

**Evaluations of Venturi Oxygen Stripping™ as a Ballast Water Treatment
to Prevent Aquatic Invasions and Ship Corrosion**

Mario N. Tamburri^{1*}, Brenda J. Little², Gregory M. Ruiz³, Jason S. Lee², and Peter D. McNulty⁴

1 Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science

2 Naval Research Laboratory, Stennis Space Center

3 Smithsonian Environmental Research Center

4 NEI Treatment Systems, Inc.

* Chesapeake Biological Laboratory
University of Maryland Center for Environmental Science
P.O. Box 38 / One Williams Street
Solomons, MD 20688, USA
Telephone: 410-326-7440
Fax: 410-326-7428
Email: tamburri@cbl.umces.edu

Abstract:

Invasions by non-native species have resulted in significant ecological changes and enormous economic cost. Although there are several vectors that can transport aquatic invaders, by far the most important is through ship ballast water. Currently, however, there is no environmentally friendly ballast water treatment that is truly effective at reducing introductions and yet also acceptable to the shipping industry in terms of safety, time, and cost. Deoxygenation may however be such a treatment with benefit for ship owners through corrosion prevention, while simultaneously limiting the number of aquatic organisms surviving transport in ballast tanks.

Our current investigations are providing the critical information required to evaluate the efficacy and feasibility of deoxygenation as a ballast water treatment to prevent aquatic invasions and tank corrosion. Specifically, we are: (1) evaluating the Venturi Oxygen Stripping™ system developed by NEI Treatment Systems, Inc. to optimize the deoxygenation process, (2) examining the impact of this oxygen stripping technique on the immediate and long-term survival of natural Chesapeake Bay planktonic organisms, and (3) quantifying corrosion rates and establishing the corrosion mechanism under deoxygenated conditions (with particular emphasis on microbiologically influenced corrosion and the production of hydrogen sulfide). These results will ultimately lead to a full-scale shipboard evaluation of deoxygenation as a cost-saving ballast water treatment.

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 2003		2. REPORT TYPE		3. DATES COVERED 00-00-2003 to 00-00-2003	
4. TITLE AND SUBTITLE Evaluation of Venturi Oxygen Stripping Trademark as a Ballast Water Treatment to Prevent Aquatic Invasions and Ship Corrosion				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science, P.O. Box 38/One Williams Street, Solomons, MD, 20688				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Introductions:

Statement of Problem – Invasions by non-native aquatic species are increasingly common worldwide in coastal habitats and it is widely accepted that ballast water is the most important vector responsible for transporting and introducing non-native species to new biogeographic regions (Carlton and Geller 1993; Cohen and Carlton 1998). It has proven challenging, however, to find an environmentally friendly ballast water treatment that is effective at reducing the potential for introductions and yet also acceptable to the shipping industry in terms of safety, time, cost, and space constraints. For instance, the offshore exchange of ballast water is currently recommended to reduce introductions (since coastal organisms are unlikely to invade open ocean areas, and vice versa), but the process is time-consuming (thus costly) cannot be performed in rough sea conditions, and has limited effectiveness in some environments and for certain vessel designs (e.g., Cooper et al. 2002; Ruiz et al. unpublished data).

Analysis of different ballast water treatments by the National Research Council (1996) suggested that intensive filtration, thermal treatment, and biocides were the most promising options. However, discharging warm water or water laden with biocides potentially threaten biological communities around ports, some biocides can be dangerous to crew members, and fine filtration systems are expensive to install and maintain (National Research Council 1996). For any ballast water management strategy to be successful, the shipping industry must be willing and able to comply (e.g., non-conflicting with other regulations such as those designed for crew safety). However, the shipping industry does appear prepared to embrace technologies that are effective, safe, and efficient.

The acceptance and implementation of effective ballast water treatment measures would be hastened by providing the shipping industry with economic incentives for doing so. Our previous and ongoing work suggests that deoxygenation may be such a treatment. The economic benefit for ship owners involves significant corrosion reduction, while simultaneously limiting the number of aquatic organisms surviving transport in ballast tanks (Tamburri et al. 2002).

Corrosion of ballast tanks from exposure to seawater is typically destructive and costly for individual vessels and the shipping industry as a whole. Currently painting and sacrificial anodes are used almost exclusively as the means to prevent ballast tank corrosion, but they are expensive and time-consuming. Investigators from Sumitomo Heavy Industries, Ltd. of Japan have therefore proposed an alternative corrosion prevention technique that purges oxygen from ballast tanks with nitrogen gas (Matsuda et al. 1999). This new anticorrosion technology was derived from the basic concept that removing oxygen from the ballast tanks will limit the oxidation of metallic structures and thus greatly reduce the problems associated with corrosion. Our initial proof-of-principle and laboratory studies on the effectiveness of deoxygenation to prevent the transport of non-native species and the full-scale, field study on ballast tank corrosion demonstrated that this approach may both save the shipping industry money on corrosion prevention while removing a large proportion of the organisms typically found in ballast waters (Tamburri et al. 2002).

Current Objectives – While results from the initial proof-of-principle studies are promising, clearly additional work is needed to determine if deoxygenation is a feasible and effective treatment for shipboard application to prevent aquatic invasions and tank corrosion. Our current NOAA funded investigations are focused on a laboratory scale proof-of-technology. Specifically, we are: (1) evaluating the Venturi Oxygen Stripping™ system developed by NEI Treatment Systems, Inc. to optimize the deoxygenation process, (2) examining the impact of this oxygen stripping technique on the immediate and long-term survival of natural Chesapeake Bay planktonic organisms, and (3) quantifying corrosion rates and establishing the corrosion mechanism under deoxygenated conditions (with particular emphasis on microbiologically influenced corrosion). Although the effects of low oxygen or hypoxia (< 1.0 mg/l oxygen) on aquatic organisms (see reviews by Grieshaber et al. 1994, Diaz and Rosenberg 1995; Tamburri et al. 2002) and corrosion (e.g., Hardy and Bown 1984; Lee et al. 1993a) are well documented, our current work is the first large-scale, direct investigation of both simultaneously. Furthermore, by conducting the experiments across different scales, we are collecting the critical data required to evaluate

the feasibility of deoxygenation as a shipboard ballast water treatment. These results will ultimately lead to a full-scale evaluation of deoxygenation as a cost-saving ballast water treatment onboard active vessels.

Background and Previous Work on Ballast Water Invasions – Sumitomo Heavy Industries found that deoxygenating ballast waters (purging with nitrogen gas to drop oxygen levels to approximately 0.2 mg/l) decreases the rate of uniform corrosion by 90% and represents a significant saving for ship owners when compared to other corrosion prevention approaches currently available (approximately \$80,000/year/vessel saved when compared to the standard painting and maintenance; Matsuda et al. 1999). These results are supported by the anecdotal observations of the Hellepont Group, who state that corrosion in ballast tanks on their tankers has been “completely arrested” after the addition of anodes and low-sulphur inert gasses.

To test whether deoxygenation may also limit invasion, we carried out laboratory oxygen tolerance experiments on the larvae of three widely introduced aquatic nuisance species (Australian tubeworm *Ficopomatus enigmaticus*, European zebra mussel *Dreissena polymorpha*, and European green crab *Carcinus meanas*) using oxygen levels comparable to those in the shipboard corrosion study (< 0.8 mg/l). Significant levels of mortality were found in nitrogen treated water after only two or three days (Tamburri et al., 2002). Two separate literature reviews of oxygen tolerance for various aquatic species further support the conclusion that few organisms will be able to withstand extended periods of exposure to deoxygenated ballast water (Table 1). For example, by far the most abundant animals found in ballast water are copepod crustaceans (Carlton and Geller 1993; Smith et al. 1999) and shallow water and estuarine species that are unable to withstand 24 hours of exposure to hypoxia (e.g., Roman et al., 1993; Lutz et al. 1994; Stalder and Marcus 1997).

Table 1. A representative sample of time until significant mortality (LD₅₀, LT₅₀, or survivorship in treatment significantly less than control) was found for aquatic organisms held under various low oxygen concentrations. Adapted from Tamburri et al., 2002.

Species	O ₂ level (mg/l)	Time to significant mortality	Source
<i>Astronotus ocellatus</i> fish – adults	0.4	24 hours	Muusze et al. 1998
<i>Ophiura albida</i> brittle star - adults	0.1	60 hours	Vistisen and Vismann, 1997
<i>Gammarus pseudolimnaeus</i> amphiod - adults	1.5	24 hours	Hoback and Barnhart, 1996
<i>Platichthys flesus</i> fish – juveniles	1.0	2 hours	Tallqvist et al. 1999
<i>Meganyctiphanes norvegica</i> krill – adults	1.8	2 hours	van den Thillart et al. 1999
<i>Cancer irroratus</i> crab – larvae	1.7	4 hours	Vargo and Sastry, 1977
<i>Crassostrea virginica</i> oyster – larvae	0.02	18 hours	Widdows et al. 1989

Small plant and algal parts (fragments, spores, and seeds) as well as single-celled phytoplankton, protozoists, fungi, and bacteria are also often transported in ballast water. These microscopic components of ballast water have not been thoroughly characterized. However, it appears from our reviews that their tolerances for low oxygen environments will vary greatly. There are examples of species that are very sensitive to hypoxic conditions (e.g., filamentous fungi, Padgett et al. 1989; zoospores of the seaweed *Undaria pinnatifida*, Mountfort et al. 1999), as well as counter-examples of species that can withstand low oxygen levels (e.g., resistant cysts of dinoflagellates, Hallegraeff 1998). Marine bacteria, in particular, will have dramatically different responses to the conditions created in nitrogen treated ballast tanks. While most obligate aerobic strains will be unable to grow over extended periods of hypoxia, some facultative and obligate anaerobic bacteria may actually thrive under the conditions found in treated ballast. We therefore conclude that ballast water deoxygenation (maintaining hypoxia) would likely be highly effective at reducing introductions of aquatic animals (larvae, juveniles, and adults stages) but may have mixed success at eliminating introductions by members of other taxa.

Although other ballast water treatment options might be more comprehensively effective, they come at greater environmental and financial cost. For example, some biocides may be hazardous for the crew as well as for native organisms in the vicinity of the ballast discharge (National Research Council 1996). Moreover, these techniques come at a significant price for ship owners. Our previous work suggested that widespread voluntary adoption of deoxygenation may result if the economic benefits for controlling corrosion are demonstrated definitively and become well known. While ballast water treatments have been controversial, raising conflicts between environmentalists and ship owners, we felt that deoxygenation represented a working solution that should appeal to both parties and that deserved further investigation.

Background and Previous Work on Ballast Tank Corrosion – The vast majority of the world's fleet of ships, including military and commercial vessels, are constructed of carbon steel. Steel corrodes quickly when exposed to oxygen and water. Ocean-going vessels are particularly susceptible to corrosion, due to the accelerated corrosion rate in exposure to salt water. Corroded steel structures on a vessel decrease seaworthiness so extensive measures are taken to prevent corrosion and, inevitably, in repair. The cost to prevent, maintain, and repair corrosion on individual vessels can run into the millions of dollars (e.g., \$5.5 million to replace 1400 tonnes of ballast tank steel on *Wind Conquest*, Marine Engineering Review 1991).

One area in a ship where corrosion is of particular concern is in the ballast tanks. Prolonged exposure of the ballast tank structure to water (often salt water) creates a condition conducive to rapid corrosion. The cost to paint ballast tanks is typically at least \$5.00 to \$10.00 per square meter with the cost to repair corroded areas at approximately \$500 per square meter (Fairplay 1993). With large cargo vessels and oil tankers having hundreds of thousands of square feet of ballast tank surface area, preventing and treating corrosion is extremely costly.

Therefore, any measure for controlling aquatic invasive species in ballast tanks cannot be evaluated without consideration of the impact on corrosion. For example, both chlorination (McCracken 2001) and ozonation (Andersen 2001) of seawater are believed to exacerbate corrosion of steel. Clearly, removal or reduction of oxygen will eliminate or reduce direct oxidation reactions related to corrosion. However, deoxygenation could increase corrosion resulting from the activities of naturally occurring microaerophilic, facultative or obligate anaerobic bacteria. Acid-producing bacteria (APB) and sulfate-reducing bacteria (SRB) grow under anoxic conditions and produce corrosive metabolic by-products (organic acids and sulfides, respectively).

The corrosion rate of carbon steel is not influenced by pH over the range of 4.5 to 9.5 in distilled and tap waters (Boyer and Gall 1985). Over this range, corrosion products maintain a pH of 9.5 at the metal surface. Below pH 4.0, hydrogen evolution begins and corrosion increases dramatically. Although it is extremely unlikely that APB will change the bulk pH of carbonate buffered seawater, APB can reduce pH locally under colonies and produce corrosion in carbon steel (Pope 1995).

All seawater contains 2 gm l^{-1} sulfate than can be reduced to sulfide by SRB in the absence of oxygen. Reviews by Miller and Tiller (1970), Iverson (1974) and Postgate (1979) provide examples and details of microbiologically influenced corrosion of iron and mild steel under anaerobic conditions caused by SRB. Microbiologically influenced corrosion failures have been reported for mild steel piping and equipment exposed in the marine environment (Sanders and Hamilton, 1986; Eidsa and Risberg 1986; Eashwar et al. 1990) soil (King et al. 1983; Kasahara and Kajiyama 1986; Alanis et al. 1986; Pope et al. 1988; Dias and Bromel 1990), oil refining industry (Winters and Badelek 1987), fossil fuel and nuclear power plants (Soraco et al. 1988; Licina 1988, Pope 1986 and 1987; Bibb 1986) and process industries (Pacheco, 1987; Honneysett 1985; Tatnall et al. 1981). Deoxygenation can also result in putrefaction, anaerobic breakdown of sulfur-rich proteins, and levels of sulfides will not be limited to the sulfate concentration in the seawater. Sulfide reacts with iron oxide, formed in the atmosphere or in oxygenated seawater, to produce a non-tenacious iron sulfide layer that can be removed with stress or converted back to an oxide by the introduction of oxygen. In either case the sulfide layer is not uniformly removed or oxidized, creating adjacent anodic and cathodic regions and aggressive corrosion.

The most corrosive operating condition is one in which carbon steel is exposed to alternating oxygenated/deoxygenated conditions (Hardy and Bown 1984; Lee et al. 1993a; Lee et al. 1993b). Under constant oxygenation an oxide will form that provides corrosion resistance. Under anaerobic conditions a sulfide layer will form and corrosion rate will decrease until oxygen is introduced. The result of alternating operating conditions is severe pitting. Additionally, concentrations of sulfides can produce sulfide assisted stress corrosion cracking in carbon steel. Most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium (Hamilton 1986). Anaerobic conditions and sulfides form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations. Exposure of iron sulfide corrosion products to oxygen creates differential aeration cells and localized corrosion. However, because aerobic microorganisms form biofilms, continuous deoxygenation to prevent biofilm production has been suggested as a way to reduce microbial induced corrosion (Lutey 200; Pope and Pope 2001).

Methods:

Optimizing Deoxygenation – A key to the success of deoxygenation as a ballast water treatment is to design and develop the most efficient method for maintaining levels of oxygen in tanks that both kills the majority of aquatic organisms while also reducing corrosion rates – below 1.0 mg/l . The deoxygenation method proposed by Sumitomo Heavy Industries for ballast water treatment entails bubbling an inert gas into the ballast tanks after they have been filled. The shipboard trial by Matsuda and colleagues (1999) included vertical pipes installed into a ballast tank from which pure nitrogen gas was pumped into the water for the “sparging” of oxygen. The tank was also sealed at the deck to permit nitrogen purging of the headspace. This method may achieve some deoxygenation through the contact of the nitrogen bubbles with the water, but primarily relies on diffusion of oxygen through the water surface in the tanks. Although hypoxic conditions were achieved, the sparging and purging of oxygen took days and relied on both the presence of a large headspace in the ballast tank filled with nitrogen gas (a free surface condition that is typically avoided since it can destabilize the vessel as water moves within tanks) and on large volumes of expensive inert gas. Although the basic principles are sound and experimental results on corrosion significant, the method used by Sumitomo Heavy Industries for deoxygenation appears to be inefficient and relatively costly to employ (approximately \$3.5 million for installation on a vessel).

Other deoxygenation methods (e.g., vacuums, horizontally placed diffuser plates, biological processes) use techniques with varying degrees of effectiveness. However, our investigations suggest that the most efficient way to remove oxygen from ballast water is through introducing microfine bubbles of an inert gas as water is being pumped into the tanks. The smaller a bubble, the higher the ratio of surface area to volume and thus the higher gas-to-water contact surface where transfer takes place. Therefore, we

have begun work with NEI Treatment Systems, Inc. to evaluate the deoxygenation of ballast water through Venturi Oxygen Stripping™.

Survivorship of natural planktonic organisms subjected to deoxygenated water – Dockside, mesocosm experiments are being conducted at the Chesapeake Biological Laboratory (CBL), University of Maryland Center for Environmental Science, in Solomons, Maryland (Figure 1). Natural seawater is pumped from one meter below the surface into 10 identical 25-gallon, airtight fiberglass cylinders, held inside a laboratory at the end of the CBL pier. All water first passes through a 1 cm screen (the mesh size commonly used to filter intake into ship ballast tanks) and the cylinders are kept in the dark during the trials to mimic the light environment onboard vessels. In five control cylinders, seawater is delivered directly from the pump. In five treated cylinders, the seawater first passes through the Venturi Oxygen Stripping™ system. Physical conditions such as oxygen, temperature, pH, and conductivity are monitored throughout the experiments with sensors sealed within the cylinders. Oxygen levels in the control cylinders are always above 8.0 mg/l whereas water in the treated cylinders enters and remains hypoxic (< 0.9 mg/l) throughout the experiments.

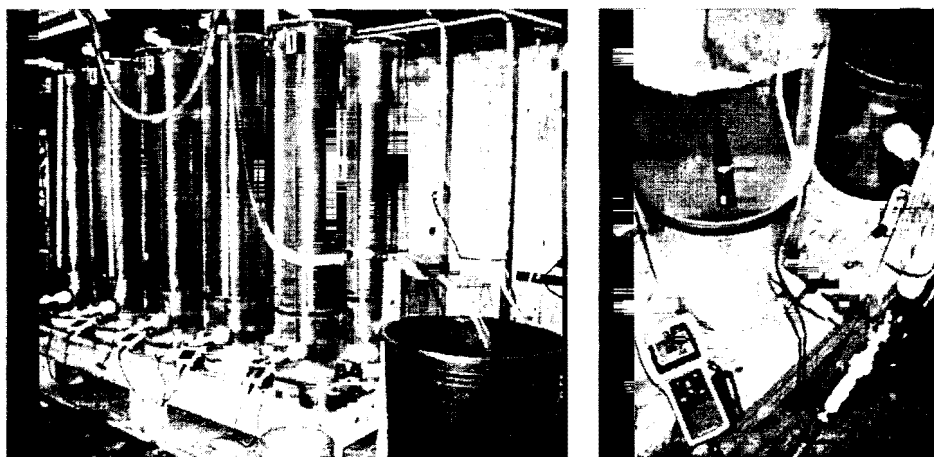


Figure 1. Mesocosm experimental setup to examine the effectiveness of Venturi Oxygen Stripping™ at killing natural planktonic organisms found in Chesapeake Bay.

To examine mortality over time as a result of deoxygenation, one treated and one control cylinder are drained completely through a bottom valve 1, 24, 48, 72, and 96 hours after filling. The treated and control cylinder at each sampling period are then compared for abundance or mortality of three separate planktonic community components. Zooplankton mortality is examined by sieving the entire volume through a 50 μm screen and determining total abundance and living versus dead individuals. The percentages of living individuals are quantified by examining reactivity or movement under a dissecting microscope. Relative abundances of phytoplankton are analyzed by determining chlorophyll-a concentrations using standard extractive fluorometry techniques. Subsamples are also examined under a compound microscope to identify major algae groups. Finally, the densities of bacterial cells in each cylinder are determined by flow cytometry.

Additionally, subsamples of abundant zooplankton (such as copepods and barnacle larvae) that are scored as dead after the 48-hour deoxygenation treatment are being placed in aerated natural seawater to determine their ability to recover and resume swimming after removal from hypoxic conditions. These entire dockside/mesocosm trials are being repeated five times during the seasons when planktonic organisms are most abundant (April through September 2003) in the Chesapeake Bay.

Rates and mechanism of corrosion under deoxygenated conditions – Laboratory experiments are underway to examine: A) how deoxygenation influences bulk water chemistry, biofilm formation and biofilm/metal interfacial chemistry, B) if microbiologically influenced corrosion occurs under deoxygenated conditions and if so by what mechanism, and C) the impact of O₂ on corrosion mechanisms and rates under deoxygenated conditions. The corrosion experiments are being conducted at the Naval Research Laboratory (NRL), Corrosion Facility in Key West and at NRL Stennis Space Center.

Five identical chambers were built to expose 1020 carbon steel (common ballast tank material) and natural seawater to different conditions (Figure 2). Three chambers are alternating immersion treatments where for two weeks the chambers are filled with water, then two weeks with gas, and this cycle is repeated for one year. The first chamber is alternating between raw, oxygenated seawater and air. The second chamber is alternating between natural seawater that is first deoxygenated by passing through the Venturi Oxygen Stripping™ system and air. The third chamber is alternating between deoxygenated water and inert gas containing only trace amounts of oxygen. The two remaining chambers are held stagnant for one year (no cycling). One was filled with raw, oxygenated seawater and is being left open to air while the other was filled with deoxygenated seawater and is being stored in an anaerobic hood. The experimental design is summarized in Table 2.

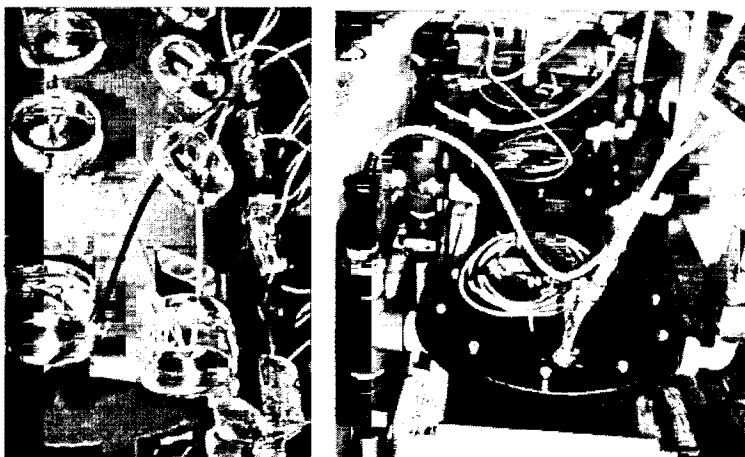


Figure 2. Experimental setup to examine rates and mechanism of corrosion under the deoxygenated conditions produced by the Venturi Oxygen Stripping™ system.

Samples are collected every month over one year to assess changes in dissolved and particulate water chemistry (dissolved oxygen, dissolved organic carbon and nitrogen, particulate organic carbon and nitrogen, bulk pH, sulfide concentration) using standard techniques. Serial dilutions are used to determine most probable numbers of APB, SRB, general heterotrophic aerobes, and anaerobes (Bioindustrial Technologies, Inc.).

The carbon steel coupons have been oriented in rows both horizontally and vertically in each chamber to simulate tank bottoms and sidewalls, respectively. Triplicate samples from both containers are removed every two months, fixed in glutaraldehyde and examined to assess the extent of biofilm formation and corrosion morphology. Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) are being used to characterize the corrosion morphology, biofilm structure and corrosion product composition on the metal surface. Swabs made of the coupon surface and serial dilutions are used to determine the microbial composition of the biofilm and microelectrodes are used to make O₂ profiles through the biofilms. Finally, polarization resistance and open-circuit potential is being used to monitor electrochemistry and corrosion of the carbon steel continuously over the one year experiment.

Table 2. Experimental design for the one year corrosion experiment being conducted at NRL facilities.

Chamber	Treatment	Cycle	Location
1	Alternating Immersion	Two weeks oxygenated water then two weeks air	Key West, FL
2	Alternating Immersion	Two weeks deoxygenated water then two weeks air	Key West, FL
3	Alternating Immersion	Two weeks deoxygenated water then two weeks inert gas	Key West, FL
4	Stagnant Immersion	Oxygenated water open to air no cycling	Stennis, MS
5	Stagnant Immersion	Deoxygenated water in anaerobic hood no cycling	Stennis, MS

Results:

Optimizing Deoxygenation – Evaluations of several approaches and a series of pilot studies have led to the conclusion that Venturi Oxygen Stripping™ represents the most effective and economical method of deoxygenation for use aboard vessels. Venturi Oxygen Stripping™ is a patent-pending rapid, in-line deoxygenation system that mixes inert gas directly into ballast water as it is drawn into the vessel. The inert gas is produced by combusting low-sulfur marine diesel (generating mostly nitrogen with small amounts of carbon dioxide and only trace levels of oxygen) in a device similar to the inert gas generators commonly used on tankers. The gas is mixed with the ballast water using a venturi injector that is installed in-line, just down-stream of the ballast pump. The venturi injector creates a micro-fine bubble emulsion where dissolved oxygen quickly diffuses out of the water into the gas. Because adding carbon dioxide in solution forms both carbonic and carboxylic acid, the pH of treated water is also reduced. This system is designed so that the same inert gas is also used to blanket all headspaces and the entire ballast tank when empty to maintain permanent hypoxia. Continuously maintaining a deoxygenated environment in ballast tanks appears to be a critical factor for corrosion prevention (see below).

Laboratory experiments performed under a variety of environmental conditions show that the time until low-oxygen equilibrium condition in the water is reached is less than 10 seconds. Treated water also reoxygenates within seconds after release from test tanks. Further design, development, and testing by NEI Treatment Systems has found that this ballast water treatment will be simple to install, operate, and maintain because several component parts are similar to equipment already commonly used onboard vessels. Finally, cost analysis show that the Venturi Oxygen Stripping™ system will be relatively inexpensive to install (\$100,000 - \$700,000 depending on vessel design) and operation (\$15,000 - \$50,000 / year). These values do not consider the significant decrease in ballast tank maintenance costs through corrosion prevention.

Survivorship of natural planktonic organisms subjected to deoxygenated water – Although the experiments on the ability of Venturi Oxygen Stripping™ to kill planktonic organisms are still ongoing, initial results are striking. The dissolved oxygen levels and pH in the control cylinders were between 8.18 – 11.01 mg/l and 7.61 – 8.20 respectively, whereas the dissolved oxygen levels and pH in the treated cylinders dropped to 0.26 – 0.87 mg/l and 5.46 – 5.62 respectively. In treated tanks, these changes to the

physical environment lead to a greater than 99% mortality of Chesapeake Bay zooplankton (copepods, barnacle larvae, polychaete larvae, cladocerans, crustacean nauplii, bivalve larvae, and nematodes) in less than 48 hours while the majority of zooplankton survived in the control cylinders (Figure 3). In addition to hypoxia and lowered pH, many of the larger zooplankton (mostly copepods) also appeared to be killed instantaneously by being damaged as they passed through the venturi injector which created large amounts of cavitation and turbulence (Figure 4). Furthermore, no intact individuals scored as dead after 48 hours recovered after being placed back in aerated water for 24 hours. Therefore zooplankton are not simply narcotized but are being effectively killed.

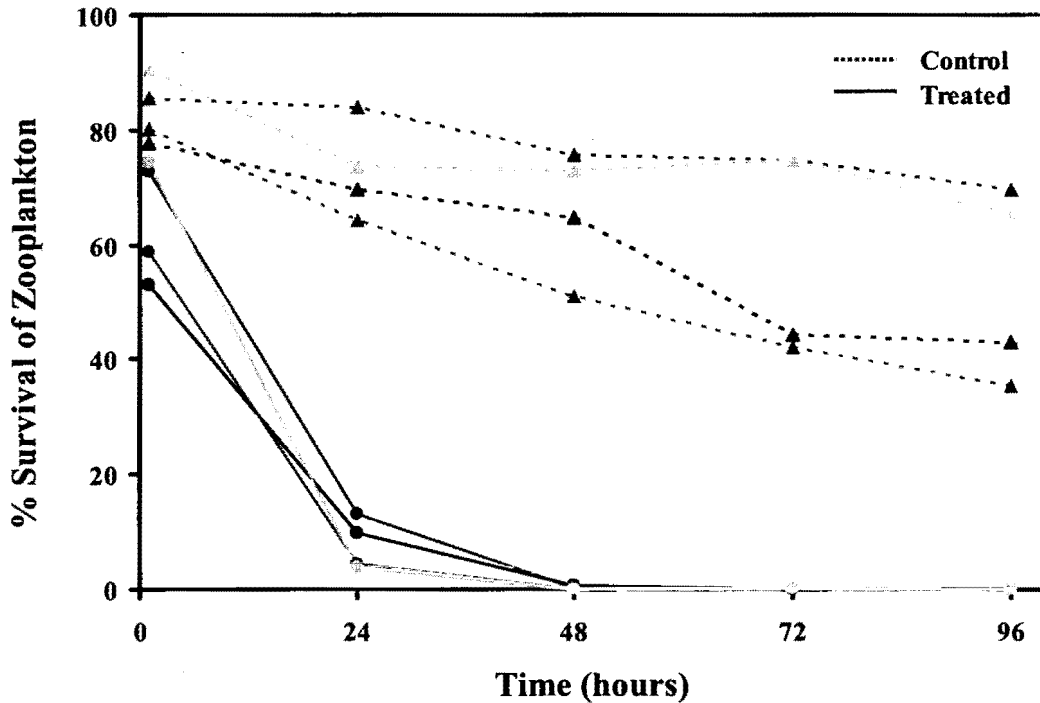
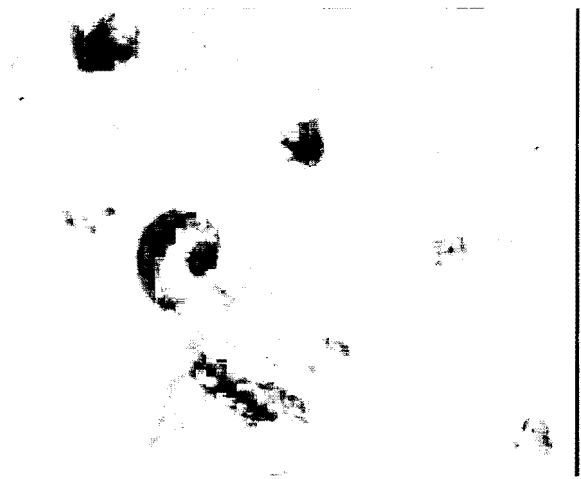


Figure 3. Percent survival of natural Chesapeake Bay zooplankton (copepods, barnacle larvae, polychaete larvae, cladocerans, crustacean nauplii, bivalve larvae, and nematodes) in control and treated (deoxygenated) chambers after 1, 24, 48, 72, and 96 hours for the first four replicate trials of an ongoing experiment.

Figure 4. A damaged copepod (lower middle) after passing through the Venturi Oxygen Stripping™ system. In all current trials examining the impacts of this treatment on zooplankton, the initial (after 1 hour) percent survival is 5 to 20 percent lower in treated versus control (see Figure 3) because of physical damage to larger individuals.



It also appears that the Venturi Oxygen Stripping™ system may reduce the abundance of phytoplankton (Figure 5). However, because large reductions in chlorophyll-a were also found in the control cylinders over time, impacts of deoxygenation on phytoplankton are difficult to discern at this point. Although additional experiments are being run, it is obvious that the abundances of algae are generally decreasing due to the darkened test conditions (which are meant to mimic ship ballast tank light levels) regardless of treatment.

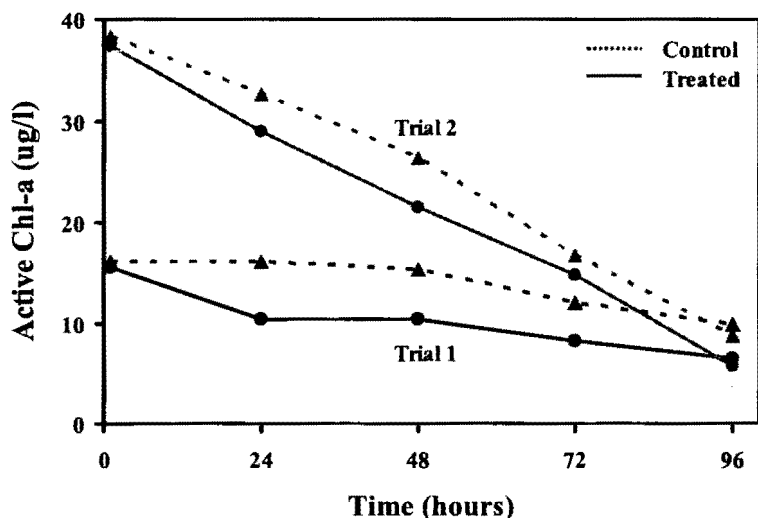


Figure 5. Active chlorophyll-a concentrations in control and treated (deoxygenated) chambers after 1, 24, 48, 72, and 96 hours for the first two trials of an ongoing experiment.

Finally, the deoxygenated environment and relatively high organic material available (dead plankton) after treatment with the Venturi Oxygen Stripping™ system does not appear to enhance bacterial growth or cause blooms. Initial measurements are showing no obvious difference in bacterial abundances in control versus treated through time (Figure 6).

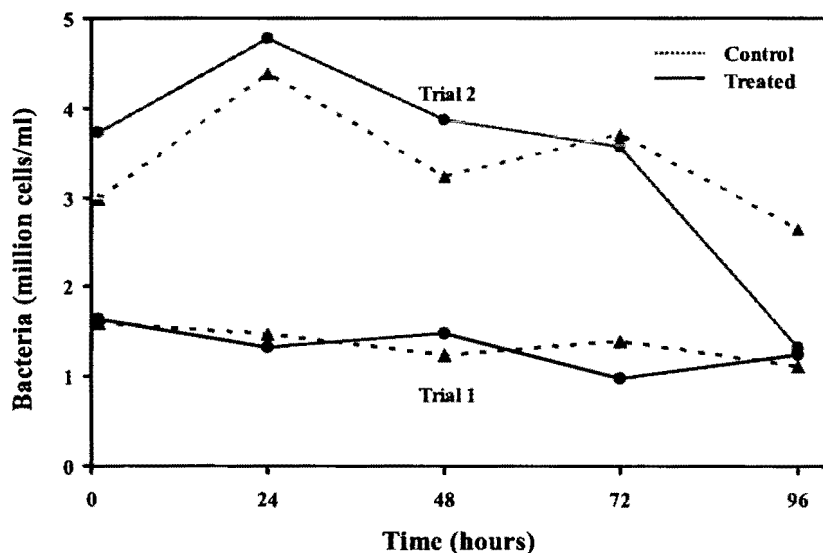


Figure 6. Abundance of bacterial cells in control and treated (deoxygenated) chambers after 1, 24, 48, 72, and 96 hours for the first two trials of an ongoing experiment.

Rates and mechanism of corrosion under deoxygenated conditions – Corrosion, biofilm formations, and changes to seawater chemistry as a result of deoxygenation are relatively slow processes. Therefore, conclusions can only be drawn after the year long study is completed. However, initial results from the IR compensated Linear Polarization Resistance analyses (only one of the many parameters being studied) suggested that instantaneous corrosion rates are significantly lower when the carbon steel in the alternating immersion trials are kept continuously in a hypoxic environment. In fact, alternating back and forth from water that is deoxygenated to air may enhance corrosion rates.

Conclusion:

Ballast water treatment technologies should be: 1) effective at killing potentially damaging invaders, 2) safe for shipboard crew, 3) environmentally benign, and 4) affordable for ship owners. As we have discussed above, deoxygenation through Venturi Oxygen Stripping™ is highly effective at killing animal invaders but may be less effective for other taxa. However, the number of individuals from resistant taxa that do survive this treatment may be below the threshold which poses a significant threat for the establishment of non-native populations (Williamson, 1996; Bailey et al., 2003; Drake et al., 2003). Furthermore, because most of the components of Venturi Oxygen Stripping™ system are already found onboard vessels and existing regulations require the measurement of ballast tank oxygen levels prior to entry, there are no major threats to crew safety. Deoxygenated water itself is also relatively benign when discharged. Treated water will reoxygenate and mix rapidly with receiving water in harbors (particularly if released above surface) and therefore create little danger for native estuarine organisms, which can withstand brief reductions in oxygen levels. However, if required, water can also be actively reoxygenated prior to release by simply adding an additional venturi injector connected to air on the outflow piping system. Finally, this ballast water treatment admirably meets the fourth criterion. Rather than an added expense for ship owners, it actually represents a net savings, due to the significant decrease in corrosion. To our knowledge, this is the only example of a ballast water treatment technique with economic incentives for the shipping industry.

An additional consideration when evaluating any ballast water treatment is how operational efficacy will be measured and how compliance with regulations will be monitored. Given the results of our work and the wealth of literature on the oxygen tolerance of aquatic organisms (Grieshaber et al. 1994, Diaz and Rosenberg 1995; Tamburri et al. 2002), determining efficacy and compliance with future regulations may simply entail continuous measurements of dissolved oxygen levels with perhaps only periodic biological sampling for validation.

Our fundamental goal is to provide the science necessary for the development of effective ballast water management strategies and policies. Through rigorous laboratory and dockside/mesocosm experiments, our work is providing the information required to evaluate the efficacy and feasibility of deoxygenation through Venturi Oxygen Stripping™ as a ballast water treatment to prevent aquatic invasions and will be the basis for a definitive shipboard study planned for the near future.

In summary, it appears that rapid and efficient reduction of oxygen levels in ballast water both causes substantial mortality of a large proportion of transported organisms and minimizes ballast tank corrosion. As such, it represents a rare example of a solution that simultaneously has benefits for marine conservation and industry.

References:

- Alanis, I., Berardo, L., De Cristofaro, N, Moina, C., and Valentini, C., 1986. In *Biologically Induced Corrosion*, 102, Houston, National Association Of Corrosion Engineers.
- Andersen, A. B., 2001. Ballast Water Treatment by Ozonation, presented at International Ballast Water Treatment R&D Symposium, IMO London, March 26-27.
- Bailey, S.A., I.C. Duggan, C.D.A. van Overdijk, P.T. Jenkins and H.J. MacIsaac. 2003. Viability of invertebrate diapausing eggs collected from residual ballast sediment. *Limnology and Oceanography*. 48:1701-1710.

- Bibb, M., 1986 In *Biologically Induced Corrosion*, 96, Houston, National Association Of Corrosion Engineers.
- Boyer, H. E. and Gall, T. L., 1985. *Metals Handbook*, American Society for Metals: Metals Park, OH.
- Carlton, J. T., and Geller, J. B., 1993. Ecological roulette: The global transport of nonindigenous marine organisms. *Science*, 261, 78-82.
- Cohen, A. N., and Carlton, J. T., 1998. Accelerating invasion rate in a highly invaded estuary. *Science*, 279, 555-558.
- Cooper, W. J., Dinnel, P. A., Gensemer, R. W., Herwig, R. P., Kopp, J. A., Ruiz, G. M., Sonnevil, G., Stubblefield, W. A., and VanderWende, E., 2002. Ozone, Seawater and Aquatic Nonindigenous Species: testing a full-scale ozone ballast water treatment system on an American Oil Tanker. 11th International Conference on Aquatic Invasive Species, Alexandria, VA.
- Dias, O. C., and Bromel, M. C., 1990. *Material Performance*, 29: 53.
- Diaz, R. J., and Rosenberg, R., 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioral responses of benthic macrofauna. *Oceanography and Marine Biology Annual Review*, 33, 245-303.
- Drake, J. M., Lodge, D. M., and Lewis, M., 2003. Combining allometric parameters of biological processes with recent progress in invasion theory: Implications for ballast water standards. 12th International Conference on Aquatic Invasive Species, Windsor, Ontario, Canada.
- Eashwar, M., Subramanian, G., Chandrasekaran, P., and Balakrishnan, K., 1990. In *Proc. Corrosion '90*, No. 120; Las Vegas, National Association Of Corrosion Engineers.
- Eidsa G. and Risberg, E., 1986. In *'Biologically Induced Corrosion'*, 109, Houston, National Association Of Corrosion Engineers.
- Fairplay, April 1993. Special Report: Paints and Coatings - Covering the Costs.
- Grieshaber, M. K., Hardewig, I., Kreutzer, U., and Poertner, H. O., 1994. Physiological and metabolic responses to hypoxia in invertebrates. In: Blaustein, M. P. (Ed.), *Reviews of Physiology Biochemistry and Pharmacology* 125. Springer-Verlag, New York, pp. 43-147.
- Hallegraef, G. M., 1998. Transport of toxic dinoflagellates via ships' ballast water: Bioeconomic risk assessment and efficacy of possible ballast water management strategies. *Marine Ecology Progress Series*, 168, 297-309.
- Hamilton, W. A. and Maxwell, S., 1986. Biological and Corrosion Activities of Sulphate-Reducing Bacteria within Natural Biofilms. *Biologically Induced Corrosion*, Dexter, S. C. ed., National Association of Corrosion Engineers: Houston, TX, pp. 131- 136.
- Honeysett, D. G., Van Den Bergh, W. D. and O'brien, P. F., 1985. *Material Performance*, 24: 34.
- Hardy, J. A. and Bown, J. L., 1984. The Corrosion of Mild Steel by Biogenic Sulfide Films Exposed to Air. *Corrosion*, 40, 650-654.
- Hoback, W. W., and Barnhart, M. C., 1996. Lethal limits and sublethal effects of hypoxia on the amphipod *Gammarus pseudolimnaeus*. *Journal of the North American Benthological Society*, 15, 117-126.
- Iverson, W. P., 1974. *Microbial Iron Metabolism*, New York, Academic Press.
- Kasahara, K. and Kajiyama, F., 1986. In *Biologically Induced Corrosion*, 171, Houston, National Association Of Corrosion Engineers.
- King, R. A., Skerry, B. S., Moore, D. C. A., Stott, J. F. D. and Dawson, J. L., 1986. In *Biologically Induced Corrosion*, 83, Houston, National Association Of Corrosion Engineers.
- Lee, W. C., Lewandowski, Z., Okabe, S., Characklis, W. G., and Avci, R., 1993. Corrosion of Mild Steel Underneath Aerobic Biofilms containing Sulfate-Reducing Bacteria Part I: At Low Dissolved Oxygen Concentration. *Biofouling* 7, 197-216.
- Lee, W. C., Lewandowski, Z., Morrison, M., Characklis, W. G., Avci, R., and Nielsen, P. H., 1993. Corrosion of Mild Steel Underneath Aerobic Biofilms containing Sulfate-Reducing Bacteria Part I: At High Dissolved Oxygen Concentration, *Biofouling* 7, 217-239.
- Licina, G. C., 1988. *Sourcebook For Microbiologically Influenced Corrosion In Nuclear Power Plants*, Palo Alto, Electric Power Research Institute.

- Lutey, W. L. 2001. Treatment for the Mitigation of MIC, In A Practical Manual on Microbiologically Influenced Corrosion, Vol. 2, NACE Press.
- Lutz, R. V., Marcus, N. H., and Chanton, J. P., 1994. Hatching and viability of copepod eggs at two stages of embryological development: anoxic/hypoxic effect. *Marine Biology*, 119, 199-204.
- Marine Engineering Review, January 1991. Life Corrodes Away.
- Matsuda, M., Kobayashi, S., Miyuki, H., and Yoshida, S., 1999. An anticorrosion method for ballast tanks using nitrogen gas. Ship and Ocean Foundation Technical Report.
- McCracken, W., 2001. Ballast Water Treatment with Available Biocides, presented at International Ballast Water Treatment R&D Symposium, IMO London, March 26-27.
- Miller, J. D. A. and Tiller, A. K., 1970. In *Microbial Aspects Of Metallurgy*, 61, New York, Elsevier.
- Mountfort, D. O., Hay, C., Dodgshun, T., Buchanan, S., and Gibbs, W., 1999. Oxygen deprivation as a treatment for ships' ballast water: laboratory studies and evaluation. *Journal of Marine Environmental Engineering*, 5 (3).
- Muusze, B., Marcon, J., Van Den Thillart, G., and Almeida-Val, V., 1998. Hypoxia tolerance of Amazon fish: respirometry and energy metabolism of the cichlid *Astronotus ocellatus*. *Comparative Biochemistry and Physiology A*, 120, 151-156.
- National Research Council, 1996. Stemming the tide: controlling introductions of nonindigenous species by ship's ballast water. National Academy Press, Washington, D.C.
- Pacheco, A., Dishinger, T. D. and Tomlin, J. L., 1987. In Proc. Corrosion '87, No. 376, San Francisco, National Association Of Corrosion Engineers.
- Padgett, D. E., Celio, D. A., Hearth, J. H., and Hackney, C. T., 1989. Growth of filamentous fungi in a surface-sealed woody substratum buried in salt-marsh sediments. *Estuaries*, 12, 142-144.
- Pope, D. H., 1986. A Study Of MIC In Nuclear Power Plants And A Practical Guide For Countermeasures, Final Report Np-4582, Palo Alto, Ca, Electric Power Research Institute.
- Pope, D. H., 1987. Microbial Corrosion In Fossil-Fired Power Plants - A Study Of Microbiologically Influenced Corrosion And A Practical Guide For Its Treatment And Prevention, Palo Alto, Electric Power Research Institute.
- Pope, D. H. and Morris, E. A., 1995. Some Experiences with Microbiologically Influences Corrosion of Pipelines. *Materials Performance*, 34, 23-28.
- Pope, D. H., Zintel, T. P., Kuruvilla, A. K. and Siebert, O. W., 1988. In Proc. Corrosion 88, No. 79, St. Louis, Mo, National Association Of Corrosion Engineers.
- Pope, D. H. and Pope, R. M., 2001. Microbiologically Influenced Corrosion in Fire Protection Sprinkler Systems; By; A Practical Manual on Microbiologically Influenced Corrosion, Vol. 2, NACE Press.
- Postgate, J. R., 1979. *The Sulphate Reducing Bacteria*, Cambridge, England, Cambridge University Press.
- Roman, M. R., Gauzens, A. L., Rhinehart, W. K., and White, J. R., 1993. Effects of low oxygen waters on Chesapeake Bay zooplankton. *Limnology and Oceanography*, 38, 1603-1614.
- Sanders, P. F. and Hamilton, W. A., 1986. In *Biologically Induced Corrosion*, 47, Houston, National Association Of Corrosion Engineers.
- Smith, L. D., Wonham, M. J., McCann, L. D., Ruiz, G. M., Hines, A. H., and Carlton, J. T., 1999. Invasion pressure to a ballast-flooded estuary and an assessment of inoculant survival. *Biological Invasions*, 1, 67-87.
- Stalder, L. C., and Marcus, N. H., 1997. Zooplankton responses to hypoxia: behavioral patterns and survival of three species of calanoid copepods. *Marine Biology*, 127, 599-607.
- Tallqvist, M., Sandberg-Kilpi, E., and Bonsdorff, E., 1999. Juvenile flounder, *Platichthys flesus* (L.), under hypoxia: effects on tolerance, ventilation rate and predation efficiency. *Journal of Experimental Marine Biology and Ecology*, 242, 75-93.
- Tamburri, M.N., Wasson, K., and Matsuda, M., 2002. Ballast water deoxygenation can prevent aquatic introductions while reducing ship corrosion. *Biological Conservation*, 103, 331-341.
- Tatnall, R., Piluso, A., Stoecker, J., Schultz, R. and Kobrin, G., 1981. *Material Performance*, 19: 41.

- van den Thillart, G., George, R. Y., and Stromberg, J. O., 1999. Hypoxia sensitivity and respiration of the euphausiid crustacean *Meganyctiphanes norvegica* from Gullmarn Fjord, Sweden. *Sarsia*, 84, 105-109.
- Vargo, S. L., and Sastry, A. N., 1977. Acute temperature and low dissolved oxygen tolerances of brachyuran crab (*Cancer irroratus*) larvae. *Marine Biology*, 40, 165-171.
- Vistisen, B., and Vismann, B., 1997. Tolerance to low oxygen and sulfide in *Amphiura filiformis* and *Ophiura albida* (Echinodermata: Ophiuroidea). *Marine Biology*, 128, 241-246.
- Widdows, J., Newell, R. I. E., and Mann, R., 1989. Effects of hypoxia and anoxia on survival, energy metabolism, and feeding of oyster larvae (*Crassostrea virginica*, Gmelin). *Biological Bulletin*, 177, 154-166.
- Williamson, M., 1996. *Biological Invasions*. Chapman and Hall, London.
- Winters, M. A. and Badelek, P. S. C., 1987. In *Proc. Corrosion 87*, No. 156, San Francisco, National Association Of Corrosion Engineers.

Acknowledgements:

We would like to thank K. Wasson, M. Matsuda, M. Bednarski, and K. McPherson, for their help with various aspects of this work. The National Oceanic and Atmospheric Administration is funding our current investigations. Other supporters of our work include Alaska Tanker Company, Polar Tankers, Inc. (ConocoPhillips), Southern California Marine Institute/Port of Los Angeles, and NEI Treatment Systems, Inc.