPCR was used to estimate SRB abundance. SRB abundances typically ranged from 1.9 to 7.4 x 10^4 *dsr*A copies/cm^{-2}. But at one site, DSPA Berth 4, SRB abundance on steel coupons was as high as 63 x 10^4 *dsr*A copies/cm^{-2} (Bostrom 2010).

The activities of sulfate-reducing bacteria are thought to cause pitting of steel structures. Classic theory suggests that the dissimilatory sulfite reductase (DSR) enzyme catalyzes the conversion of sulfite to sulfide (Kondo *et al.* 2004, Kondo *et al.* 2008) and hydrogenase activity that produces hydrogen intermediates carry electrons away from the steel surface causing pitting (Beech 2003, Beech and Sunner 2004). Other reactions produce compounds such as iron-sulfide (FeS) that help develop galvanic cells, which also leads to pitting corrosion (Hamilton 1985, Beech 2003, Beech and Sunner 2004).

A multiple linear regression model was developed to predict steel corrosion rates at harbors along the north shore of Lake Superior. The corrosion rate of a steel structure at Silver Bay, MN (0.057 mm/yr) was overestimated by this model (0.084 ± 0.012 mm/yr;

Table 6). And, the model underestimated (0.067 mm/yr) the actual corrosion rate of a steel structure at another site in the Knife River Marina (0.106 mm/yr; Table 6). Several factors may explain this outcome. Steel structures on the north shore of Lake Superior tended to have less tubercles that were physically harder to break apart than those in the DSH, and pitting seemed to be confined to a few deep pits under larger tubercles. Pitting seemed more sporadic on steel at the north shore sites and more uniform on steel structures in the DSH, where corrosion pits often overlapped. This model should be tested at additional locations before governments or private dock owners use it because of the limited number of samples and sites that were available to validate the model. Analysis of samples from new sites within the DSH, harbors that are similar to the DSH such as Thunder Bay, Ontario, and harbors along the south shore of Lake Superior should help to further validate the model.

It is interesting that alkalinity was positively related to the steel corrosion rate in the regression model while other studies have shown that alkalinity can have a protective effect (Larson and Skold 1958, Melchers 2006). High alkalinity can lead to denser corrosion products (Melchers 2006). This might limit oxygen diffusion through corrosion tubercles leading to greater anoxia under corrosion tubercles, which would be conducive to the metabolism of anaerobic bacteria like SRB. Melchers and Wells (2006) indicated that nutrients trapped in corrosion products can be utilized by SRB to increase their metabolism when anoxic conditions exist and in turn increase rates of corrosion.

It is unclear why the abundance of *Gallionella* bacteria was not related to the long-term steel corrosion rate or included as a parameter in the multiple regression model

while the abundance of SRB was an important parameter. This was particularly baffling considering that iron-oxidizing bacteria similar to *Gallionella* may account for up to 30% of the bacteria within corrosion tubercles on steel structures in the DSH. Beech and Sunner (2004) suggested that different SRB species may have different metabolic activities in biofilms and that two similar systems may thus demonstrate different corrosion rates. In the future, measuring rates of iron oxidation and sulfate reduction by microorganisms within corrosion tubercles may lead to models that better predict corrosion rates of steel. Although methods exist to measure bacterial rates of iron oxidation and sulfate reduction in laboratory cultures, accurate and easy methods to measure these rates in corrosion tubercles *in situ* do not exist now.

Considering all available data, it is clear that the corrosion of steel structures is accelerated in the DSH compared to other freshwater environments and that some water quality parameters like alkalinity and oxygen are correlated with this corrosion. However, it appears that water chemistry alone is not likely the sole cause of accelerated steel corrosion in the DSH, but rather a combination of microbiological and chemical factors appear to influence the corrosion of steel structures in this harbor. Other factors affecting steel corrosion like the presence and activities of iron-oxidizing and sulfate-reducing bacteria have to be considered. From this study, alkalinity, sulfate concentration, and the abundance of sulfate-reducing bacteria appear to be important factors to consider to predict corrosion rates of steel structures in the Duluth-Superior Harbor and the north shore of Lake Superior.

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Appendix

Table 7. Water quality measurements made at sites in the Duluth-Superior Harbor between August 9 and 10, 2010.

Sample Site Location	Alkalinity (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Larson Skold Index	Conductivity (µS/cm)	pH	DO (mg/L)	DOC (mg/L)	Dissolved Copper (mg/L)	Temperature (°C)
Duluth Entry (lake side)	44	2.4	3.6	0.16	101.0	8.17	11.17	1.77	0.00082	24.3
Superior Entry	54	5.2	7.4	0.28	123.4	7.93	11.33	5.59	0.0012	20.9
Cargill Dock	77	12	31	0.64	219.6	7.80	8.93	12.66	0.0015	24.4
Army Corps	77	12	33	0.67	215.4	7.72	9.12	12.95	0.0030	23.5
DSPA Berth 4	80	12	29	0.59	195.2	7.86	9.80	12.23	0.0083	22.1
Cutler Maner	75	11	14	0.40	220.1	8.04	9.27	13.30	0.0019	23.6
Cenex Harvest States	90	12	35	0.59	247.5	7.96	8.78	15.62	0.0018	24.0
Midwest Energy	91	14	17	0.41	239.0	7.94	8.75	16.08	0.0016	23.3
Hallett Dock 5	95	12	30	0.51	240.1	7.87	8.43	16.18	0.0018	23.2
Oliver Bridge	68	9.4	49	0.97	176.3	7.71	8.80	18.99	0.0020	22.6

Table 8. Water quality measurements made at sites in the Duluth-Superior Harbor and the north shore of Lake Superior between July 26 to 27, 2011.

Sample Site Location	Alkalinity (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Larson Skold Index	Conductivity (µS/cm)	pH	DO (mg/L)	DOC (mg/L)	Dissolved Copper (mg/L)	Temperature (°C)
Duluth Entry (harbor side)	57	7	10	0.36	146.2	6.88	8.7	9.41	0.0013	19.6
Cargill Dock	64	9.6	14	0.44	177.1	6.79	7.46	13.01	0.0015	21.8
Army Corps	61	7	10	0.33	161.4	6.83	7.64	11.02	0.0023	20.7
Cutler Magner	65	9.9	13	0.42	186.7	6.90	8.01	13.37	0.0016	23.0
Midwest Energy	73	13	15	0.47	215.3	7.07	7.29	17.66	0.0016	22.7
Hallett Dock 5	70	9.7	14	0.40	190.5	7.48	6.78	17.43	0.0017	21.8
Oliver Bridge	81	7.5	10	0.26	203.6	6.71	7.01	19.27	0.0013	23.9
Knife River Marina	45	1.4	3.3	0.12	83.4	8.00	10.85	1.30	0.0029	16.5
Two Harbors	43	2.7	3.5	0.17	84.8	7.63	10.28	1.20	0.0011	15.4
Silver Bay	53	1.8	3.5	0.12	83.2	6.83	10.11	1.18	<0.0008	15.6
Taconite Harbor	380	1.4	3.4	0.01	48.0	7.05	10.38	1.83	0.0015	ND

Table 9. Long-term corrosion rate measurements made in the Duluth-Superior Harbor between July 18, 2006 and September 1, 2006.

Sample Site Location	Latitute	Longitude	Years Steel in Service	Average Corrosion Rate (mm/year)	Standard Deviation Corrosion Rate (mm/year)
Duluth Entry 1	46.7809	92.08855	19	0.072	0.047
Duluth Entry 2	46.78086667	92.08843333	19	0.098	0.032
Duluth Entry 3	46.78016667	92.0901	19	0.083	0.027
Duluth Entry 4	46.77961667	92.09183333	19	0.071	0.023
Duluth Entry 5	46.77943333	92.0945	19	0.148	0.032
Duluth Entry 6	46.77803333	92.09328333	19	0.143	0.048
Duluth Entry 7	46.77895	92.09125	19	0.083	0.024
Duluth Entry 8	46.77965	92.08946667	19	0.128	0.030
Duluth Entry 9	46.77985	92.08841667	19	0.069	0.016
Duluth Entry 10	46.78006667	92.08801667	19	0.162	0.057
Superior Entry 1	46.71021667	92.00633333	97	0.062	0.016
Superior Entry 2	46.71165	92.00775	97	0.069	0.023
Superior Entry 7	46.70736667	92.01266667	97	0.014	0.004
Superior Entry 8	46.70738333	92.01306667	97	0.012	0.004
Superior Entry 9	46.7067	92.01471667	97	0.004	0.002
Superior Entry 10	46.70465	92.01678333	97	0.003	0.001
DECC	46.46765	92.05906	42	0.099	0.046
Cargill	46.46166	92.06312	29	0.170	0.079
Cargill A	46.73503	92.14468	29	0.113	0.059
Cargill B	46.70118657	92.03368148	29	0.138	0.106
Cargill C	46.72	92.14361667	29	0.122	0.064
Army Corps 1	46.77521667	92.09233333	38	0.063	0.028
Army Corps 2	46.77528333	92.09206667	38	0.037	0.014
DSPA Berth 1	46.45495	92.06151	49	0.064	0.023
DSPA Berth 4	46.4548	92.05776	49	0.094	0.033
DSPA Berth 6	46.45495	92.06151	49	0.075	0.038
Lakehead 1	46.46457	92.05563	3	0.369	0.113
Lakehead 2	46.46454	92.05522	30	0.090	0.054
Community Sailing Dock	46.43932	92.03408	26	0.140	0.056
Cutler Magner	46.43993	92.04498	46	0.062	0.029
CHS 1	46.44399	92.05965	43	0.067	0.026
CHS 2	46.44377	92.06155	49	0.046	0.015
CHS 3	46.44406	92.06151	4	0.227	0.068
MWE 1	46.44571	92.06891	31	0.061	0.018
MWE 2	46.44571	92.06891	31	0.126	0.056
Hallett Dock 5	46.44734	92.07943	18	0.207	0.076
Bong Bridge Range Cell	46.43882	92.086668	26	0.092	0.034
Spirit Lake Marina	46.42433	92.12172	21	0.073	0.019
Oliver Bridge	46.39391	92.12165	90	0.045	0.023
CN Two Harbors	47.00931	91.40258	94	0.023	0.008
William A Irvin			68	0.065	0.013
John Sherwin			48	0.083	0.023