Critical Review of a Ballast Water Biocides Treatment Demonstration Project Using Copper and Sodium Hypochlorite

(A Science Report to Governor John Engler)

Prepared by
Michigan Environmental Science Board
Ballast Water Biocides Investigation Panel

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PREFACE

Michigan Environmental Science Board

The Michigan Environmental Science Board (MESB) was created by Governor John Engler by Executive Order 1992-19 on August 6, 1992. The MESB is charged with advising the Governor, the Natural Resources Commission, the Michigan Department of Natural Resources and other state agencies, as directed by the Governor, on matters affecting the protection and management of Michigan's environment and natural resources. The MESB consists of nine members and an executive director, appointed by the Governor, who have expertise in one or more of the following areas: engineering, ecological sciences, economics, chemistry, physics, biological sciences, human medicine, statistics, risk assessment, geology, and other disciplines as necessary. Upon the request of the Governor to review a particular issue, a panel, consisting of MESB members with relevant expertise, is convened to evaluate and provide recommendations on the issue. The MESB is neither a state policy body nor an advocate for or against any particular environmental or public health concern.

Major Findings and Conclusions

Over 160 nonindigenous aquatic nuisance species (ANS) of plants and animals have been introduced into the Great Lakes Basin since the 1800s. Of these, more than one-third of the known Great Lakes ANS have been introduced in the last half of the 20th Century, with the greatest number of the introductions coinciding with the expansion of the St. Lawrence Seaway in 1959. Seventy percent of the ANS discovered since 1985 in the Great Lakes are native to fresh and brackish waters of the Ponto-Caspian region (Black, Caspian and Azov Seas) in Eurasia. The introduction of ANS has played a major role in modifying aquatic ecosystems within the Great Lakes Basin. The primary route of ANS entry into the Great Lakes has been through ballast water exchange from ocean-going ships. Although federal law mandates open water exchange to help reduce the risk of ANS found in ballast tanks and sediments, it does not ensure protection of the Great Lakes since many older and larger vessels cannot safely execute open water exchange and it does not address ballast water exchange that takes place on ships between Great Lakes ports.

In May 2001, the Michigan Department of Environmental Quality (MDEQ) issued a request for proposals for shipboard testing of two ballast water tank biocides, hypochlorite and copper ion, to determine their effectiveness against ANS. Fleet Technology Ltd. of Kanata, Ontario and ESG International of Guelph, Ontario was selected as the prime and subcontractors, respectively. The final draft report of the demonstration project (Study), entitled *Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides* was completed in April 2002. On April 10, 2002, Governor John Engler requested that the Michigan Environmental Science Board (MESB) review the final draft Study and evaluate the scientific validity of the conclusions reached regarding the efficacy of the two biocides evaluated; corrosivity to ballast tanks resulting from the two biocides; and discharge concentrations for each biocide needed to meet regulatory standards. Major findings and conclusions of the MESB are summarized below.

♦ **Copper Ion Biocide.** Copper as an ion (e.g., Cu^{2+}) is a naturally occurring chemical in the environment and necessary for various metabolic processes. At high concentrations, copper is toxic and is used to control algae and bacteria in swimming pools and lakes. Because of its toxic effects on biota such as fish, copper discharge to surface water is of concern. If a copper biocide treatment is used for ballast discharge, then this discharge water would most likely need to be regulated. The Study's test results demonstrated that the copper ion biocide was only 33 percent effective at 167 parts per billion (ppb) in freshwater and 70 percent effective at 68 ppb in reducing bacteria in freshwater and simulated seawater experiments, respectively. These results suggest that at the concentrations tested, copper treatment was not effective. In order to be effective, even higher concentrations of copper would be needed, which would result in the further exceedance of the range of theoretical allowable discharge concentration levels (2 ppb to 48 ppb) determined by the Study for the Great Lakes jurisdictions.

In addition to potential limits on copper concentrations that could be used, the efficacy of copper in killing biota ballast water is influenced by the natural geochemical behavior of copper in the environment. For example, copper is a particle reactive chemical. This means that it will tend to be adsorbed to sediments, whether suspended or settled. Consequently, the presence of sediment in the ballast tank would reduce the efficacy of copper as a biocide and higher concentrations of copper would need to be used compared to water in the absence of the sediment. This issue was not addressed in the Study.

The behavior and toxic effects of copper in water also are altered by natural processes, such as the formation of ion pairs in solution. In solution solutes, copper (Cu^{2+}) can bond with other solutes, such as bicarbonate (HCO_3^-), to form new dissolve chemical species known as an ion pair or complex. The formation of this ion pair decreases the toxicity of a copper. Since copper in solution is particularly influenced by the presence of dissolved organic matter, bicarbonate, and carbonate in water, changes in the relative abundances in these solutes might necessitate different amounts of copper concentrations needed as a biocide. This point is important to consider when interpreting the results of the Study's simulated seawater experiments since, if the simulated solution did not contain proper amounts of solutes, such as sulfate and bicarbonate, the experimental results observed in the Study might not represent the true behavior of copper.

Copper ion concentrations in water of 0.02 to 0.05 ppm can cause severe corrosion of aluminum. For this reason, discharge of copper ion treated water from ballast tanks could cause significant corrosion of nearby aluminum-hulled boats and aluminum structures. It would be important to evaluate this issue further prior to proceeding with any additional consideration of copper ion as a ballast water biocide.

In summary, the Study's toxicity data, as a whole, suggest that in sufficiently high concentrations, copper ion could be an effective biocide. However, at the concentrations needed to achieve the desired effectiveness, the level would be far too high to be discharged into the Great Lakes. Given this, and in the absence of any known neutralizing agent that would allow copper to be safely discharged into the Great Lakes, the MESB Panel concludes that copper ion cannot be considered to be a viable ballast water biocide alternative at this time.

♦ **Sodium Hypochlorite Biocide.** The Study's conclusions regarding the effectiveness of sodium hypochlorite as a viable ballast water biocide alternative from the shipboard and laboratory toxicity tests are limited and can only be considered preliminary at best. However, despite the problems outlined in this critique regarding the testing protocols used, the MESB Panel suggests that the use of sodium hypochlorite as a ballast water biocide can have a high degree of efficacy when treating the majority of organisms that were tested in the Study, assuming sufficient active hypochlorite concentration can be attained to account for sediment loads from both suspended and deposited material. Considerable more work will need to be conducted before any definitive statement regarding its efficacy within an actual ballast water tank environment can be made. In particular, well planned and controlled toxicity tests need to be conducted that will evaluate the biocide's effectiveness on both benthic and resting stages of ANS in the presence of both suspended and bottom sediment similar to that found in ballast water tanks. Also, a mechanism needs to be developed and a careful analysis needs to be conducted that will determine how much chlorine remains available over time in the ballast tank in order to: (1) ensure the presence of an effective concentration of the biocide at the time when it is needed, and (2) allow for a determination to be made as to how much neutralizing compound would be needed for dechlorination prior to ballast water discharge.

♦ **Biocide Discharge Concentrations.** There exists no state or federal permitting requirements specifically for ballast water discharges and ballast water discharges are exempted from point-source discharge regulations. However, discharges of ballast water treated with sodium hypochlorite still would need to be of such quality so as to protect the designated uses of receiving waters. While the Study did attempt to address the issue of discharge of treated ballast water, the MESB Panel concludes that insufficient information (too few tests and lack of data as to what requirements would need to be met throughout the Great Lakes jurisdictions), was provided to definitively address the question regarding if such discharges could be safely and legally discharged into Great Lakes waters. Additional studies involving the use of actual ballast water treated with the biocide and a clear indication as to what would be required by the various U.S. and Canadian Great Lakes jurisdictions in order to meet Great Lakes water quality standards would be useful.

The MESB Panel also concludes that biocide treatment in the absence of some other mechanism to address ballast water sediment, such as filtration, will result in an incomplete elimination of ANS. Future studies will need to address this problem by investigating the efficacy and the practicality of shipboard use of combined treatment methodologies.

♦ **Biocide Corrosivity.** The biocide corrosion tests that were conducted in the Study were of too short a duration to allow prediction of long-term corrosion rates or coating degradation rates. Corrosion is not always constant over time, and, unless the time-dependence of corrosion rate is known, it is not possible to extrapolate data from short-term tests to predict long-term performance. In particular, coating degradation typically has an incubation time when the corrosive constituents are diffusing through the coating to the base metal underneath. For ballast water tank coatings, this incubation time can be many months. In addition, the tests should have used natural seawater and should have included cathodic protection for some of the exposures to better simulate the actual ballast water tank environment.

The hypochlorous acid that is proposed as a biocide is an oxidant and can increase the corrosion of steel in water if present in quantities similar to the other oxidant in seawater, dissolved oxygen. The effect may become noticeable at concentrations of 1 part per million (ppm) or more if the kinetics of the reactions is favorable. Just as important, this oxidant may negatively affect the performance of paint systems on steel. Therefore, a new corrosion test would need to be conducted to determine the magnitude of these effects.

Based on the information presented in the Study, the MESB is unable to reach definitive conclusions regarding the nature and extent of detrimental corrosion effects of either biocide on ballast tank structural integrity. Additional, better designed and longer duration tests will be needed to more fully evaluate this concern.

Critical Review of a

Ballast Water Biocide Treatment Demonstration Project

Using Copper and Sodium Hypochlorite

(A Science Report to Governor John Engler)

Introduction

Over 160 nonindigenous aquatic nuisance species (ANS) of plants and animals have been introduced into the Great Lakes Basin since the 1800s. Of these, more than one-third of the known Great Lakes ANS have been introduced in the last half of the 20th Century, with the greatest number of the introductions coinciding with the expansion of the St. Lawrence Seaway in 1959 (Ricciardi, 2001; Mills *et al.*, 1993). According to Ricciardi and MacIsaac (2000), 70 percent of the ANS discovered since 1985 in the Great Lakes are native to fresh and brackish waters of the Ponto-Caspian region (Black, Caspian and Azov Seas) in Eurasia.

The introduction of ANS, such as the sea lamprey (*Petromyzon marinus*), zebra mussel (*Dreissena polymorpha*), European ruffe (*Gymnocephalus cernuus*), tubenose goby (*Proterorhinus marmoratus*), round goby (*Neogobius melanostomus*), spiny water-flea (*Bythotrephes cederstroemi*), curly leaf pondweed (*Potamogeton crispus*), and Eurasian water milfoil (*Myriophyllus spicatum*), has played a major role in modifying aquatic ecosystems within the Great Lakes Basin (Ricciardi, Neves, and Rasmussen, 1998; MacIsaac, 1996; Mills *et al.,* 1993; Keast, 1984; Coffey and McNabb, 1974). Freed from natural competitors, predators, parasites, pathogens, and other factors that regulate the ANS populations in their native environments, ANS can grow at or near their potential exponential growth rate and out-compete the native species for food and/or habitat (Mack *et al.,* 2000). Consequently, many of the ANS have severely disrupted Great Lakes native plant and animal species populations and ecosystem functions (Mack *et al.*, 2000; Lubomudrov, Moll and Parsons, 1997; Allan and Flecker, 1993).

The primary route of ANS entry into the Great Lakes has been through ballast water exchange from ocean-going ships (Parsons and Harkins, 2000; Mills *et al*., 1993). A ballasted ocean freighter entering the Great Lakes typically carries three million liters of ballast water, which is discharged before taking on cargo. According to Locke *et al.* (1993), approximately 800 million liters of ballast water are released into the system every year. Pursuant to the federal Nonindigenous Aquatic Nuisance Prevention and Control Act of 1990, as amended (NANPCA, 1990), some ships are now required to exchange their ballast water at sea, flushing out organisms and raising the salinity of the ballast water to kill freshwater organisms that might remain alive in the ballast tank. Although open water exchange helps reduce the risk of ANS found in ballast tanks and sediments, it does not ensure protection of the Great Lakes since for many older and larger vessels, open water exchange may not be feasible or safely executed (Designers & Planners, Inc and Herbert Engineering Corp., 1998; Ryle, 1995). In addition, current federal regulations apply only to those vessels that claim to be carrying ballast on board (BOB). Vessels that enter with no ballast on board (NOBOB) are exempt from the regulations. NOBOB ships can still contain substantial amounts of unpumpable water and sediment in their ballast tanks and, therefore, harbor adult organisms, dinonflagellate cysts, and diatom resting spores. Consequently, other control methods such as filtration, heat, ultraviolet light, and a variety of different types of biocides treatments also are being studied in an effort to find an effective method or combination of methods to control ANS (Oemcke, 1999; Lubomudrov, Moll and Parsons, 1997; Lloyd's Register Engineering Services, 1995; Laughton, Moran and Brown, 1992).

In April 2000, the Michigan Department of Environmental Quality (MDEQ) convened a workgroup of technical experts from international and domestic shipping industries, and the U.S. Coast Guard to examine potential ballast water treatments including technologies, management practices, and biocides. The Ballast Water Working Group (BWWG) focused on what was currently available and practical, and what could be put into use as an interim measure while other related research continued. The BWWG concluded that the only currently available methods for dealing with the problem were management practices and biocides. The BWWG defined a *currently available method* as: (1) not needing extensive research to establish the efficacy of the biocide, (2) not needing extensive ship retrofitting, and (3) not requiring any shore-side facilities.

In May 2000, the BWWG concluded that: (1) management practices and biocides are the only two methods currently available to minimize the introduction of ANS, (2) hypochlorite and glutaraldehyde are potentially currently available ballast water biocides, and (3) shipboard field-testing of the biocides should be carried out as soon as possible. In February 2001, the BWWG recommended that a third biocide, copper ion, be added to the list of potential biocides. In May 2001, the MDEQ issued a request for proposals for shipboard biocide testing of hypochlorite and copper ion (a test of glutaraldehyde was proceeding under a separate grant). FedNav, a major transoceanic shipping company plying the Great Lakes, agreed to provide a ship (*Federal Yukon*) for the experimental work. Fleet Technology Ltd. of Kanata, Ontario, was selected as the prime contractor. The subcontractor was ESG International of Guelph, Ontario. The final draft report of the demonstration project (Study), entitled *Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides* (BMT Fleet Technology, Ltd. and ESG International, Inc. 2002, see Appendix 1), was completed in April 2002.

Charge to the Michigan Environmental Science Board

On April 10, 2002, Governor Engler (Engler, 2002) requested that the Michigan Environmental Science Board (MESB) review the final draft Study and evaluate the scientific validity of the conclusions reached regarding the:

1. Efficacy of the two biocides evaluated;
2. Corrosivity to ballast tanks resulting from the two biocides; and
3. Discharge concentrations for each biocide needed to meet regulatory standards (see Appendix 2).

On April 14, 2002, a Ballast Water Biocides Investigation Panel (Panel), composed of four MESB members and five guest scientists, was formed to begin the investigation. The investigation consisted of an initial independent review of the Study by the Panel members and a meeting (May 29, 2002) of the Panel, at which testimony and Study's supportive documentation were presented and discussed (Harrison, 2002).

Overview of the Biocides Study

The Study was comprised of three parts: (1) a shipboard demonstration on board the *Federal Yukon*, (2) toxicology testing in a biological laboratory, and (3) corrosion testing in the materials laboratory (see Attachment 1).

Shipboard Toxicity Tests. The purpose of the field demonstration portion of the Study was to examine the shipboard application of the two biocides and assess the efficacy of treatment on a single typical voyage, and to further determine whether the application of biocides adversely affects the real-life operations of the ship. The Study was not allowed to interfere with the commercial operations of the ship and certain on-site modifications to the experimental plan were necessary to accommodate the local biological conditions and engineering difficulties encountered. The tests were conducted on the deck of the ship using 55-gallon plastic barrels as test chambers. Additionally, a deck-mounted decant tank (a metal tank typically reserved for capturing cargo wash water prior to discharge) was modified and coated with paint used in the ballast tanks for additional hypochlorite tests.

A typical voyage profile for a ship on international trade into the Great Lakes consists of loading cargo overseas and transiting the ocean as a NOBOB. On arrival at a Great Lakes port, the ship discharges its cargo and takes on ballast to transit to a second Great Lakes port. Here, the ship will discharge that ballast and take on an out-bound cargo. The shipboard demonstration was conducted during one such typical international voyage to four ports:

- Coastal Port #1 (ocean saltwater port): Cargo was offloaded and ballast water taken on.
- Coastal Port #2 (ocean saltwater port): Cargo was taken on and ballast water discharged, creating a NOBOB condition.
- Great Lakes Port #1 (Great Lakes freshwater port): Cargo was off-loaded and ballast water taken on.
- Great Lakes Port #2 (Great Lakes freshwater port): Cargo was taken on and ballast water discharged.

Laboratory Toxicity Tests. The purpose of the laboratory toxicity testing portion of the Study was to quantify the efficacy of the biocides as it relates to the treatment of organisms in ballast water. The toxicity testing was conducted on freshwater and saltwater fish, invertebrates, algae, and bacteria. In addition, the toxicity of the biocides to selected ANS resting stages was evaluated. In certain instances, the toxicity of the biocides was tested in both laboratory and ballast water collected from the ship. A limited number of tests were conducted with and without the presence of clean control sediment for characterizing the effect of sediment on biocide efficacy.

Laboratory Corrosion Tests. The purpose of the laboratory corrosion testing portion of the Study was to examine the possible detrimental effects that the addition of biocide to ballast water may have on the structural integrity of the vessel. The effects of biocide-treated water on coating systems and base metals typically used in the construction of ships ballast tanks were investigated in a specially adapted corrosion tank. The different conditions of metal exposure within a ballast tank to ballast water (e.g., fully submerged, a splash zone or area of periodic immersion, and damp spaces) were simulated along with a "buried" experiment to show the effects on structure covered with sediment. The experiment used an accelerated corrosion testing concept to compare the effects of adding biocide to both fresh and saltwater. Corrosion tests were conducted on bare metal coupons, metal coupons coated with typical marine coating systems, and coated metal coupons that were scribed through the paint thickness to examine the effects of coating damage.

Summary of Study Conclusions. Two shipboard ballast water biocide treatment trials conducted during a typical saltwater and freshwater voyage indicate that sodium hypochlorite (dosed to a residual of approximately 10 parts per million - ppm) significantly reduced (>90%) ambient zooplankton and bacteria levels relative to the controls after a two-hour treatment. In freshwater trials, copper ion treatment (<0.2 ppm) was capable of reducing ambient zooplankton levels greater than 30 percent relative to the control. For both biocides applied at these levels, numerous organisms were capable of surviving treatment in settled sediments.

Laboratory biocide toxicity tests conducted on freshwater and saltwater fish, invertebrates, algae, and bacteria, in test conditions that simulate those in a ballast tank showed that sodium hypochlorite was effective (i.e., achieved LC_{99} – the lethal concentration of substance that results in 99% mortality in a population) with the majority of species tested at less than a total residual chlorine of 10 ppm. Higher sodium hypochlorite levels were required to kill encysted life stages. The LC_{99} and EC_{99} (the effective concentration of a substance that results in 99% growth reduction, hatchability, or mortality in a population) values of the majority of species tested were at total copper levels below 200 ppm. The encysted life stages of certain test organisms were not killed at higher total copper levels. The presence of high levels of sediment negatively impacted the efficacy of both biocides.

Accelerated (short-term) corrosion tests conducted on bare, coated, and scribed metal coupons under a variety of conditions (e.g., fully submerged, periodic immersion, damp spaces, and buried in simulated sediment) in saltwater and freshwater suggests that coupons exposed to sodium hypochlorite tend to experience slightly more corrosion and paint damage than the control samples; however, the effect is not quantifiable in terms of metal life expectancy from the analysis. No failures were observed in any unscribed coating system due to the presence of sodium hypochlorite. Short-term corrosion tests in solutions containing copper suggest that in the aggressive corrosion environment of salt water and periodic immersion, there is a slight increase in corrosion, but there were no increases in coating failures.

Michigan Environmental Science Board Critique

The following MESB critique addresses concerns regarding the general experimental protocols used and conclusions reached in the Study. The critique focuses on sodium hypochlorite, although most of the methodological and interpretation concerns also apply to copper ion.

Shipboard Toxicology Testing Protocol. In general, the MESB Panel found that the shipboard experimental design was not clear and was further complicated by the following issues:

1. The distribution of treatments among container types was unbalanced within and between biocide and water types, with a lack of replication for some containers;

2. The source and chemical make-up of sediments used was different between freshwater and seawater trials. This difference confounds the ability to ascribe differences in efficacy between the source waters to differential activities of the chemicals alone;

3. The source of water was different between treatments, controls, and water sources. Some containers were filled through fire mains, thus bypassing ballast tanks, while others were filled from ballast tanks. This difference confounds the ability to ascribe differences solely to the presence of the biocide, or to compare among combinations of biocides and water types (fresh or salt);

4. Physical conditions, as indicated by the amounts of suspended material present, were different between decant tanks and 55-gallon barrels;

5. The methods for dosing hypochlorite to the decant tanks and 55-gallon barrels were not provided but were evidently different from that used to dose the copper ion. The former two types of containers were dosed after they were filled with water while the latter were dosed during filling of ballast tanks; and

6. There is confusion regarding where the efficacy tests were conducted (e.g., in the decant tanks and 55-gallon barrels, or in 20-liter buckets using dosed water drawn from the tanks/barrels and organisms collected from the intake water/plankton tows).

In addition to the problems with the experimental design, many of the specifics for the methods used in the shipboard tests were missing, including such critical items as methods of collection and addition of organisms to test chambers, number of samples per container, procedures for handling samples, and methods for calculating and comparing data.

Sediment chlorine demand was found to be a major issue that had to be adjusted for to provide appropriate target loads. The method for adjusting for the chlorine demand of the suspended sediment was not provided. The amount of sediment added to the test tanks was one percent on a volume-to-volume basis. The justification for the amount and the type of sediments used in the test should have been included in the Study based on the range of sediment quantity and type expected.

The quantitative toxicology for the shipboard tests focused solely on pelagic organisms, while the data for the benthic organisms were circumstantial. It was clear from the Study that an effective dose would need to have been larger than the 10 ppm employed in the Study based on the presence of cysts and live benthic organisms found in the sediment. Recent work at the Great Lakes Environmental Research Laboratory (Landrum, 2002) indicates that concentrations in excess of 1,000 ppm would be required to be effective for sediment dwelling organisms in order to account for the chlorine demand of the sediment.

Additional organisms from the local area had to be added to the shipboard test tanks to ensure that there were sufficient numbers to detect a response. There was nothing in the Study protocols to indicate how this was done. In addition, there was no testing of the health of the collected organisms to allow for comparison to the laboratory data. The tests were only performed with pelagic organisms and the exposures were done with a sub-sample of the water of unknown volume. It was not clear if the number of organisms at the end of the exposure was compared relative to controls or relative to t=0 for each tank. The Study indicated that the 55-gallon barrels from the copper ion test served as controls for the hypochlorite test; however, it was not clear whether these were performed at the same time using the same ballast water. Additional detail in the protocols regarding this issue could not be found in the Study. The protocols suggest that there would be an n of 4 for treatments and n of 2 for controls except for the decant tank, but the number of replicates and the data for both treatment and control tanks were not provided.

The Study provides data suggesting 90 to 96 percent declines in the zooplankton on exposure to hypochlorite, but the method for determining these values was not provided. Because of the absence of the supporting information, it is not possible to be certain about the validity of these values. There was an indication in the Study that significant numbers of organisms could not be recovered at the end of the trials. It was not clear, however, if this was just for the treatments or also for the controls.

The temperature of the shipboard tests varied from 12 to 20 degrees centigrade (^oC), but the laboratory tests were performed at 15^oC. The impact of the temperature on the toxicity testing was not evaluated. Changes in temperature will affect both the degradation of the hypochlorite and the response of the organisms to the toxicant. While this does not affect the shipboard test results directly, it does make the setting of a toxicant dose from laboratory data problematic.

Finally, the conditions that existed the Study's decant tanks and 55-gallon barrels cannot be considered identical to what would be expected to exist in the ballast tanks, and the dosing procedures used in the Study for hypochlorite and copper ion biocides cannot be considered as being what would be needed for actual ballast tank disinfection. Given the inability of the Study to duplicate ballast tank structure and the complications of mixing in an actual ballast tank environment, the biocide exposures observed in the Study cannot be considered to be necessarily representative of what would be expected to take place in the ballast tank environment.

Laboratory Toxicology Testing Protocol. The Study's laboratory toxicity tests employed a wide range of organisms and life stages, which is appropriate for evaluation of a proposed biocide. However, while the range of organisms was large (ranging from bacteria to fish), the logic for the selection of the organisms was not provided. Also, selection of a different set of test organisms, representing the same range of sizes and taxonomic groups might have led to different conclusions about the sensitivity to the hypochlorite. Consequently, the toxicity testing employed in the Study only can be considered preliminary because of the limited number of organisms per treatment, the small number of replicates per treatment, and the range of responses in the definitive tests.

Further, it was not possible to fully evaluate the protocols used for the toxicity testing because in many cases the protocols were not available and the protocols that were supplied were not the ones used (e.g., there are protocols for 10-day toxicity tests with *Hyalella azteca* and *Chironomus tentans*, but neither were used). In several cases, the protocols used were *In House* protocols and were not described as part of the Study. Even where specific protocols were cited (e.g., for *Artemia salina* cysts), the full citation was not provided and the protocols could not be located. The data sheets were the only source of information on how tests were performed. Unfortunately, the problem was further complicated by the absence of some of the data sheets.

In addition to the above, the presentation of the data and analyses was confusing. For example: (1) differences in water chemistry are identified in the Study, but the significance of these differences in the interpretation of results is not discussed; (2) LC_{99} numbers for saltwater tests referred to in the text of the Study do not match the numbers in the summary table for saltwater tests; and (3) test results for *Eohaustorius estuaries* in laboratory and ballast saltwater are called "similar," even though the ranges of the data are non-overlapping.

The temperature selected for the studies was 15^{o}C. This temperature is not standard for many of the organisms studied and there should have been justification provided for the use of this temperature. The exposure duration selected for use with the Study was 48 hours with no justification provided for its selection. However, the actual duration used varied in some instances based on the test organism (e.g., in the case of the Microtox test, the duration was only 15 minutes). For toxicity testing, a typical definitive test is conducted with five replicates with 5 - 20 organisms per replicate for each treatment. While the minimum number of test organisms per treatment is given as 20

(ASTM, 1998; USEPA, 1993), the usual number is generally more. The definitive tests did meet the standard criteria for minimum numbers of organisms per treatment, except for the tests with *Daphnia* neonates where n = 12; however, in many treatments, the range of response was either zero or 100 percent. Consequently, the ability to provide reliable estimates of the LC_{99} is limited.

The analysis of the toxicity testing data was not conducted in a manner that permits any evaluation of the uncertainty of the response. In most cases, the data were analyzed by a linear interpolation and not by a more standard approach, such as use of logit or probit analysis. As a result, the 95 percent confidence limits for the LC_{99} have been minimized. For instance in Test 4121 (*Bacillus subtilis* spore), the data were analyzed with both the probit and linear extrapolation methods and it is clear that the more standard probit method leads to substantially larger confidence limits. The need to use the linear interpolation stems from the limited partial mortality data in many of the data sets. Often the result is either zero or 100 percent response. Further, in some cases (e.g., for *Lubricous variegates*, Test 4031), the control mortality was sufficient that it would invalidate the test. The method of addressing control mortality was not provided in the Study, which invalidates the results of that test.

Finally, as with the shipboard tests, there was no quality control information provided on the health of the organisms used in laboratory toxicity tests. There should have been reference toxicity tests performed to ensure that the organisms used in the Study were of adequate health.

Impact of Sediment. The shipboard and laboratory toxicity tests did not fully investigate the influence of sediments on the response to hypochlorite. There were range-finding tests performed in the presence of sediment, but the Study indicates that there were significant technical difficulties such that definitive tests could not be performed. Reasons for and information about the difficulties were not provided. The problems that were encountered in the laboratory have implications in the application of hypochlorite to systems where there are bedded sediments. Since it is clear from the Study that the amount and character of the sediments in the vessel will affect the amount of hypochlorite that must be used, obtaining definitive testing in the presence of sediment and developing a method to address the hypochlorite demand of sediments is crucial to proper application of hypochlorite as a ballast water disinfectant. The lack of any pertinent information on this factor further compromises the conclusions of the Study.

Another consideration not addressed in the Study is the potential release of metals from ballast tank sediments as the result of the use of sodium hypochlorite. Treating soil and sediment samples with an oxidizing solution such as sodium hypochlorite or hydrogen peroxide is a common method of removing metals bound to the organic fraction of the soil or sediment (e.g., Laforce and Fendorf, 2000; Basta and Gradwohl, 2000; Usero *et al*., 1998). It is possible that during the treatment of ballast water containing sediments with sodium hypochlorite, metals could be released from the sediments. The amount of metal released would depend on the contact time of the sediment with the sodium hypochlorite, the amount of metal associated with the sediment, the amount of sediment, and the fate of the metal when released to solution (e.g., does it reabsorb to the sediment).

Biocide Discharge into the Great Lakes. Chlorine is widely used to disinfect drinking water and effluents from sewage treatment facilities. Hypochlorite solutions (e.g., sodium hypochlorite) are typically used and are very effective for chlorination. However, when chlorination is used to disinfect wastewater, residual chlorine that is discharged to surface waters can be toxic to aquatic life. Additionally, chlorination can form various chlorination by-products in water (i.e., disinfection by-products), depending on the amounts and type of organic matter that is present. At high levels, by-products formed by the chlorination of drinking water have been shown to cause cancer and developmental and reproductive problems in laboratory animals (e.g., trihalomethanes, haloacetic acids, and bromate) (USEPA, 2002). Ocean-going vessels take on ballast in various locations where the waters can have different constituent profiles. The varying characteristics of ballast water will likely affect the types and amounts of chlorinated compounds that are formed.

Dechlorination reduces the toxic effects of chlorinated wastewater and reduces the formation of chlorination by-products. The use of sulfur salts (e.g., sulfur bisulfite) is a typical method for dechlorination. However, dechlorination to near zero amounts can be difficult. Additionally, over-dechlorination can lead to the formation of sulfates, reduced dissolved oxygen, and reduced pH in the effluent (USEPA, 2000).

The effectiveness of sodium bisulfite at neutralizing chlorine was evaluated in the Study through total residual chlorine measurements of ballast water test solutions before and after chlorination/dechlorination. In addition, a laboratory simulation test was conducted to assess potential formation of organic chemicals and related ballast water discharge acceptability to the state of Wisconsin. The results indicated that when sodium bisulfite was properly added and mixed with chlorinated ballast water, all theoretical total residual chlorine requirements (rather than actual since regulatory standards do not exist) for the state of Wisconsin could be met. No other Great Lakes jurisdictions were similarly evaluated. Also, the Study suggested that the levels of organic by-products formed through dechlorination would not exceed Michigan Water Quality Standards for a “typical, short-term intermittent discharge.” In both instances, insufficient information (too few tests and lack of data as to what the standards would be for the various other Great Lakes jurisdictions) was provided in the Study to definitively address the questions regarding the safety and legality of discharging chlorinated and/or dechlorinated ballast water into Great Lakes waters. Additional information and actual testing will be needed before this question can be addressed.

The environmental effects of a full-scale implementation of a standardized chlorine ballast water treatment protocol of all Great Lakes transversing ocean-going ships were not addressed in the biocides Study. Small concentrations of the biocides within the ballast tanks of numerous ships could add up quickly when ballast tanks from multiple ships are discharged into local harbors. This question should be evaluated in future studies.

Laboratory Corrosion Testing Protocol. The Study's choice of 3.5 percent sodium chloride as the test media for the corrosion tests was not reasonable since seawater is a medium with multiple living organisms that can affect corrosion rate, either by their physical presence (shielding), their metabolism (use and creation of corrosive compounds at the metal surface), and death (products of decay). A more realistic choice would have been to use fresh, natural seawater.

Fifteen days was too short a time period to conduct the corrosion tests performed in the Study. Although water will permeate most coatings within this time period, anions like chloride will take much longer. Incubation times for coating degradation of epoxies can be over one year. For bare steel alone, the types of corrosion products that accumulate on the surface determine corrosion rate, and these products take much longer than 15 days to come to an equilibrium configuration. Any corrosion data generated in 15 days on bare steel will be difficult to extrapolate to exposure times associated with ship service, while no corrosion effects are likely to show up on properly coated steel in this time frame. Any conclusions resulting from an investigation as short as that provided for in the Study cannot be considered definitive.

In addition to the above, the Study's lack of application of basic statistics in its analysis of some sections and its flawed use of statistics in other sections were problematic. For example, the Study's conclusions regarding the significance of corrosion rates are not supported with any statistical analyses. It is unlikely that, if an analysis of variance had been performed on the data, there would have been any statistically significant effects of any of the variables except at the 95 percent confidence level. Similarly, the Study's conclusions regarding creepage (coating deterioration) also are not supportable, since a 15-day test is too short to overcome incubation time for coating deterioration in some cases. Again, if an analysis of variance was done on these data, it is unlikely that the results would show that any variable caused statistically significant change in creepage.

Finally, a large environmental effect of discharging ballast water containing copper was not addressed in the Study. Extremely small amounts of copper, on the order of 20 parts per billion (ppb), can cause catastrophic corrosion of aluminum by a process called heavy metal ion corrosion. This involves plating out of the copper on the aluminum to form micro-galvanic cells. This effect occurs in both fresh and salt water and can result in pitting depth growth rates on aluminum on the order of an inch per year (Hack, 2002) While the impact of such action would not be noticed by the large commercial ships, it would be by every owner of an aluminum-hulled boat that would be damaged. This issue would need to be investigated further in the event that future studies consider copper ion as a possible biocide for consideration.

Conclusions

The following presents the MESB's conclusions regarding efficacy of the two biocides evaluated, their ability to be discharged into waters of the Great Lakes, and their corrosion impact on ballast water tanks.

Copper Ion Biocide Efficacy and Discharge Concentrations. Copper as an ion (e.g., Cu^{2+}) is a naturally occurring chemical in the environment and necessary for various metabolic processes. For example, copper acts as a catalyst in the formation of hemoglobin, the iron-containing respiratory pigment in red blood cells (Sandstead, 1995). At high concentrations, copper is toxic and is used to control algae and bacteria in swimming pools and lakes. The amount of copper to control algae depends on the other types of life forms in the water body. For example, if fish are present, then lower amounts of copper ion are used.

Because of its toxic effects on biota such as fish, copper discharge to surface water is of concern. If a copper biocide treatment is used for ballast discharge, then this discharge water would most likely need to be regulated. The Study's test results demonstrated that the copper ion biocide was only 33 percent effective at 167 ppb in freshwater and 70 percent effective at 68 ppb in reducing bacteria in freshwater and simulated seawater experiments, respectively. These results suggest that at the concentrations tested, copper treatment was not effective. In order to be effective, even higher concentrations of copper would be needed, which would result in the further exceedance of the range of the theoretical allowable discharge concentration levels (2 ppb to 48 ppb) determined by the Study for the Great Lakes jurisdictions.

In addition to potential limits on copper concentrations that could be used, the efficacy of copper in killing biota ballast water is influenced by the natural geochemical behavior of copper in the environment. For example, copper is a particle reactive chemical. This means that it will tend to be adsorbed to sediments, whether suspended or settled. Consequently, the presence of sediment in the ballast tank would reduce the efficacy of copper as a biocide and higher concentrations of copper would need to be used compared to water in the absence of the sediment.

The behavior and toxic effects of copper in water also are altered by natural processes, such as the formation of ion pairs in solution. In solution solutes, copper (Cu^{2+}) can bond with other solutes, such as bicarbonate (HCO_3^-), to form new dissolve chemical species known as an ion pair or complex. In the example given, the ion pair would be copper bicarbonate ($CuHCO_3^-$). The formation of this ion pair decreases the toxicity of a copper (Stumm and Morgan, 1996). Since copper in solution is particularly influenced by the presence of dissolved organic matter, bicarbonate, and carbonate in water, changes in the relative abundances in these solutes might necessitate different amounts of copper concentrations needed as a biocide. This point is important to consider when interpreting the results of the Study's simulated seawater experiments since, if the simulated solution did not contain proper amounts of solutes, such as sulfate and bicarbonate, the experimental results observed in the Study might not represent the true behavior of copper.

Copper ion concentrations in water of 0.02 to 0.05 ppm can cause severe corrosion of aluminum. For this reason, discharge of copper ion treated water from ballast tanks could cause significant corrosion of nearby aluminum-hulled boats and aluminum structures. It would be important to evaluate this issue further prior to proceeding with any additional consideration of copper ion as a ballast water biocide.

In summary, the Study's toxicity tests, as a whole, suggest that in sufficient concentrations, copper ion could be an effective biocide. However, at the concentrations needed to achieve the desired effectiveness, the level would be far too high to be discharged into the Great Lakes. Given this, and in the absence of any known neutralizing agent that would allow copper to be safely discharged into the Great Lakes, the MESB Panel concludes that copper ion cannot be considered to be a viable ballast water biocide alternative at this time.

Sodium Hypochlorite Biocide Efficacy and Discharge Concentrations. The Study's conclusions regarding the effectiveness of sodium hypochlorite as a viable ballast water biocide alternative from the shipboard and laboratory toxicity tests are limited and can only be considered preliminary at best. However, despite the problems outlined in this critique regarding the testing protocols used, the MESB Panel suggests that the use of sodium hypochlorite as a ballast water biocide can have a high degree of efficacy when treating the majority of organisms that were tested in the Study, assuming sufficient active hypochlorite concentration can be attained to account for sediment loads from both suspended and deposited material. Considerable more work will need to be conducted before any definitive statement regarding its efficacy within an actual ballast water tank environment can be made. In particular, well planned and controlled toxicity tests need to be conducted that will evaluate the biocide's effectiveness on both benthic and resting stages of ANS in the presence of both suspended and bottom sediment similar to that found in ballast water tanks. Also, a mechanism needs to be developed and a careful analysis needs to be conducted that will determine how much chlorine remains available over time in the ballast tank in order to: (1) ensure the presence of an effective concentration of the biocide at the time when it is needed, and (2) allow for a determination to be made as to how much neutralizing compound would be needed for dechlorination prior to ballast water discharge.

According to the Study, there exists no state or federal permitting requirements specifically for ballast water discharges and ballast water discharges are exempted from point-source discharge regulations. However, discharges of ballast water treated with sodium hypochlorite still would need to be of such quality so as to protect the designated uses of receiving waters. While the Study did attempt to address the issue of discharge of treated ballast water, the MESB Panel concludes that insufficient information (too few tests and lack of data as to what requirements would need to be met throughout the Great Lakes jurisdictions), was provided to definitively address the question regarding if such discharges could be safely and legally discharged into Great

Lakes waters. Additional studies involving the use of actual ballast water treated with the biocide and a clear indication as to what would be required by the various U.S. and Canadian Great Lakes jurisdictions in order to meet Great Lakes water quality standards would be useful.

Finally, as seen in this Study and other investigations (e.g., Lubomudrov, Moll and Parsons, 1997) involving the use of only biocides to address ANS, the MESB Panel also concludes that biocide treatment in the absence of some other mechanism to address ballast water sediment, such as filtration, will result in an incomplete elimination of ANS. Future studies will need to address this problem by investigating the efficacy and the practicality of shipboard use of combined treatment methodologies.

Impact of Biocides on Ballast Tank Corrosion. The biocide corrosion tests that were conducted in the Study were of too short a duration to allow prediction of long-term corrosion rates or coating degradation rates. Corrosion is not always constant over time, and, unless the time-dependence of corrosion rate is known, it is not possible to extrapolate data from short-term tests to predict long-term performance. In particular, coating degradation typically has an incubation time when the corrosive constituents are diffusing through the coating to the base metal underneath. For ballast water tank coatings, this incubation time can be many months. In addition, the tests should have used natural seawater and should have included cathodic protection for some of the exposures to better simulate the actual ballast water tank environment.

The hypochlorous acid that is proposed as a biocide is an oxidant and could increase the corrosion of steel in water if present in quantities similar to the other oxidant in seawater, dissolved oxygen. The effect may become noticeable at concentrations of 1 ppm or more if the kinetics of the reactions is favorable. Just as important, this oxidant may negatively affect the performance of paint systems on steel. Therefore, a new corrosion test should be conducted to determine the magnitude of these effects.

Copper ion concentrations in water of 0.02 to 0.05 ppm can cause severe corrosion of aluminum. For this reason, discharge of copper ions from treated ballast tanks may cause significant corrosion of nearby aluminum-hulled boats and aluminum structures. It would be important to evaluate this issue further prior to proceeding with any additional consideration of copper ion as a ballast water biocide.

Based on the information presented in the Study, the MESB is unable to reach definitive conclusions regarding the nature and extent of detrimental corrosion effects of either biocide on ballast tank structural integrity. Additional, better designed and longer duration tests will be needed to more fully evaluate this concern.

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Appendix 1

Executive Summary
[Draft] Final Report: Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides

BMT Fleet Technology, Ltd. and ESG International, Inc. [2002]. *[Draft] Final Report: Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides*, April 12, 2002. Kanata, Ontario. 730p.

Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides

[Draft] FINAL REPORT

12 April, 2002

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Surface Water Quality Division
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EXECUTIVE SUMMARY

Numerous mechanical, physical, and chemical treatments, that may reduce aquatic nuisance species (ANS) introductions through the ballast water vector, are presently being investigated. This study was initiated to help the State of Michigan to determine if hypochlorite and copper can be recommended for general application as ballast water biocides.

The biocidal properties of sodium hypochlorite and copper as they relate to ballast water treatment were evaluated in shipboard trials aboard the MV *Federal Yukon*, and in laboratory toxicity tests. Additionally, the potential detrimental effects of routine application of the biocides in ballast tanks were explored using accelerated corrosion experiments in the laboratory. Shipboard trials, conducted during a typical saltwater and freshwater voyage, indicate that sodium hypochlorite (dosed to a residual of ~10 ppm) significantly reduced (>90%) ambient zooplankton and bacteria levels relative to the controls after a two-hour treatment. In freshwater trials, copper ion treatment (< 0.2 ppm) was capable of reducing ambient zooplankton levels greater than 30% relative to the control. For both biocides, applied at these levels, numerous organisms were capable of surviving treatment in settled sediments.

Laboratory toxicity tests were conducted on freshwater and saltwater fish, invertebrates, algae, and bacteria, in test conditions that simulate those in a ballast tank. Sodium hypochlorite was effective (i.e., achieved LC99) at killing the majority of species tested at less than Total Residual Chlorine (TRC) 10 ppm. Higher sodium hypochlorite levels were required to kill encysted life stages. The LC99 and EC99 values of the majority of species tested were at total copper levels below 200 ppm. The encysted life stages of certain test organisms were not killed at higher total copper levels. Exploratory range-finding tests suggest that the presence of high levels of sediment will negatively impact the performance of both biocides.

Accelerated corrosion tests were conducted on bare, coated, and scribed metal coupons under a variety of conditions (i.e., fully submerged, periodic immersion, damp spaces, and buried in simulated sediment) in saltwater and freshwater. Test data suggests samples exposed to sodium hypochlorite tend to experience slightly more corrosion and paint damage than the control samples, however the effect is small and is not quantifiable in terms of life expectancy from this analysis. No accelerated failures were observed in any unscribed coating system due to the presence of sodium hypochlorite. Accelerated corrosion tests in solutions containing copper suggest in the aggressive corrosion environment of salt water and periodic immersion there is a slight increase in corrosion but there were no increases in coating failures observed.

Numerous operational issues and constraints were identified during the conduct of the study. These include;

- The removal of bottom sediment from ballast tanks and suspended sediment in incoming ballast water would likely have additional treatment benefits for both biocides.
- Appropriate dosing and monitoring and distribution equipment will be required to ensure accurate biocide levels have been reached.
- There are un-addressed safety issues surrounding the use of hypochlorite on ships, and classification societies and regulatory bodies would require special consideration of any on-board facility.
- There are environmental discharge concerns associated with using copper.
- The ranges of water qualities, particularly amount of sediment that can be expected to require treatment have yet to be identified.
- Sodium hypochlorite is readily available throughout the Great Lakes ports or can be generated on board.

- Copper ion generators are capable of supplying copper ions to the ballast water intake.

Economic models of typical on-board installations required to apply sodium hypochlorite or copper directly at the ballast water intake were investigated. It was shown that the life cycle cost of an onboard sodium hypochlorite generator and application system would increase the required charter rate necessary to maintain a return on the ship by $207 per day or 2.3% of a typical daily charter rate. To use manufactured sodium hypochlorite of a high concentration would cost $125 per day but increase the safety concern of handling on-board. The life cycle cost of a copper ion generator similar to that installed on the *Federal Yukon* using the same operational parameters would be $48 per day or an increase in charter rate of 0.5%.

The issue of sediment load and the detrimental effects it can have on the efficacy of biocides needs to be addressed: it should be quantified from both a tank bottom and intake water sediment perspective. Furthermore, it is possible that treatment of ballast water using biocides at every ballast operation may create a cumulative effect and tend to inactivate sediment borne biota.

Appendix 2

April 10, 2002 Correspondence to the Michigan Environmental Science Board from Governor John Engler

Engler, J. [2002]. *Correspondence to Dr. Lawrence Fischer, Michigan Environmental Science Board*, April 10, 2002. Office of the Governor, Lansing. 2p.

STATE OF MICHIGAN
OFFICE OF THE GOVERNOR
LANSING

JOHN ENGLER
GOVERNOR

April 10, 2002

Dr. Lawrence Fischer, Chair
Michigan Environmental Science Board
P.O. Box 30680
Lansing, Michigan 48909-8180

Dear Dr. Fischer:

Over 160 non-native aquatic and terrestrial species of plants and animals have been introduced into the Great Lakes Basin since the 1800s. Introductions of non-native aquatic nuisance species, such as the sea lamprey, zebra mussel, Eurasian ruffle, round goby, and spiny water flea, whether intentionally or unintentionally, play a major role in modifying aquatic ecosystems of the Great Lakes. Second only to habitat loss, many aquatic nuisance species severely impact and alter native species' communities and ecosystem functions. The primary route of entry into the Great Lakes for these non-native species has been through ballast water exchange.

On August 6, 2001, I signed into law Public Act 114 (Act). Among other charges, the Act requires the Department of Environmental Quality (DEQ) to determine whether one or more ballast water treatment methods, which protect the safety of the vessel, its crew, and its passengers, could be used by oceangoing vessels to prevent the introduction of aquatic nuisance species into the Great Lakes. A field demonstration project was initiated by the DEQ in 2001 to evaluate the effectiveness and safety of two different biocides, sodium hypochlorite and copper ion. A draft report of this demonstration project, entitled, *Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides*, recently has been completed.

I am requesting that the Michigan Environmental Science Board (MESB) review the draft DEQ report to evaluate the scientific validity of the conclusions reached regarding the:

1. Efficacy of the two biocides evaluated;

2. Corrosivity to ballast tanks resulting from the biocides; and

3. Discharge concentrations for each biocide needed to meet regulatory standards.

I am directing the DEQ to fully cooperate with and support the MESB's investigation. I would encourage the MESB to seek assistance in this assignment from recognized experts in the academic and scientific communities. Please provide me with your evaluation as soon as possible.

Thank you for your continuing service to the citizens of Michigan.

Sincerely,

John Enger
Governor

cc: Mr. Russell J. Harding, Director, DEQ
Mr. David Ladd, Director, Office of the Great Lakes, DEQ
Mr. Keith G. Harrison, Executive Director, MESB

Michigan Environmental Science Board

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