

STUDIES TO ADDRESS THE ISSUES  
RAISED BY THE MESB (2002)  
CRITICAL REVIEW OF A BALLAST  
WATER BIOCIDES TREATMENT DEMONSTRATION  
PROJECT USING SODIUM HYPOCHLORITE

FINAL REPORT

May 2004

Submitted to:

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**BMT FTL DOCUMENT QUALITY CONTROL DATA SHEET**

**PROPOSAL/REPORT:** Studies to Address the Issues raised by the MESB (2002)  
Critical Review of a Ballast Water Biocide Treatment  
Demonstration Project Using Sodium Hypochlorite

**DATE:** May, 2004

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- Michigan Great Lakes Protection Fund
- Office of the Great Lakes, Michigan Department of Environmental Quality
- Transport Canada Marine Safety Branch

## 2. EXECUTIVE SUMMARY

A series of “at ship” field trials and laboratory tests were performed in 2002 to establish the effects of using Copper Ion and Sodium Hypochlorite as Biocides in Ballast Water [1]. These tests were conducted under contract to the Michigan Department of Environmental Quality (DEQ) to support their determination of whether these chemicals could be recommended for use as biocides in Ballast Water for Ships on the Great Lakes. Such determinations are mandated under Michigan Act 114 of 2001.

Following a public meeting discussing the above report, Governor Engler charged the Michigan Environmental Review Board to review the work on the 10th April, 2002. The MESB issued its review in September 2002 [2]. This report outlines the work conducted by BMT Fleet Technology Limited and Stantec Consulting Ltd. It supplements the findings of the 2002 project and addresses the issues raised by that review.

### 2.1 Temperature Impacts on Hypochlorite Toxicity

A review of the available literature indicated that a definitive statement regarding the impact of temperature on the efficacy of sodium hypochlorite was not possible.

Although an increase in temperature was generally accompanied by an increase in the toxicity of hypochlorite to the numerous species tested, it could not be determined whether the results were related to thermal stress or increased physiological requirements of the test organisms or to an increase in the chemical activity of hypochlorite as it relates to toxicity.

### 2.2 Sediment Impacts on Chlorine Toxicity

A series of laboratory tests involving simulated ballast waters were conducted to determine the effects of sediment on chlorine toxicity to *Hyalella azteca*. Simulated ballast waters were prepared using water collected from Hamilton Harbour and sediments collected from bulk carriers' ballast tanks prior to the ballasting operations. Sediments were added to the harbour water in controlled amounts to bracket expected ranges of sediment loadings in ships' ballast tanks. Chlorine as sodium hypochlorite was added in controlled dosages. Sub samples of the simulated ballast waters were removed for toxicity testing upon stabilizing the concentration of total residual chlorine (TRC) and for determination of the presence of disinfection by-products.

In the present study, sediment concentration was shown to be a significant contributor to chlorine demand (defined as any inorganic or organic compound which is capable of reducing the amount of chlorine added to a solution). As such, any substance capable of contributing to chlorine demand will also reduce its efficacy by lowering the residual chlorine level. An attempt was made to satisfy the chlorine demand, by maintaining each target chlorine residual for a period of five minutes prior to initiation of the static test exposure.

Sediment concentration had no effect on the toxicity of chlorine to *Hyalella azteca* at sediment concentrations (0 (nominal) to 100 ppm), but reduced toxicity marginally at higher concentrations (1,000 ppm). The 48-h LC90s (defined as the concentration of test substance that is estimated to kill 90% of the test organisms within the test period) for Total Residual Chlorine (TRC) were generally similar for the 0, 10 and 100 ppm sediment concentrations of sediments #1 and #2. The 48-h LC90s were also similar for the highest sediment concentration (1,000 ppm) of sediments #1 and #2, but marginally higher than those observed for the 0 to 100 ppm sediment concentrations. A similar trend was observed for sediment #3, except that 48-h LC90s were higher than those observed for sediments #1 and #2. The observed differences may have been related to the (ten-fold) lower concentration of ammonia in sediment #3 relative to sediments #1 and #2.

Sediment concentration also had no effect on the survival time of *H. azteca* if chlorine concentration was high enough (10 ppm). This effect was clear for sediment #3, and for the 0, 10 and 100 ppm concentrations of sediments #1 and #2. The range of LT90s observed for the highest chlorine concentration (10 ppm) for all sediment levels was 14.6 to 18.7 h.

### 2.3 Chlorination Byproducts

The main by-products of treatment of simulated ballast water with sodium hypochlorite (to a TRC concentration of 10 mg/l) were chloroform, dichloroacetic acid, and trichloroacetic acid. The other trihalomethanes (THM) and haloacetic acids (HAA) that were formed were less significant contributors to the total THM and HAA. The THM and HAA concentrations increased with increasing sediment concentrations, undoubtedly due to the increase in organic precursors in the added sediment.

Chloroform and other THM concentrations were within Michigan's theoretical permit effluent limits. HAA has not been directly regulated by Michigan. This needs to be addressed by regulatory agencies. However, if permit effluent limits were of the same order of magnitude as for THM, the HAA would be within those theoretical limits.

Acid extractible organics (e.g., phenol and o-cresol) and base neutral organics (e.g., naphthalene and pyrene) showed no evidence of being increased as a result of the chlorination process.

Metals showed no evidence of any significant liberation from the sediments as a result of the chlorination process. Dissolved metals showed no significant increase with increasing sediment addition.

The amount of chlorinating chemicals needed to be used to treat all ballast water discharged in the Great Lakes (to the TRC concentration of 10 mg/l) would be small in relation to other uses of chlorinating chemicals in the Great Lakes Watershed.

## 2.4 Dechlorination

Dechlorination is needed due to potential acute toxicity of chlorine residual in the ballast water discharge. No direct toxicity of bisulfite residual is expected, provided reasonable control of overdosing is maintained. Dissolved oxygen was not significantly affected by dechlorination. Dechlorination reduced pH by about 0.5 units. This is not expected to cause problems in the receiving water.

## 2.5 Structural Integrity

The addition of hypochlorite at the dose levels necessary to be biologically effective has no effect on the standard ship type coating system (paint permeability).

There is no significant increase in the rate of ballast tank coating damage experienced by exposure to hypochlorite over a 90-day period.

Corrosion rates of bare steel are increased by the presence of hypochlorite at the biologically effective dose rates under constant exposure conditions. However, the amount of corrosion increase is not considered significant over the life of a ship due to the relatively small amount of time that elevated hypochlorite concentrations would be present.

Under the most aggressive corrosion conditions found in a ship ballast tank (splash zones) the life cycle for steelwork replacement to normal Classification Society standards is reduced by less than 5%.

## 2.6 Shipboard Dosing System

A shipboard dosing/monitoring system can be developed. However, there is no readily available automated system suitable for the ship board working environment.

The cost to shippers using hypochlorite as a ballast tank biocide on ships typical of those trading internationally into the Great Lakes represents a 0.8% increase in daily charter rates (cost of shipping).

To ensure that hypochlorite is effectively and conservatively applied as a biocide, it is necessary to ensure that sediment loads are minimized. Ship owners must adopt best management practices respecting ballast operations

### 3. INTRODUCTION

A series of “at ship” field trials and laboratory tests were performed in 2002 to establish the effects of using Copper Ion and Sodium Hypochlorite as Biocides in Ballast Water [1]. These tests were conducted under contract to the Michigan Department of Environmental Quality (DEQ) to support their determination of whether these chemicals could be recommended for use as biocides in Ballast Water for Ships on the Great Lakes. Such determinations are mandated under Michigan Act 114 of 2001.

The results of that work were presented to the Michigan Ballast Water Working Group meeting in Detroit on 20 March 2002. At that meeting, it was decided that there should be a review of the report prior to any DEQ recommendation that either of these ballast water treatment methods could be used by ocean-going vessels.

The Michigan Environmental Review Board (MESB) was asked to review the work on the 10th April 2002. The MESB issued its review in September 2002 [2].

The Office of the Great Lakes issued a call for work to address these findings and further assist the DEQ in its determination of the suitability of Hypochlorite as a ballast water biocide. (Copper as a biocide was abandoned due to concerns of biocide efficacy and of achieving discharge limits.)

This work reports on the further experimental and engineering efforts developed and carried out to address the major issues raised in the MESB review viz:

**Temperature: The effect of typical Great Lakes ballast water temperature ranges on the efficacy of sodium hypochlorite as a biocide.**

During a typical shipping season, water temperatures in the Great Lakes vary from lows of 1 to 3°C in cooler months to 15 to 22°C during summer and fall depending on the water depth. As is the case with many oxidizing chemicals, the temperature of hypochlorite application may impact its biocidal properties. To address this, toxicity of hypochlorite across a temperature range representative of a Great Lakes shipping season was researched and is detailed in Section 4, Literature Review.

**Sediments: The effects of sediment on the efficacy of chlorine (as sodium hypochlorite) as a biocide.**

There are generally accepted best management practices (BMPs) to minimize the sediments that include the biota ingested by a ship’s ballast system, however, they cannot eliminate the presence of organic and inorganic material suspended in the water. It is this material that consumes the hypochlorite, which is then left ineffectual as a biocide. The issue to be addressed is: what is the chemical demand on the biocide resulting from the sediment content? Laboratory work using ship collected sediments were conducted and are reported in Section 5, Effects of Sediment on Chlorine Toxicity.

**Byproducts: The quantification and impact of the formation of chlorinated compounds by typical sodium hypochlorite treatment of ballast tanks in Great lakes waters.**

The mixing of hypochlorite in a ballast tank containing water and sediment is expected to produce some level of disinfection by-products (DBPs). The DBP formation issue was investigated through a literature review (Section 4) and a series of laboratory experiments (Section 6). The results of the laboratory experiments conducted to determine the amount and types of DBPs that may be produced from the interaction of hypochlorite with the sediments and water associated with ballast tanks, are presented and discussed in Section 6. This is reported in Section 6, Presence of Disinfection By-products.

The analytical data developed in the Disinfection By-product laboratory work is examined as they relate to the discharge requirements of the regulatory agencies for states and provinces adjacent to the Great Lakes. This is addressed in Section 7, Regulatory issues.

**Structural Integrity: The effects of Hypochlorite on steel corrosion kinetics, paint permeability and overall corrosion enhancement.**

A series of coating experimental examinations and longer term corrosion tests were conducted and reported in Section 8, Structural Integrity.

**Shipboard: The practical implementation, on board ship, of a sodium hypochlorite chlorination and de-chlorination system control mechanism to ensure effect and efficient use (minimization) of chemical additives.**

This is referred to as a Monitoring and Dosing system and the practicality of implementing such a system is developed in Section 9.

## 4. LITERATURE REVIEW

### 4.1 Introduction

A literature review was conducted prior to the initiation of the laboratory experimental studies to help address the issues of:

- extent of Disinfection By-product (DBP) formation during ballast water treatment with sodium hypochlorite;
- impact of temperature on the efficacy of sodium hypochlorite, and;
- the discharge of treated ballast water to the Great Lakes ecosystem.

The literature review is reported in Appendix A, the conclusions are presented below;

### 4.2 Summary/Conclusions

#### 4.2.1 Disinfection By-products

No studies were found in the scientific literature that directly involved Disinfection By-products (DBP) formation from the chlorination of ship ballast. However, DBP formation from the chlorination of natural waters, wastewater, and drinking water supplies has been extensively studied and is well-documented in the scientific literature.

The literature suggests that trihalomethanes (THMs) and haloacetic acids (HAAs) are the most abundant and regularly detected DBPs formed during the chlorination of natural waters. Given that the organic material and precursors found in drinking water studies are likely similar to those in ballast water, the formation of the same types and relative predominance of DBPs are expected during the treatment of ballast water.

#### 4.2.2 Temperature Issues

The literature suggests that, in general terms, an increase in temperature results in an increase in the toxicity of hypochlorite to numerous species. However, the increase in toxicity seen in these studies may be more related to thermal stress or increased physiological requirements (and therefore increased exposure of key physiological systems to higher chlorine exposure) than to an increase in the chemical activity of hypochlorite as it relates to toxicity.

There are also indications that changes in hypochlorite toxicity due to exposure temperature may be species specific, likely depending on thermal tolerance limits of the species in question. This suggests that organisms that have protected resting stages may not be impacted by temperature-induced increases in toxicity, as the relative physiological requirements of the resting stages are low.

From a chemical perspective, some authors suggest that, due to an increase in THM formation, sodium hypochlorite may be more reactive at higher temperatures. However, other literature suggests that less of the reactive hypochlorous acid species is present at higher temperatures. The net impact of the reactivity of hypochlorite as it relates to efficacy is not well researched.

Due to the variety of different species and temperature conditions that are encountered during the treatment of ballast water, and the limited testing that has been conducted to date, a definitive statement regarding the impact of temperature on the efficacy of sodium hypochlorite cannot be made. Additionally, given the large number of variables (i.e., test species, temperature ranges, life-stages, water quality conditions, etc.) that would need to be addressed in a laboratory study, it is not likely that a laboratory investigation within the scope of this project would provide a definitive answer to this issue.

#### 4.2.3 Discharge of chlorinated water

Discharge limits for TRC are regulated around the Great Lakes and are similar across jurisdictions. The limits are based on acute toxic effects on aquatic life.

Studies in the effects of chlorinated/de-chlorinated discharges of waste water displayed site-specific results.

The present study uses the laboratory work to provide answers to the MESB concerns regarding the contents of discharge related to ballast water and potential for reactions with the likely sediments found therein.

## 5. EFFECTS OF SEDIMENT ON CHLORINE TOXICITY

A series of laboratory tests involving simulated ballast waters were conducted to determine the effects of sediment on chlorine toxicity to *Hyalella azteca*. Simulated ballast waters were prepared using water collected from Hamilton Harbour and sediments collected from bulk carriers' ballast tanks prior to the ballasting operations. Treatments included harbour water alone (i.e., no sediment added) and harbour water spiked with 10, 100 and 1,000 ppm sediment (i.e., 0.001, 0.01 and 0.1%). The highest concentration was considered a "worst case" scenario. Chlorine as sodium hypochlorite was added in controlled dosages. Sub samples of the simulated ballast waters were removed for toxicity testing upon stabilizing the concentration of total residual chlorine (TRC) and for determination of the presence of disinfection by-products. Additional details of these procedures are provided in the following sections.

### 5.1 Sample Collection

#### 5.1.1 Sediment Samples

Sediment samples (S#1, S#2 and S#3) were collected from the ballast tanks of three different ships immediately after reaching their first port of call in the Great Lakes. Table 5.1 summarizes the sediment collection information.

**Table 5.1: Sediment Collection Information**

<b>Description</b>	<b>Sediment 1</b>	<b>Sediment 2</b>	<b>Sediment 3</b>
Date Sampled	2003-05-22	2003-06-06	2003-07-02
Ship Port	Hamilton Harbour	Toronto Harbour	Hamilton Harbour
Ship Type	Bulk Carrier	Bulk Carrier	Bulk Carrier
Tank Location	Forepeak	Starboard #5	Forepeak

Approximately 14 L of sediment were collected from the ballast tanks of each ship. Sediment samples were collected using clean stainless steel sampling spoons or sampling shovels depending on the depth of the sediment. Sediments samples were collected in new, clean 7 L polyethylene cylindrical pails lined with a food-grade polyethylene liner. Each liner was closed with a plastic cable tie and the pail was sealed with a leak-proof plastic lid. A label indicating the sample location, ship name, contents, time/date sampled, sampler, and affiliation, was placed on each sample bucket and lid. A sample chain-of-custody form was completed for each sampling to document the conditions during sampling and transport of the sample. The materials that were used in the sampling of the ballast water/sediments are listed in Appendix B, Table B.1.

#### 5.1.2 Harbour Water Samples

Samples of Hamilton Harbour Water (HW) were collected on May 27, 2003 (HW-1), June 16, 2003 (HW-2) and August 11, 2003 (HW-3). Harbour water, as opposed to ballast water, was used for preparing the simulated ballast water on the basis that it was representative of typical ballast water in the Great Lakes and that it provided a source of non-contaminated water (i.e., non-acutely toxic to the test organism).

Approximately 250 L of harbour water were collected in association with each sediment sampling event. All samples were collected using a stainless steel pail and stored in 22.5 L new,

clean plastic pails lined with a food-grade polyethylene (bag). Each bag was sealed with a plastic cable tie and the pail was sealed with a leak-proof plastic lid. Water quality parameters including temperature, pH, Dissolved Oxygen (DO), conductivity/salinity were measured at the time of sampling using a portable hand-held multi-meter (Table 5.2).

### 5.1.3 Sample Handling and Storage

Sediment and harbour water samples were transported by field crew directly to Stantec's Ecotoxicity Testing Laboratory located in Guelph, Ontario. The harbour water samples were composited in a single 280-L polyethylene mixing tank and filtered (60 µm Nyltex mesh screen). Water quality parameters including DO, pH, temperature and conductivity were measured and recorded. Harbour water was then re-distributed among the 20L sample buckets and stored at 4 to 8°C until required for use in tests.

Sediment samples were pressed through a 1000 µm stainless steel sieve to remove large debris, composited in a clean 20 L polyethylene container and re-distributed to the 7 L sample pails with new polyethylene liners. Sediment samples were stored in the laboratory at 4 to 8°C until required for use in testing.

**Table 5.2: Analyses Conducted on Ballast Water Samples**

Parameter	*Method	QL	Matrix	Lab Performing Analysis
pH	pH electrode	0.1 pH unit	Water	Field/STANTEC
Temperature	Temperature Probe	0.1 °C	Water	Field/STANTEC
Dissolved Oxygen	Oxygen Electrode	0.1 ppm	Water	Field/STANTEC
Conductivity	Conductivity Probe	1 µmhos	Water	Field/STANTEC

\*Based on procedures provided by the manufacturer.

### 5.1.4 Chemical Analysis of Water and Sediment Samples

Sub samples of each of the three composited sediments were submitted to Philip Analytical Services for analysis of Total Organic Carbon (TOC), particle size, and total metals (Table 5.3). Percent moisture was determined in-house by laboratory staff. Sub samples of the harbour water were analysed for humic substances, Dissolved Organic Carbon (DOC), TOC, and dissolved metals.

**Table 5.3: Summary of Analyses Performed on Sediments and Hamilton Harbour Water**

Analysis	Task/Matrix	
	Ballast Sediment	Hamilton Harbour Water
Metals <sup>1</sup>	X	X
Humic substances		X
Particle Size	X	
TOC	X	X
DOC		X
General Water Quality <sup>2</sup>		X
Percent Moisture	X	

<sup>1</sup>Metals include those listed in Appendix C. Analyses of sediment were for total metals; analyses of harbour water were for dissolved metals.

<sup>2</sup>DO, pH, temperature, and conductivity/salinity.

## 5.2 Laboratory Toxicity Tests with Simulated Ballast Waters

Laboratory toxicity tests were undertaken to determine the effect of sediments on the efficacy of chlorine (as sodium hypochlorite) using the post-juvenile form (i.e., 2 to 15 d old) of the freshwater amphipod (*Hyalella azteca*). *Hyalella* was chosen for the following reasons: the species is tolerant of a broad range of salinities expected to be found in ballast waters, the organism is epibenthic, and lives in close proximity to sediments, it represents an ecological niche typical of a ballast water organism, and it is easily cultured in the laboratory. Total residual chlorine (TRC) concentrations were measured at specific times during the toxicity exposures to monitor chlorine decay in the test system. Table 5.4 summarizes the treatments used to evaluate the efficacy of sodium hypochlorite in the presence of sediment.

**Table 5.4: Study Design Summary for the Evaluation of the Efficacy of Sodium Hypochlorite in the Presence of Sediment**

Treatment	Number
Hamilton Harbour Water	3 (HW-1, HW-2, HW-3))
Sediment from the Ballast Tanks of 3 Different Ships	3 (S#1, S#2, S#3)
Sediment Concentrations	4 (0, 10, 100, and 1000 ppm)
Hypochlorite Levels	6 (5 hypochlorite treatment levels plus control)
Replicates per Treatment	3
No. of organisms per replicate	10
<b>Organisms per Treatment</b>	30
Total No. of Treatments Treatment	72

### 5.2.1 Test Organism and Acclimation

Organisms for testing were obtained from Stantec Consulting Ltd., Brampton, ON. Animals were shipped at 2-15 days of age. On arrival to the laboratory, the organisms were unpacked, and transferred to a 4-L food-grade plastic container. During acclimation of the organisms, instantaneous temperature change did not exceed  $\pm 3^{\circ}\text{C}$ , and daily temperature changes did not exceed  $\pm 1^{\circ}\text{C}$  from the previous days reading while temperature was slowly adjusted to  $15 \pm 1^{\circ}\text{C}$ . Acclimation to Hamilton Harbour water was done in a stepwise fashion by removing small volumes (100 mL) of the original culture water and adding similar volumes of the harbor water each day.

### 5.2.2 Preparation of Simulated Ballast Waters (Chlorinated and Non-Chlorinated)

Prior to the addition of any sediment, pH of the harbour water was adjusted from an initial pH of approximately 8.4 to  $7.5 \pm 0.1$  with dilute sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to enhance the disinfection efficiency of free chlorine. Hypochlorous acid ( $\text{HOCl}$ ) is more reactive than hypochlorite ( $\text{OCl}$ ) and the relative proportion of  $\text{HOCl}$  to  $\text{OCl}$  is inversely related to pH. At pH 7.5, the two types of free chlorine appear equally. However, below pH 7.5, hypochlorous acid predominates and above pH 7.5 the hypochlorite ion is the main form (Singer, 1988).

Simulated ballast waters (i.e., HW-1 plus S#1, HW-2 plus S#2, HW-3 plus S#3) were prepared by adding an appropriate amount of sediment in 30 to 50 L sub samples of harbour water to achieve the following nominal sediment concentrations of 0 (control), 10, 100 and 1,000 ppm (on a volume:volume basis) using a chlorine-mixing apparatus (see Appendix B).

A sufficient amount of chlorine (as  $\text{NaOCl}$ ) was added to each 30 to 50 L water:sediment mixture to achieve each target concentration of chlorine in sequence, beginning with 0 ppm TRC and increasing sequentially from lowest to highest concentration (i.e., 0.63, 1.25, 2.5, 5.0 and 10 mg/L). After each TRC level was achieved and maintained for a period of approximately five minutes, sub samples of the mixture were removed for toxicity testing and for additional testing related to formation of disinfection by products (see Section 6). Toxicity tests were initiated on average within 20 minutes of achieving each TRC level. The total elapsed time for a given sediment level (i.e., from initiation of chlorine dosing to initiation of the toxicity exposure for the highest TRC level) on average was 95 minutes. While it is recognized that this procedure resulted in some differences in contact time between low and high chlorine concentrations, the differences were considered to be negligible in light of the total duration of the toxicity test exposure (i.e., 48 hr).

The mixing system consisted of a 100 L polyethylene cylindrical tank (Appendix B). Mixing was accomplished by means of a centrifugal pump mounted externally to the tank such that the tank contents were drawn from the bottom and returned to the top of the tank. An automated dosing system was replaced by manual dosing of sodium hypochlorite into the solution tank after it was determined that the chlorine probe was not able to detect the changes in the chlorine levels as rapidly as they occurred.

Sub samples of the simulated ballast waters from the highest chlorine treatments (10 ppm TRC) were analysed for Total Suspended Solids (TSS) as a measure of the efficiency of the mixing apparatus. All chlorine concentrations were verified by measurement using the DPD Colorimetric method for Total Chlorine Residual (Hach Method 8167). The total amount of hypochlorite required to achieve set-points, volumes of solutions dosed, and dosing times were recorded for each treatment level.

Upon stabilization of each total residual chlorine concentration, a 1 L sample was removed and split into four 250-ml sub samples for toxicity testing. Three of the sub-samples were transferred to 300-ml test chambers to be used as the replicate solutions for the toxicity test, while the fourth was used to measure general water quality parameters. Additionally, a 5L sample of the test solution was collected from the lowest (0 ppm TRC) and highest (10 ppm TRC) and set aside for additional testing related to the formation of disinfection by-products. All sub-samples were collected while the mixing apparatus was operational to ensure that the samples were homogeneous. Sediment levels in each of the individual replicate exposures were observed to be similar but this was not verified by analytical measurement, except for the 10 ppm non-chlorinated control treatments (i.e., one replicate analysed for TSS at the 0, 10, 100 and 1000 ppm sediment, 10 ppm TRC).

### 5.2.3 Bioassay Procedures

Laboratory toxicity tests were conducted at  $15 \pm 1^\circ\text{C}$ . This temperature was considered representative of the average Great Lakes temperature when treatment is likely to occur (i.e., between March and December), and within the preferred thermal range of a variety of aquatic species in the Great Lakes. Test results were based on a static, acute 48-hour exposure using 2 to 15 d old *Hyalella azteca*. The calculated endpoints were the 48-h LT90 (i.e., time in hours estimated to cause 90% mortality of the test organisms within a 48-h period) and 48-h LC90 (i.e., the concentration of test material in water estimated to cause 90% mortality of the exposed organisms within a 48-h period). A summary of the toxicity test conditions is provided in Appendix D.

Sodium hypochlorite efficacy testing was conducted in a zero (i.e., 0 ppm nominal, no sediment added), low (i.e., 10 ppm), intermediate (i.e., 100 ppm) and an elevated (i.e., 1,000 ppm) level of sediment. The sediment levels were chosen to represent the possible range of solids that may be taken up in ballast water during ballasting in the Great Lakes, including what is expected to be an elevated sediment level (i.e., 1,000 ppm) as a worst-case scenario.

Records of mortality, temperature, pH, dissolved oxygen (DO), and TRC concentration were taken throughout the testing period at 0 hr, 2 hr, 24 hr, and 48 hr. All data were recorded and then entered into an electronic bench sheet. Appendix B, Table B.2 details the lab equipment that was used in the laboratory toxicity testing. Tests were considered invalid if the mean survival for the control treatment was <90%.

### 5.2.4 Reference Toxicant Testing

Reference toxicant tests were conducted to evaluate the health of the test organisms, the suitability of the test system, and the performance of the technical staff. The reference toxicant used was copper sulphate. Control charts documenting this performance are provided in Appendix D.

### 5.2.5 Statistical Analysis

48-h LC90 and LT90 and their 95% confidence limits were calculated using linear interpolation method with the program TOXSTAT (West and Gulley, 1996). The LC90 is defined as the concentration of the test substance that is estimated to be lethal to 90% of the animals exposed to that concentration within a prescribed time interval. The LT90 is defined as the time that is estimated to cause death to 90% of the test animals at a specified exposure concentration.

## 5.3 Results

### 5.3.1 Chemical Characterization of Water and Sediment Samples

After the water samples were composited, a sub sample was analyzed for DO, pH, temperature and conductivity. Results for the initial sample collected on May 27<sup>th</sup> are provided in Table 5.5.

**Table 5.5: General Water Chemistry Characteristics of Hamilton Harbour Water (May 27, 2003)**

Parameter	Measured In the Field	Measured In the Laboratory
pH	8.39	8.5
Temperature (°C)	13.8	15.0
Dissolved Oxygen (mg/L)	12.5	11.3
Conductivity (µs)	802	838

Additional water quality characteristics of the Hamilton Harbour water (pH adjusted to  $7.5 \pm 0.1$ ) are shown in Table 5.6. Harbour waters collected in May and June had similar concentrations of TOC, DOC, humic substances and ammonia. The sample collected in August had similar levels of TOC and DOC, but had lower concentrations of ammonia (order of magnitude), and to a lesser extent, humic substances.

**Table 5.6: Hamilton Harbour Water Characteristics**

Sample Description	Ammonia as N	TOC	DOC	Humic Substance
	ppm	ppm	ppm	ppm
EQL	0.05	0.5	0.5	-
HW-1 (May 27, 2003)	0.98	4.2	3.6	7.7
HW-2 (Jun 16, 2003)	0.85	4.3	3.8	7.7
HW-3 (Aug 11, 2003)	0.09	5	3.8	5.8

Sediment samples were characterized for certain physical (including particle size and % moisture) and chemical parameters (including DOC and metals). From Table 5.7 it can be seen that the sediments were similar in terms of particle size distribution with the largest components consisting of silt and clay. TOC levels were similar for sediments #1 and #2 (2.5 to 2.6 ppm), but slightly lower than sediment #3 (4.48 ppm). In terms of the heavy metals, concentrations of copper, zinc and iron were higher in sediment #3 than sediments #1 and #2, while barium was higher in sediment #1 relative to sediments #2 and #3.

**Table 5.7: Sediment Characterization**

<b>Analysis</b>	<b>Units</b>	<b>S#1</b>	<b>S #2</b>	<b>S #3</b>	<b>EQL<sup>a</sup></b>
<b>Total Metals</b>					
Aluminum, Al	(mg/kg)	17100	16200	12700	5
Barium, Ba	(mg/kg)	694	81	93	4
Beryllium, Be	(mg/kg)	1.2	1.2	0.9	0.5
Boron, B	(mg/kg)	21	19	36	2
Cadmium, Cd	(mg/kg)	<0.5	<0.5	<0.5	0.5
Calcium, Ca	(mg/kg)	28800	35400	10800	10
Chromium, Cr	(mg/kg)	18	46	113	2
Cobalt, Co	(mg/kg)	15	12	32	2
Copper, Cu	(mg/kg)	93	48	401	2
Iron, Fe	(mg/kg)	10600	33600	158000	4
Lead, Pb	(mg/kg)	91	69	136	5
Magnesium, Mg	(mg/kg)	10600	10400	6500	2
Manganese, Mn	(mg/kg)	950	1910	2140	2
Mercury, Hg	(mg/kg)	0.17	0.34	0.5	0.01
Molybdenum, Mo	(mg/kg)	2	<2	23	2
Nickel, Ni	(mg/kg)	70	30	121	5
Potassium, K	(mg/kg)	2810	4220	2420	20
Silver, Ag	(mg/kg)	<1	<1	<1	1
Sodium, Na	(mg/kg)	8620	21400	839	50
Strontium, Sr	(mg/kg)	84	125	95	2
Titanium, Ti	(mg/kg)	608	298	285	2
Total Phosphorus, P	(mg/kg)	1100	1430	2990	5
Vanadium, V	(mg/kg)	60	44	66	2
Zinc, Zn	(mg/kg)	1460	496	3950	1
<b>Particle Size</b>					
Total Gravel	%	<0.1	<0.1	0	0.1
Total Sand	%	8.8	2.0	6.8	0
Total Silt	%	60.2	54.8	54.7	0
Total Clay	%	30.9	43.2	38.5	0
<b>TOC (as C)</b>	%	2.52	2.60	4.48	0.01
<b>Percent Moisture</b>	%	63.8	65.3	53.2	

<sup>a</sup> EQL – Estimated Qualification Limit

### 5.3.2 Toxicity Test Results

All toxicity tests were conducted in triplicate and all test solutions were checked for mortalities and concentrations of TRC at 0, 0.5, 2.0, 24 and 48 hrs. All raw data (including observations of mortality, water quality parameters, concentrations of TRC) along with graphical illustration of the chlorine decay rates are summarized in the toxicity test reports (Appendix D).

In the present study, sediment concentration was shown to be a significant contributor to chlorine demand (defined as any inorganic or organic compound which is capable of reducing the amount of chlorine added to a solution). As such, any substance capable of contributing to chlorine demand will also reduce its efficacy by lowering the residual chlorine level. When interpreting the following results, it should be noted that an attempt was made to satisfy the chlorine demand, by maintaining each target chlorine residual for a period of five minutes prior to initiation of the static test exposure.

Toxicity test results were expressed in terms of an LC90 (i.e., the concentration of test substance, in this case mg/L TRC, that is estimated to cause 90% mortality of the test organisms within the 48-h exposure period), and in terms of an LT90 (i.e., the time estimated to cause 90% mortality of the test organisms for a given exposure concentration of TRC). All results were based on measured concentrations at the beginning of the test. As such, estimates of the LC/LT90s should be viewed as conservative, since the concentration of chlorine decreased over time.

#### 5.3.2.1 Effect of Sediment Level on Chlorine Toxicity over Time

From Table 5.8, it can be seen that sediment concentration had no effect on the toxicity of chlorine to *H. azteca* at low to intermediate sediment concentrations (0 (nominal) to 100 ppm), but reduced toxicity marginally at higher concentrations (1,000 ppm). The 48-h LC90s for chlorine (as TRC) were generally similar (2.4 to 3.1 ppm) for the 0, 10 and 100 ppm sediment concentrations of sediments #1 and #2. The 48-h LC90s were also similar (4.45 to 4.50) for the highest sediment concentration (1,000 ppm) of sediments #1 and #2, but marginally higher than those observed for the 0 to 100 ppm sediment concentrations. A similar trend was observed for sediment #3, except that 48-h LC90s were higher (4.49 to 4.56 for 0 to 100 ppm sediment; 9.08 for the 1000 ppm sediment) than those observed for sediments #1 and #2. The reduced efficacy of chlorine observed in sediment #3 relative to sediments #1 and #2 may have been related to a (ten-fold) lower concentration of ammonia (Table 6.2).

Reactions of chlorine with ammonia produce combined chloramines (mono-, di- and trichloramines). While the toxicity of chloramines relative to free chlorine is not well established, there is evidence to suggest that chloramines are more toxic than free chlorine (Crumley et al. 1980, White 1999). It was also observed that TRC levels at the end of the test were generally lower in sediment #3 relative to sediments #1 and #2, which may also have been related to ammonia concentration. A slower rate of decay would tend to enhance overall efficacy of chlorine.

### 5.3.2.2 Effect of Sediment Level on Survival Time at Various Chlorine Concentrations

The effects of sediment level on survival time of *H. azteca* exposed to varying concentrations of chlorine in the simulated ballast waters are summarized in Table 5.9. Overall, sediment concentration had no effect on the survival time of *H. azteca* if the chlorine concentration was high enough (10 ppm). This effect was clear for sediment #3, and for the 0, 10 and 100 ppm concentrations of sediments #1 and #2.

The range of LT90s observed for the highest chlorine concentration (10 ppm) was 14.6 to 18.7 h. Results for the highest sediment and TRC concentration for sediments #1 and #2 are somewhat anomalous, since  $\geq 90\%$  mortality was not achieved within the 48h exposure period. However, results may be explained by examination of the chlorine decay rates (Appendix D), where at the highest sediment concentration, chlorine decay was more rapid for sediments #1 and #2, than for sediment #3.

**Table 5.8: Effect of Exposure Duration and Sediment Level on the Toxicity of Chlorinated Hamilton Harbour Water to *Hyalella Azteca*.**

Table values include LC90 concentrations and 95% confidence limits in parentheses.

Time (in hrs)	Sediment Concentration (ppm)			
	0	10	100	1000
<b>Sediment #1</b>				
0	>12.5	>10.7	>10	>9.6
0.5	>12.5	>10.7	>10	>9.6
2	>12.5	>10.7	>10	>9.6
24	3.5(3.2-3.9)	9.9(4.8-10.7)*	9.3(4.75-10.0)*	>9.6
48	3.1 (1.9-3.9)	2.62(1.4-4.8)	2.8(1.9-4.0)	4.45(4.26-4.50) <sup>1</sup>
<b>Sediment #2</b>				
Time (hrs)				
0	>12	>13	>9.8	>9.8
0.5	>12	>13	>9.8	>9.8
2	>12	>13	>9.8	>9.8
24	4.0 (3.7-4.2)	6.4 (3.9-10.5)	3.2 (2.0-3.7)	4.97(4.48-4.98) <sup>1</sup>
48	2.8 (1.7-4.3)	2.40(1.37-5.10)	2.4 (2.2-2.8)	4.5(4.1-4.7) <sup>1</sup>
<b>Sediment #3</b>				
Time (hrs)				
0	>10.2	>10.4	>10.9	>10.1
0.5	>10.2	>10.4	>10.9	>10.1
2	>10.2	>10.4	>10.9	>10.1
24	4.57 (4.46-4.73)	5.03 (4.85-5.19)	4.6(2.48-4.95)*	9.33 (9.15-9.44)
48	4.52 (4.38-4.63)	4.49 (3.15-5.30)	4.56 (4.49-4.62)	9.08 (8.44-9.43)

\*estimated value

<sup>1</sup> mortality from highest concentration removed from calculations

**Table 5.9: Effect of Sediment Level on Survival Time of *Hyaella Azteca* Exposed to Varying Concentration of Chlorine in Hamilton Harbour Water**

Table values include LT90 and 95% confidence limits in parentheses.

<b>Sediment Concentration (ppm)</b>				
<b>Nominal TRC (ppm)</b>	<b>0</b>	<b>10</b>	<b>100</b>	<b>1000</b>
<b>Sediment 1</b>				
Control	>48	>48	>48	>48
0.63	>48	>48	>48	>48
1.25	>48	>48	>48	>48
2.5	>48	>48	>48	>48
5.0	18.6(17.8-18.9)	44.7(44.5-44.8)	44.5(44.3-44.9)	44.8(24.0-48.0)*
10.0	18.0(15.6-19.5)	18.7(2.0-24.0)*	17.6(14.1-18.9)	>48
<b>Sediment 2</b>				
Control	>48	>48	>48	>48
0.63	>48	>48	>48	>48
1.25	>48	>48	>48	>48
2.5	>48	48	33.9(16.4-70.2)	>48
5.0	17.4 (14.4-19.2)	28.5(19.8-41.0)	18.7(2.0-24.0)*	21.9(15.2-55.0)
10.0	14.6(7.3-17.4)	18.2(16.9-19.3)	18.2(16.9-19.3)	>48
<b>Sediment 3</b>				
Control	>48	>48	>48	>48
0.63	>48	>48	>48	>48
1.25	>48	>48	>48	>48
2.5	>48	>48	>48	>48
5.0	18.7(2.0-24.0)*	18.7(2.0-24.0)*	18.7(2.0-24.0)*	>48
10.0	18.7(2.0-24.0)*	18.7(2.0-24.0)*	18.6(17.8-18.9)	18.6(17.8-18.9)

\*estimated value

**Table 5.10: Chlorine Demand of Simulated Ballast Waters with Different Sediment Levels Dosed to Approximately 10 ppm Total Residual Chlorine**

	<b>Sediment 1</b>	<b>Sediment 2</b>	<b>Sediment 3</b>
<b>Sediment Level (ppm sediment added)</b>	<b>chlorine (ppm)</b>		
0	7.93	1.37	2.16
10	11.35	4.97	0.25
100	14.75	6.01	-0.22
1000	15.71	19.87	4.77

The amount of sodium hypochlorite required to achieve the prescribed chlorine dose in the presence of the various levels of sediment was recorded and the amounts are provided in the test reports in Appendix C. From Table 5.10 it can be seen that the addition of sediment increased the chlorine demand (defined as the difference between the amount of chlorine added and the amount remaining for a given time) of the simulated ballast waters. A comparison of the results for the three sediments showed that chlorine demand was higher for sediments #1 and #2 as compared to sediment #3. Concentrations of ammonia, and to a lesser extent, humic substances, were higher in ballast waters prepared from sediments #1 and #2 than for those prepared from sediment #3. Humic substances and ammonia are known to contribute to chlorine demand and may account for the differences observed for these sediments.

For sediment #3, chlorine demand for the intermediate sediment concentrations (10 and 100 ppm) was lower than that observed for the lowest sediment concentration (i.e., no sediment added). These results cannot be explained at this time but may be related to sampling error, measurement error, interference or a combination of the above. Oxidized forms of manganese and chromium may react and read as chlorine (DPD Colourimetric Method). Concentrations of chromium and manganese (Table 5.7) were highest in the sediment #3 (113 and 2,140 mg/kg, respectively) as compared to sediments #1 (18 and 950 mg/kg, respectively) and #2 (46 and 1,910 mg/kg, respectively). However, dissolved concentrations in the ballast waters were below detection for chromium and did not exceed 49 ppb for manganese. Low levels of chlorine (< 0.09 ppm) were detected in the non-chlorinated ballast water samples, suggesting the presence of a small but negligible amount of interference.

## 6. EFFECT OF SEDIMENT ON THE FORMATION OF DISINFECTION BYPRODUCTS (DBPs)

This portion of the project was designed to determine the effect of sediment on the amount and type of DBPs formed during the chlorination/dechlorination of ballast water. The total residual chlorine of 10 ppm was selected as a reasonable exposure concentration, based on the results of a previous study that demonstrated inactivating most types of organisms at this level.

### 6.1 Sample Handling and Preparation

Simulated ballast water samples for determination of Disinfection By-Product (DBP) formation during ballast water treatment with sodium hypochlorite were prepared at the same time as the samples for toxicity testing, as described under Section 5. A total of 24 samples were submitted for chemical analysis (i.e., three sediments (S#1, S#2, and S#3), four sediment concentrations (0, 10, 100, and 1000 ppm), and two TRC concentrations (0 and 10 ppm). Sub-samples (approximately 5 L) from each of these treatments were stored in a new, clean, 7-L polyethylene plastic container lined with a food-grade polyethylene liner. All samples were held at 15°C in the dark for 48 hours. This time interval was considered representative of the shortest treatment time that was likely to be encountered during a short voyage in the Great Lakes.

Measurements of temperature, D.O., pH, conductivity, and TRC were made upon completion of the chlorination process and after 48 h storage at 15°C. After 48 hours, test solutions were dechlorinated using sodium bisulfite. The amount of bisulfite added was based on the TRC concentration remaining in test chambers at the end of the exposure. Dechlorination was conducted using the following formula:

$$\text{Sodium Bisulphite Dose (mg/L)} = \text{TRC (mg/L)} \times 1.34$$

The above mentioned ratio of 1.34 differs from the value of 1.46 given by White (1999) [3]. Regardless, final measurements of TRC were made to ensure dechlorination was complete (i.e., < 0.01 ppm TRC). Water quality parameters (including temperature, DO, pH and conductivity) of the ballast waters were measured after dechlorination to determine the impact of dechlorination on the test water.

### 6.2 Chemical Analyses

A summary of the non-chlorinated and chlorinated ballast water samples were analyzed for the parameters listed in Table 6.1. There were 12 samples for analysis, with one sample submitted in duplicate to establish representativeness for QA/QC (13 samples total).

**Table 6.1: Summary of Analyses Performed on Simulated Ballast Waters**

Parameters	Ballast Waters	
	Non-chlorinated (0 ppm TRC)	Chlorinated (10 ppm TRC)
TSS		X
Total Dissolved Metals <sup>1</sup>	X	X
Humic substance	X <sup>a</sup>	X <sup>a</sup>
TOC	X	
DOC	X	
HAA's <sup>2</sup>	X <sup>b</sup>	X
THM's <sup>3</sup>	X <sup>b</sup>	X
Acid Base Neutral and Extractable Organics	X	X
TRC <sup>4</sup>	X	X

<sup>1</sup>Total Dissolved Metals include those listed in Appendix C.

<sup>2</sup>Haloacetic acids: Chloroacetic acid, Bromoacetic acid, Dichloroacetic acid, Trichloroacetic acid, Bromochloroacetic acid, and Dibromoacetic acid.

<sup>3</sup>Trihalomethanes: Chloroform, Bromodichloromethane, Chlorodibromomethane, and Bromoform.

<sup>4</sup>DPD (HACH)

<sup>a</sup> 0 and 1000 ppm sediments only

<sup>b</sup> 0 ppm sediment only

## 6.3 Results

### 6.3.1 General Water Quality Characteristics of Simulated Ballast Waters

A summary of the water quality characteristics of the chlorinated and non-chlorinated ballast waters is provided in Table 6.2. Sediments #1 and #2 had similar concentrations of ammonia (0.7 to 1.0 ppm) that were an order of magnitude higher than that measured in Sediment #3. The concentrations of humic substances were also slightly higher in sediments #1 and #2, relative to sediment #3. Concentrations of humic substances increased in the presence of chlorine for sediments #1 and #2, but decreased in the case of sediment #3. It is not known if these differences are related to some interference related to the presence of chlorine. Concentrations of TOC (3.9 to 5.7 ppm) and DOC (3.3 to 4.1 ppm) were similar for all sediments and sediment levels. Total suspended solids were measured in the chlorinated samples only and reflect the amounts of sediment added to the harbor water samples.

### 6.3.2 Trihalomethanes (THMs)

The effect of chlorination on trihalomethane formation is summarized in Table C-1 (Appendix C). Simulated ballast waters were dosed at two levels of chlorine (0 and 10 ppm TRC nominal concentration). The non-chlorinated controls contained no detectable levels of THMs. However, trihalomethanes, in particular, chloroform and bromodichloromethane were detected in the treatment simulations dosed to 10 ppm TRC (nominal concentration) and generally increased with increasing sediment concentration. Chloroform was the largest contributor to trihalomethanes, followed by bromodichloromethane.

**Table 6.2: General Water Quality Characteristics of Simulated Ballast Waters.**

Sample Description			NH <sub>3</sub> as N (ppm)	TOC (ppm)	DOC (ppm)	TSS (ppm)	Humic Substance (ppm)
Sediment #	Sediment Level (ppm)	Nominal TRC (ppm)					
1	0	0	0.98	4.2	3.6	-	7.7
1	10	0	0.98	3.8	3.6	-	-
1	100	0	0.94	3.8	3.4	-	-
1	1000	0	0.87	5.5	3.3	-	10
1	0	10	-	-	-	< 5	-
1	10	10	-	-	-	6	-
1	100	10	-	-	-	86 <sup>a</sup> /101	-
1	1000	10	-	-	-	874	-
2	0	0	0.85	4.3	3.8	-	7.7
2	10	0	0.81	4.3	4.1	-	-
2	100	0	0.73	4.4	3.9	-	-
2	1000	0	0.81	5	3.9	-	9.4
2	0	10	-	-	-	< 5	-
2	10	10	-	-	-	6	-
2	100	10	-	-	-	45	-
2	1000	10	-	-	-	788	-
3	0	0	0.09	5	3.8	-	5.8
3	10	0	0.07	3.9	3.6	-	-
3	100	0	0.06	4.2	3.8	-	-
3	1000	0	< 0.05	5.7	3.3	-	4.7
3	0	10	-	-	-	< 5	-
3	10	10	-	-	-	8	-
3	100	10	-	-	-	53	-
3	1000	10	-	-	-	802	-
EQL			0.05	0.5	0.5	5	-

<sup>a</sup> Duplicate sample

### 6.3.3 Halo-Acetic Acids (HAAs)

Table C-2 (Appendix C) summarizes the results for Halo-Acetic Acids (HAAs) formation. As indicated above, simulated ballast waters were dosed at two levels of chlorine (0 and 10 ppm TRC nominal concentration). The non-chlorinated controls contained few detectable HAAs. However, HAAs in particular, dichloro-acetic acid and trichloro-acetic acid were present in the treatment simulations dosed to 10 ppm TRC (nominal concentration) and increased with increasing sediment level.

#### 6.3.4 Acid Extractable and Base Neutral Organics

Simulated ballast waters were analyzed for acid extractable organics (e.g., phenol and o-cresol) and base neutral organics (e.g., naphthalene and pyrene). Simulated ballast waters using the first and second sediment samples showed that all acid extractable organics were below the estimated qualification levels and therefore treatment simulations using the third sediment sample were not analyzed. Base neutral organics for simulations using the first sediment were all below the estimated quantification limits. For simulations using the second sediment, some base neutral organics were detected in both the chlorinated and non-chlorinated samples. However, for those detected, there was either no difference or only a slight increase between the chlorinated and the non-chlorinated samples.

#### 6.3.5 Heavy Metals

Samples were analyzed for 31 dissolved metals and major ions (Table C-3, Appendix C). Comparisons were made between the dissolved metals in the non-chlorinated controls and the treatment simulations dosed to 10 ppm chlorine (nominal concentration). Table values are included only for those metals that showed an increase in concentration relative to the non-chlorinated controls. There was no apparent increase in metal concentrations due to the addition of chlorine except for silicon, copper, manganese and sodium. The increase in sodium was to be expected as this resulted from the addition of chlorine in the form of sodium hypochlorite.

Issues related to the formation of DBPs are further discussed in Section 7.

## 7. DISCHARGE OF BALLAST WATER TREATED WITH HYPOCHLORITE

### 7.1 Legality of Treated Ballast Water Discharges

Ballast water discharges are exempted from the U. S. federal requirement to obtain a discharge permit under the National Pollutant Discharge Elimination System (NPDES Permit). This exemption is contained in regulations at 40 CFR 122.3(a). This exemption was originally promulgated in 1973, and was recently upheld by the U. S. Environmental Protection Agency (USEPA) on September 2, 2003[4]. The recent decision was in response to a petition by several West Coast organizations which were concerned about foreign invasive species in ballast water. In effect, this means that U. S. federal regulations to control ballast water will be developed by the U. S. Coast Guard (USCG) under the National Invasive Species Act (NISA), rather than regulated by USEPA under the existing NPDES Permit system which controls industrial and municipal wastewater.

Current USCG regulations to deal with the foreign species issue in ballast water require ballast water exchange on the high seas for ships entering the Great Lakes system. The ships declaring “no ballast on board” (NOBOB) have no ballast treatment or control requirements under NISA. These NOBOB ships constitute an estimated 70 to 90 percent of the ships entering the Great Lakes [5,6,11.2.1]. Certain management practices for ballasting ships are required by the St. Lawrence Seaway Management Corporation of Canada and the St. Lawrence Seaway Development Corporation as a condition of passage through the St. Lawrence Seaway.

There are currently no explicit U. S. or Canadian federal regulations of the type used to control conventional industrial and municipal discharges which directly apply to ballast water. Ballast water can be discharged legally in the Great Lakes without limitations on the foreign species it contains. For chemical residuals that could occur in ballast water discharges as a result of biocide treatment, there are some jurisdictional requirements based on state/provincial laws. These jurisdictions have been polled and their requirements are summarized in Table 7.1. As shown in Table 7.1, there is little consistency in these jurisdictional legal requirements.

Since international shippers ballast ships throughout the world, this is not just a national issue. The International Maritime Organization (IMO) has recently established standards for ballast water [7]. However, there are presently no international standards for biocidal efficacy or for protection of the receiving waters from biocide residuals. Discussions with the IMO indicate that a few countries have required biocide addition to ballast water prior to discharge. This was usually done to kill pathogenic microorganisms, such as cholera. In some cases, this was done when ships had been ballasted in locations identified by the World Health Organization as contaminated. The biocide usually employed for this purpose was sodium hypochlorite, which is readily available as household bleach. The IMO indicated that they are not aware of any legislation in any countries that specifically addresses biocide residuals in ballast water discharges.

In the U. S., biocides such as sodium hypochlorite must be registered for use as “pesticides” in each type of application. For example, sodium hypochlorite is a registered pesticide for use in disinfecting drinking water and treated sewage. However, no biocides are now listed in the U. S. EPA’s register of pesticides for use in ships’ ballast water. This would need to be done by the manufacturer of the chemical before it is used for that purpose. Part of this process entails providing written instructions on the label for use of the pesticide in each particular application. These instructions must be followed by the user. The state of New York also has a pesticide registration process, which forms its regulatory process for ballast water biocides (see Table 7.1).

## **7.2 Environmental Acceptability of Treated Ballast Water Discharges**

Although there is no clear and consistent regulatory basis for determining effluent limits for treated ballast water, there are water quality criteria and standards that apply to Great Lakes waters which receive ballast water discharges. These water quality criteria and standards can be used to determine the environmental acceptability of ballast water discharges. These water quality criteria and standards were used by the various jurisdictions to determine the “discharge limits” for residual chlorine shown in Table 7.1.

U. S. federal Great Lakes Initiative (GLI) Guidance, contained at 40 CFR 132, and State of Michigan water quality standards, which are consistent with that federal guidance, are used in this report to determine actual or theoretical discharge limits for chlorination by-products. The guidance and standards are designed to protect designated uses of the Great Lakes, including aquatic life, wildlife, and human health. All Great Lakes states are required to have state standards consistent with the GLI guidance.

**Table 7.1: Discharge Authorization Requirements for Treated Ballast Water**

Jurisdiction	Type of Authorization		Total Residual Chlorine Discharge Limit (ug/L) (actual or theoretical)	Additional Information
	Required	Request		
Illinois	none	n/a	n/a	--
Indiana	none	n/a	19	Practical limit = 60 (limit of quantitation)
Michigan	State approval under "Rule 97"	letter	38	Rule 97 is used to regulate chemicals applied for "water resource management"
Minnesota	State letter of approval needed	letter	38	Biocide is approved as a "treatment additive"
New York	Pesticide registration for use in ballast water by EPA and the State	application for registration	19	Registration is done by NY Bureau of Pesticide Management
Ohio	none	n/a	n/a	--
Pennsylvania	none	n/a	19	If ballast water were routinely treated, PA might consider regulation
Wisconsin	State general discharge permit	permit application	38	If ballast water were routinely treated, WI would issue a specific permit for ballast water
Canada (Ontario)	none	n/a	20	Environment Canada is in the process of establishing a criterion of 0.02 ppm TRC in treated sewage. A similar criterion for treated ballast water is considered scientifically appropriate

1. The US Federal government exempts ballast water discharges from the NPDES discharge permit requirement.
2. Some states, including Michigan and Indiana, allow somewhat higher TRC limits for intermittent discharges. However, that is a moot point because neutralization of TRC would still be needed.
3. Some jurisdictions have a general, non-quantitative prohibition against discharge of "harmful" substances.

### 7.3 Specific Discharge Concerns of Treated Ballast Water

The issues associated with the discharge of hypochlorite-treated ballast water include the following:

1. Acute toxicity to aquatic life due to chlorine residual (usually referred to as “total residual chlorine” or “TRC”).
2. Chlorination by-products that may exhibit acute or chronic toxicity to aquatic life or be deleterious to human health or wildlife.
3. The potential for liberation of metals from the ballast tank sediments into the overlying water and subsequent release of additional toxic metals when the ballast water is discharged.
4. The potential for harmful effects of dechlorinating chemicals, if they are added to treated ballast water to minimize the TRC in the discharge.

These issues were raised by the Michigan Environmental Science Board (MESB) during its review of the first ballast water biocide study [2]. This project developed a large amount of data to address these concerns. In order to provide adequately controlled experiments, the data were obtained by laboratory simulations of ballast water treatment.

The simulated ballast waters and controls were prepared in the laboratory by using water taken from Hamilton Harbour at times when international bulk carriers were being ballasted. Sediments from bulk carriers’ ballast tanks were collected prior to the ballasting operations. These sediments were added to the harbour water in controlled amounts to simulate various ballast water/sediment mixtures. Then, sodium hypochlorite was added in controlled dosages. After 48 hours, an approximation of the minimum voyage time, the simulated treated water was dechlorinated and analyzed. See Section 6 and the Appendices for more detail on the experimental procedures, and the actual analytical data that were generated.

The results of this project must be viewed in light of its inherent limitations: It was not possible to study all possible types of ballast water and sediment. The results are based on laboratory-scale ballast water simulations, rather than actual ballast tank testing. Statistical rigor could be increased by additional replications. However, the results discussed below add a great deal of information which can be used in making judgments on the legality and safety of discharges of ballast water treated with sodium hypochlorite.

#### 7.3.1 Acute Toxicity from Biocide Residual

Any biocide must be lethal to a wide range of species to be effective. However, residuals of the biocide must not cause significant toxicity to aquatic species when released with the discharged ballast water. This was examined as follows:

As expected in the treatment simulations, the TRC contained in the simulated ballast water decreased over time, following the initial dosing with sodium hypochlorite. However, in every ballast water simulation, there was TRC present in the simulated ballast water after 48 hours at concentrations above the acutely toxic level. Those TRC concentrations varied from 0.050 mg/l to 5.80 mg/l. The discharge concentration considered acceptable to protect aquatic life from acute toxicity varies from 0.019 to 0.038 mg/l in the Great Lakes jurisdictions (see Table 7.1). In the case of intermittent discharges, some jurisdictions allow a slightly higher level. However, it is clear from the data that neutralization of the TRC will be necessary to avoid acute toxicity in the receiving waters from these levels of TRC. Such “dechlorination” is commonly practiced at sewage treatment plants where various forms of chlorine are used for disinfection.

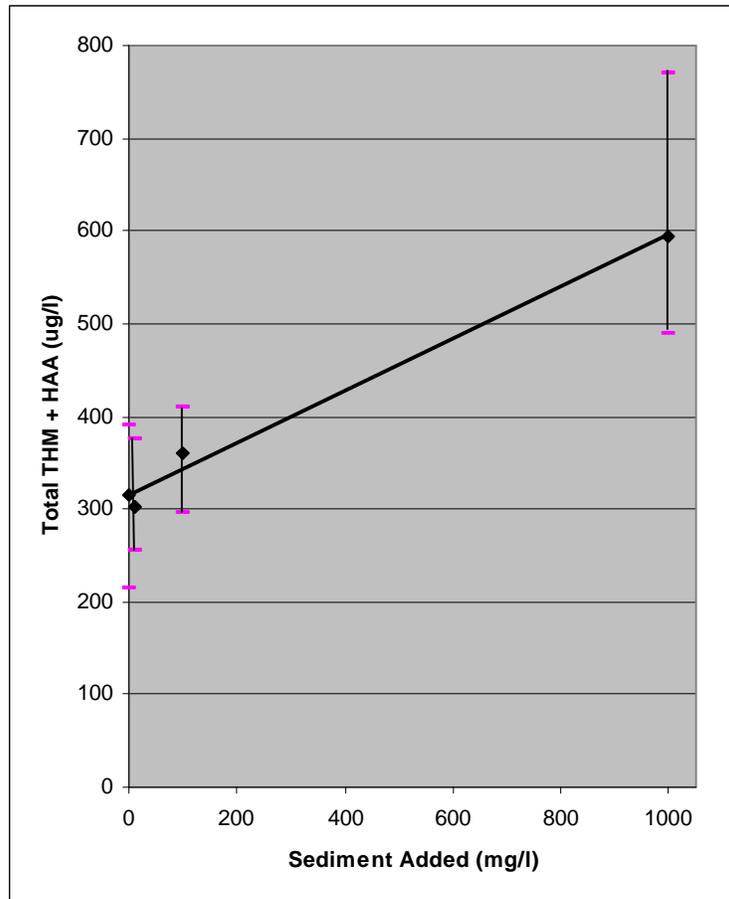
Sodium bisulfite is often used for dechlorination at sewage treatment plants, and was used in these tests to treat the simulated ballast water following the 48-hour biocide exposure. In every ballast water simulation, the dechlorination with sodium bisulfite reduced the TRC to less than 0.01 mg/l. Thus, the concern about toxicity due to TRC is resolved by using this common dechlorination technique.

### 7.3.2 Toxicity Due to Chlorination Byproducts

In addition to direct toxicity of biocide residuals, there is concern about the creation of chlorination by-products. In particular, there are many studies which demonstrate that chlorinated organic compounds can be created when water containing organic materials is treated with sodium hypochlorite or with chlorine gas [8]. In particular, the formation of chloroform and other trihalomethanes, along with halo-acetic acids has been documented. The amounts of chlorination by-products produced by treatment of ballast water were examined as follows:

Twelve types of simulated ballast waters that were dosed to 10 mg/l sodium hypochlorite, along with four types of non-chlorinated controls, were analyzed for up to 119 organic compounds, including the trihalomethanes and haloacetic acids. The samples were taken at the end of the 48-hour test period and, where applicable, following dechlorination.

The non-chlorinated controls contained no detectable trihalomethanes, and few detectable halo-acetic acids. Trihalomethanes and halo-acetic acids were present in the treatment simulations dosed to 10 mg/l sodium hypochlorite. It is clear that these compounds were formed as a result of sodium hypochlorite addition. The compounds that showed the most significant increase with chlorination were chloroform, dichloroacetic acid, and trichloroacetic acid. These data are summarized in Table 7.2. The levels of these three compounds increased somewhat with increasing sediment as illustrated in Table 7.2 and Figure 7.1. This is undoubtedly due to increasing amounts of organic precursors contained in the sediments.



Note: Although suspended solids concentrations in the harbour water were less than the estimated quantitation limit of 5 mg/l, precursors for trihalomethanes (THM) and haloacetic acids (HAA) were present. The harbour water contained an average total organic carbon content of 4.5 mg/l and an average dissolved organic carbon content of 3.7 mg/l. Humic substances averaged 7.1 mg/l. Thus, at the zero sediment added level, total THM and HAA averaged more than 300 ug/l.

**Figure 7.1: Increase in Disinfection By-products with Increasing Sediment.**

**Table 7.2: Halogenated By-products in Chlorinated Ballast Water**

Chemical Name (& Formula)	EQL (ug/l)	Average Concentrations (ug/l) in Simulated Ballast Water Discharges (dosed at 10 mg/l Cl <sub>2</sub> )				Theoretical Discharge Limits (ug/l)
		none added	10 mg/l	100 mg/l	1000 mg/l	
Sediment added						
<b>Trihalomethanes (THMs)</b>						
Chloroform (Cl <sub>3</sub> CH)	0.2	66	75	88	200	770
Bromodichloromethane (Cl <sub>2</sub> BrCH)	0.2	20	21	22	35	68
Chlorodibromomethane (ClBr <sub>2</sub> CH)	0.2	11	11	11	10	68
Bromoform (Br <sub>3</sub> CH)	0.2	0.6	0.6	0.3	0.2	520
Total THMs	n/a	96	107	122	247	n/a
<b>Haloacetic Acids (HAAs)</b>						
Monochloroacetic Acid (ClCH <sub>2</sub> -COOH)	5	n.d.	2.2	4.3	1.7	NR
Dichloroacetic Acid (Cl <sub>2</sub> CH-COOH)	5	59	60	83	142	NR
Trichloroacetic Acid (Cl <sub>3</sub> C-COOH)	5	78	58	78	126	NR
Bromochloroacetic Acid (ClBrCH-COOH)	5	15	16	18	21	NR
Bromodichloroacetic Acid (Cl <sub>2</sub> BrC-COOH)	5	20	19	19	22	NR
Chlorodibromoacetic Acid (ClBr <sub>2</sub> C-COOH)	5	18	19	17	17	NR
Dibromoacetic Acid (Br <sub>2</sub> CH-COOH)	5	2.0	3.3	3.0	4.3	NR
Dalapon (CH <sub>3</sub> Cl <sub>2</sub> C-COOH)	5	19	5.7	3.8	11	NR
Total HAAs	n/a	223	196	238	357	n/a
Total THMs & HAAs	n/a	320	304	359	603	n/a

EQL = estimated quantitation limit

n/a. = Not Applicable

NR = Not Presently Regulated in Michigan

n.d. = Not Detectable (below the analytical method detection limits)

1. THMs and HAAs were not detected in controls (unchlorinated ballast waters), except for a few minor amounts of HAAs.

2. Only the HAAs that exceeded concentrations in the controls are shown.

3. n.d. samples were assigned a value of zero when calculating averages.

4. Total THMs and HAAs may not exactly equal the sum of the individual values due to round-off errors.

5. "Theoretical discharge limits" are based on Michigan's water quality standards, which are consistent with the U. S. Federal Great Lakes Water Quality Guidance. All U. S. Great Lakes States must have standards consistent with this Guidance. The limits are considered "theoretical" because they were calculated for ballast water discharges (which are exempted from the U. S. federal requirement for discharge permits) in the same way as they are calculated for industrial and municipal discharges (which must obtain discharge permits). In accordance with the standards, the "theoretical discharge limits" for the chemicals were determined by selecting the most restrictive of several water quality values designed to protect aquatic life from acute toxicity and sub-lethal effects such as reduced growth and reproductive impairment; wildlife from sub-lethal effects such as reduced growth and reproductive impairment; and humans from cancer and non-cancer effects such as reproductive and developmental effects.

The levels of the trihalomethanes in the simulated ballast water discharges are lower than the effluent limits which would normally be applied to an industrial or municipal discharger under a Michigan NPDES Permit. The normal, or “theoretical”, NPDES Permit effluent limits are shown on Table 7.2. Therefore, at the levels shown in the testing done in this study, the trihalomethanes were within the normal acceptable ranges needed to protect the designated uses. This conclusion is considered to be conservatively protective for the following reasons:

1. The theoretical discharge limits being used are based on the assumption of continuous discharge. Even though multiple ships may de-ballast in the same general area, ballast water discharges are essentially very intermittent compared to continuous industrial or municipal discharges.
2. The trihalomethanes (and the halo-acetic acids) are relatively non-persistent in the environment. For example, the half-life of chloroform has been measured to be in the range of 36 hours to 31 days in surface waters [9].

The halo-acetic acids have not been previously regulated in Michigan discharge permits. Although it is likely that the “theoretical effluent limits” for halo-acetic acids would be of the same order of magnitude as the trihalomethanes, they have not been precisely determined by Michigan. This issue will need to be addressed by Michigan and other regulatory agencies.

Regarding other organic compounds that were analyzed, no phenolic compounds (referred to as “acid extractables”) were found at detectable levels, either in the controls or the chlorinated ballast waters. A number of benzenes and other organic compounds referred to as “base neutral extractables” were found at detectable levels in the control samples for one of the sediment types, and at similar levels in the chlorinated ballast waters using that sediment. The levels of these compounds were low, and did not appear to be affected by chlorination.

General concerns are frequently expressed about using sodium hypochlorite (or any other form of chlorine) as a ballast water biocide in the Great Lakes. These concerns are probably due to the history of finding problematic levels of chlorinated compounds in Great Lakes fish, and in birds that eat those fish. This has been a particularly insidious form of environmental contamination. Examples are the notorious compounds, DDT, Chlordane, and Dioxin. It is important to understand that those compounds were often formed as products or by-products during chemical synthesis processes that were intended to produce compounds with great environmental persistence and biocidal characteristics. These conditions are not expected to be present in the ballast tanks of ships.

Although the trihalomethanes and halo-acetic acids produced during treatment of ballast water are less environmentally troublesome than the historically notorious compounds, their creation should be minimized. The data developed in this project shows that creation of trihalomethanes and halo-acetic acids increases in water containing higher levels of sediment. For example, the highest level of sediment studied, 1000 mg/l, a level much higher than would be expected in properly managed ballasting operations, showed the highest levels of trihalomethanes and halo-acetic acids.

Therefore, it is important to minimize sediment taken on ships during ballasting operations. This reduces losses in ship carrying capacity, reduces the need to clean out ballast tanks, reduces the need and costs for sodium hypochlorite, and reduces the generation of unwanted chlorination by-products.

One other comment should be made regarding the relative risks of using sodium hypochlorite to treat ballast water: The amount which would be needed for this purpose is small in relation to the amounts of chlorine and sodium hypochlorite now being used for other purposes. This is shown in Table 7.3 (updated from [11.2.3]).

**Table 7.3: Chlorine Usage in the Great Lakes Watershed**

<b>Sector</b>	<b>Total U.S. Chlorine Consumption (tons/yr)</b>	<b>Estimated Great Lakes Chlorine Consumption (tons/yr)</b>
Water Intake and Wastewater Treatment	409,000	54,400 *
Drinking Water Treatment	146,000	19,400
Household Bleaching and Swimming Pool Treatment	290,000	38,600
Total Consumption (all uses)	13,684,000	1,820,000
Estimated Potential Use for Ballast Water Treatment	--	63

1. Amounts shown are expressed as tons/year of chlorine (Cl<sub>2</sub>).
2. U.S. chlorine consumption is based on 1997 data provided by the Chlorine Chemical Council.
3. Great Lakes consumption is extrapolated from the U.S. consumption, using the 1991 ratio of total U.S. and Canada population in the Great Lakes Watershed to total U.S. population (ratio = 0.133).
4. Ballast water treatment usage estimate is based on a 10 mg/l chlorine dosage rate, and assumes that all ballast water discharged into the Great Lakes is treated. Estimated total annual ballast water discharge to the Great Lakes = 5.7 million tonnes [5].

\* More than 500 tons/year of chlorine are used for zebra mussel control at water intakes.

### 7.3.3 Release of Metals form Ballast Tank Sediments

The concern that sodium hypochlorite additions to ballast water might liberate toxic metals from the ballast tank sediments was examined as follows:

Twelve types of simulated ballast waters which were dosed to 10 mg/l sodium hypochlorite, along with twelve types of non-chlorinated controls, were analyzed for 31 dissolved metals and major ions. The samples were taken at the end of the 48-hour test period and, where applicable, following de-chlorination.

Comparisons were made between the dissolved metals in the non-chlorinated controls and the treatment simulations dosed to 10 mg/l sodium hypochlorite at various sediment levels and sediment types. There were no apparent increases due to the sodium hypochlorite addition, except for the additional sodium from the biocide, and possible minor increases in silicon and manganese. Although somewhat elevated, these particular ions do not present an environmental problem at the relatively low levels found. Thus, at the 10 mg/l dosage, there was no evidence that sodium hypochlorite significantly liberated metals from the sediments.

Comparisons were also made between the dissolved metals in the simulations at different sediment levels. There were no apparent increases due to higher sediment levels, with the possible exception of minor increases in copper (but only near the limit of the test sensitivity), manganese and silicon. Barium appeared to actually decrease slightly at higher sediment levels. Thus, there was no evidence that sediment levels significantly affected the concentrations of dissolved metals in the simulated ballast water.

#### 7.3.4 De-chlorination Issues

The concerns related to the addition of the de-chlorination agent, sodium bisulfite, are whether there is toxicity due to the presence of the de-chlorinating chemical, whether dissolved oxygen (DO) will be depleted, and whether the pH will be altered in the ballast water discharge. Analytical tests for DO and pH were done on the simulated ballast water before and after addition of sodium bisulfite. The tests showed that de-chlorination had essentially no effect on the DO concentration, but that there was a slight decrease in the pH of about 0.5 units.

Regarding the issue of toxicity of the de-chlorinating chemical, sodium bisulfite, the Michigan DEQ has done numerous whole-effluent toxicity tests on de-chlorinated effluents from sewage treatment plants that use sodium bisulfite. Toxicity due to sodium bisulfite has never been found.

In the case of oxygen, it seems intuitive that there would be a reduction in DO whenever sodium bisulfite is added in excess of the stoichiometric amount needed to neutralize the TRC. This is because sodium bisulfite acts as a scavenger of oxidizing agents such as DO, as well as TRC. However, this has not proven to be a problem in sewage treatment plants where sodium bisulfite is used. The reason for this is that the reaction to neutralize TRC is nearly instantaneous, but the reaction with DO is relatively slow, and therefore occurs in the receiving waters where there is so much more oxygen that the effect is not significant [10].

In the case of pH, the average change of 0.5 units is not particularly troublesome, as it should not cause any violation of the receiving water standards. The pH measured in the de-chlorinated simulated ballast water ranged from 7.3 to 7.9. The pH range in the harbour water used for ballast was from 7.6 to 8.0.

There do not appear to be any harmful effects due to the addition of sodium bisulfite as a de-chlorination agent. The DO and pH results are summarized in Table 7.4.

**Table 7.4: Effects of De-chlorination on Dissolved Oxygen and pH**

SAMPLE		DISSOLVED OXYGEN (mg/l)			pH		
Sediment Number	Sediment Addition (mg/l)	Before	After	Change	Before	After	Change
1	0	9.8	10.1	+0.3	8.0	7.6	-0.4
1	10	9.9	9.9	0	8.3	7.5	-0.8
1	100	9.4	9.8	+0.4	8.2	7.3	-0.9
1	1000	8.7	8.7	0	8.2	7.8	-0.4
2	0	9.3	9.2	-0.1	8.2	7.7	-0.5
2	10	9.2	9.0	-0.2	8.2	7.7	-0.5
2	100	9.2	9.0	-0.2	8.3	7.9	-0.4
2	1000	9.3	9.2	-0.1	8.1	7.9	-0.2
3	10	8.8	8.8	0	8.2	7.6	-0.6
3	100	8.8	8.7	-0.1	8.2	7.6	-0.6
3	1000	8.7	8.3	-0.4	8.0	7.9	-0.1
Average Changes				-0.036			-0.49

**NOTES:**

1. All samples of de-chlorinated water contained non-detectable concentrations of total residual chlorine (<0.01 mg/l).
2. The above samples were all taken from water originally dosed with 10 mg/l of chlorine.

## 8. STRUCTURAL INTEGRITY

### 8.1 Introduction

An earlier series of laboratory test were performed to establish the effects of using Copper Ion and Sodium Hypochlorite as Biocides in Ballast Water [1]. That test replicated the conditions of the ballast tank environment and was designed to answer the following questions;

- What is the effect on typical coating systems of exposure to the test biocides?
- What is the effect on typical corrosion rates of ship steel when exposed to the test biocides?

This report describes further work developed to address three principal questions identified viz:

#### 8.1.1 Coating Permeability

To address this issue, a protocol was developed using 90-day exposures and a significant number of replicates in accordance with the ASTM Standard “Test Method for evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D 1654-92”

A second protocol was developed to examine permeability and cathodic protection.

#### 8.1.2 Time Frame

In this regard; a new work protocol was developed which calls for a series of test times of 30 days, 60 days and 90 day exposures of bare metal test coupons and a significantly increased number of sample repetitions to enable time based rates to be established with statistically significant sample sizes.

#### 8.1.3 Use of Seawater

It is acknowledged that the chemical content of seawater is somewhat more complex than simply adding sodium chloride however; it is the single most prevalent constituent and none of the other components normally found in seawater have significant corrosion acceleration capacities. Table 8.1 provides an analysis of typical chemical contents of seawater. The ship types of relevance to this project are those which trade into the Great Lakes and thus a number of ballast operations are conducted in the fresh water conditions of the Great Lakes. The remainder of the ballast operations will be split between those conducted in the brackish water of ports around the world and deep ocean saltwater conditions.

**Table 8.1: Most Abundant Solutes in Seawater**

Constituents(Ions)	Concentration g/kg	Weight Percent(%)
Chloride (Cl <sup>-</sup> )	18.9799	1.9
Sodium (Na <sup>+</sup> )	10.5561	1.1
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	2.6486	0.3
Magnesium (Mg <sup>2+</sup> )	1.2720	0.1
Calcium (Ca <sup>2+</sup> )	0.4001	0.04
Potassium (K <sup>+</sup> )	0.3800	0.04
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	0.1397	0.01
Bromide (Br <sup>-</sup> )	0.0646	0.0065
Trace Elements	0.633	0.1
Total	35g/kg	3.5%

These conditions can be replicated by conducting tests in fresh tap water and repeated in tap water adjusted to replicate seawater by the addition of sodium chloride which from the above table is seen to be the greatest additive to seawater.

A second concern was the biota content of sea water. In this context, the number of variables is immense and beyond the capacity of this level of study to address. However, the relative effects of such factors are small and indeed if the biocide proves effective biologically then a number of them are eliminated. The previous work also showed that oxygen availability was by far the more important factor and that when samples were buried in an inert sand, corrosion was extremely low. Biological matter will be most prevalent in the ballast tank sediments, i.e., at the bottom of the tank.

## 8.2 Laboratory Testing

### 8.2.1 Permeability of Coating

An experiment was developed. The experimental methodology used to examine the permeability of the coating is based on the work of Hoare[11]. The objective of the test is to measure the take up of water within the steel coated sample over time from first submergence and this is related to the threshold of permeability at which corrosion is supported.

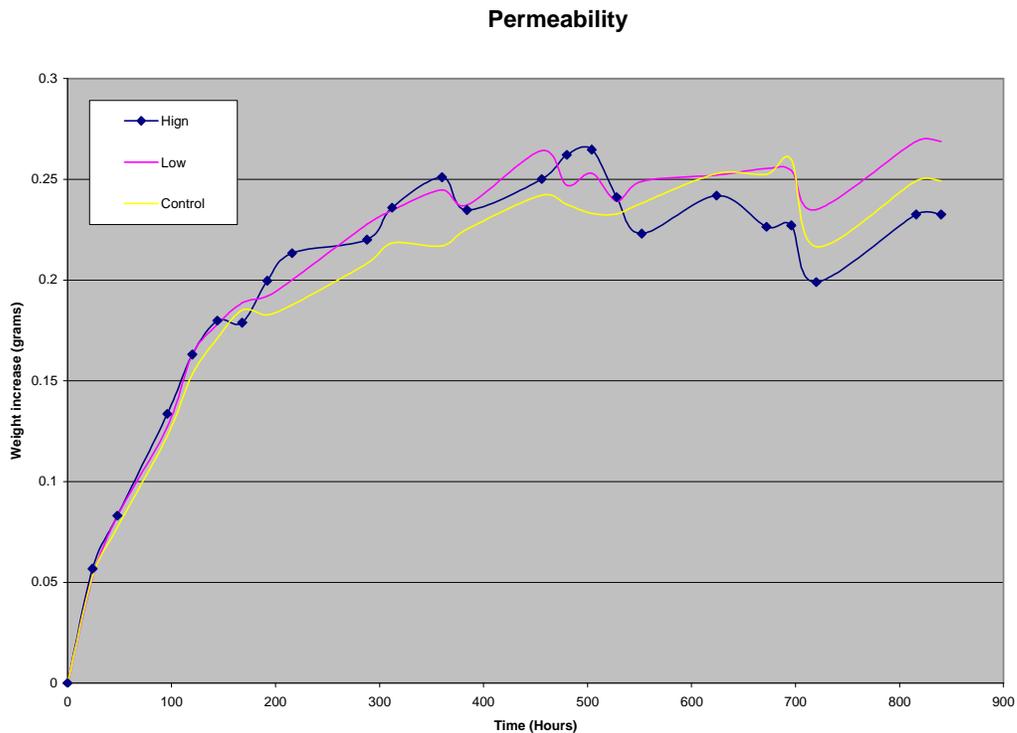
In this test, samples are prepared from standard ship building steels with fully intact coatings applied to manufacturer's specifications. These samples are then suspended in solutions with varying degrees of chlorine (Sodium hypochlorite) added. Some samples were also cathodically protected by an electrical connection to a submerged zinc ball. All samples were electrically isolated from each other and the apparatus. Figure 8.1 shows the test apparatus and a typical tests coupon.



**Figure 8.1: Permeability Test Apparatus**

Each day, each sample was removed from the solution, touch dried with a soft cloth and weighed. Four different coating and solutions of 0, 10 ppm and 40 ppm TRC were examined. TRC measurements were taken daily and additions made to ensure near constant exposure.

The following figures show the results of the tests in terms of added weight which is a measure of permeability, i.e., an average test coupon weighed 153.733 grams and over a period of 840 hours immersion in the test solution the average increase in weight was 0.25 grams.



**Figure 8.2: Increase in weight vs. Presence of Chlorine (Low 10 ppm High 40 ppm)**

From these presentations it can be seen that the presence of sodium hypochlorite does not affect the overall threshold of water take up. A more detailed discussion of the experiment is provided in Annex D.

### 8.2.2 Coating Damage

The standard used to assess the potential for coating damage is the ASTM Standard “Test Method for evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D 1654-92”. This standard rating system was used to rate the damage arising from exposure to two levels of hypochlorite exposure for four different coating systems using five identical test coupons. Scribed and unscribed test coupons were subjected to four different environments to replicate conditions in a ballast tank, these being:

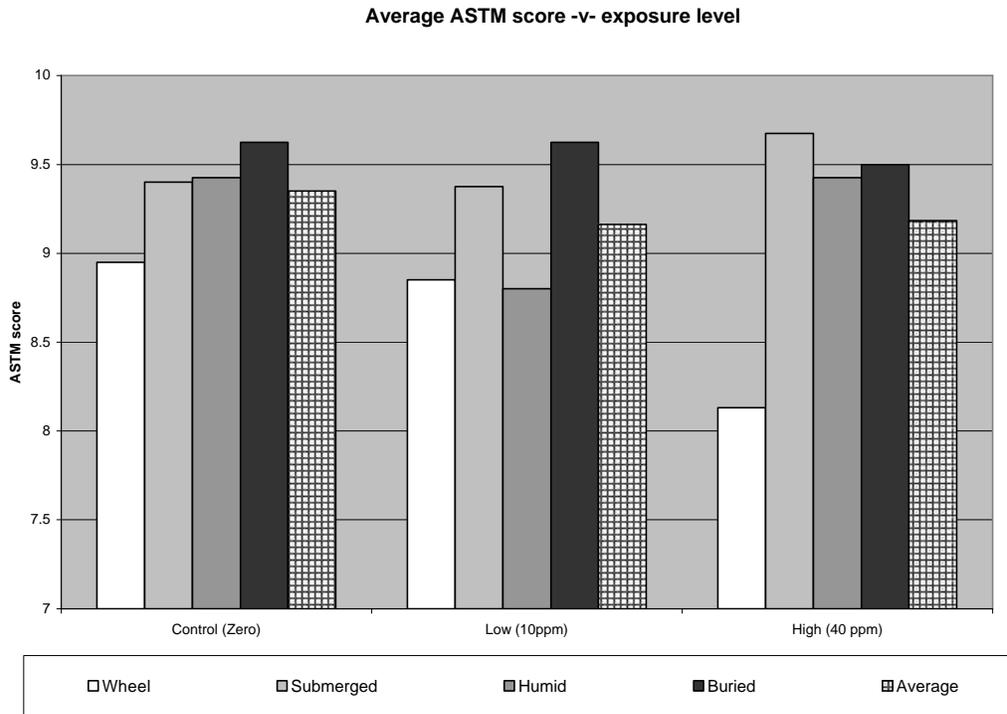
- (a) buried in an inert sand to replicate the under sediment condition at the bottom of mud laden tanks;
- (b) in the damp humid space replicating an empty ballast tank;
- (c) fully submerged to replicate a full ballast tank; and
- (d) rotating on a wheel with cyclic immersion into the test solution to replicate the splash zone in the top of a partially full tank.

The experiment results are described in full in Appendix E. Examination of the ASTM rating score for the four coating systems reveals the following:

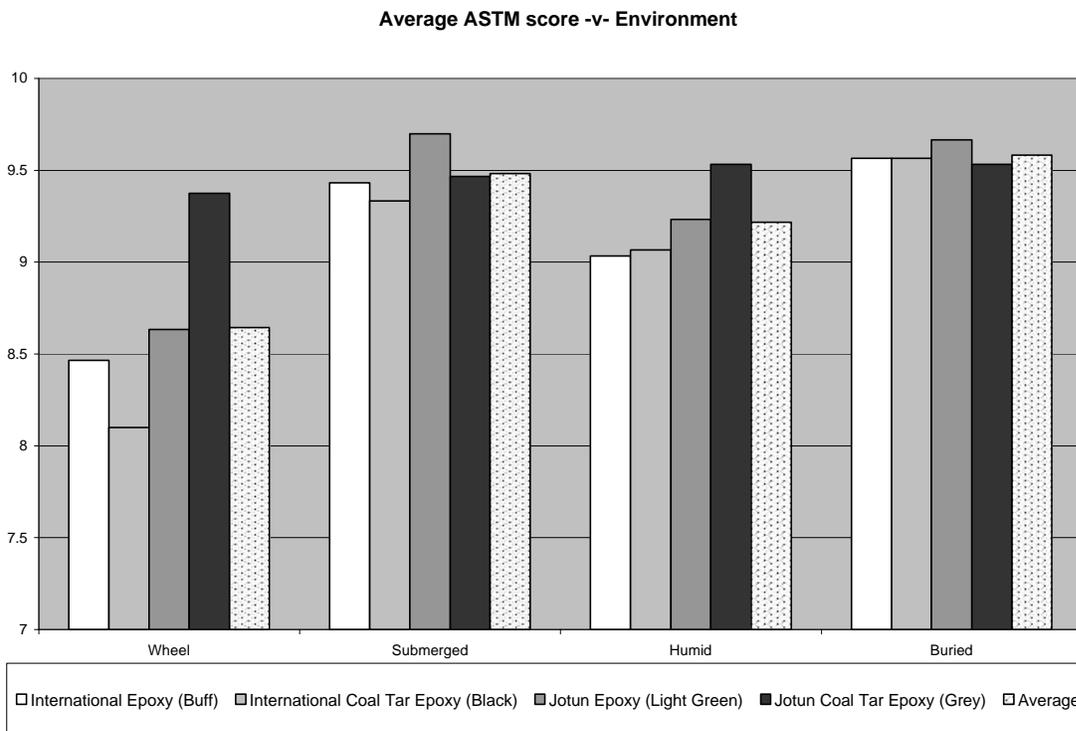
- Samples exposed to hypochlorite tend to experience slightly more damage than the control samples; however, this does not appear to be proportional to level of hypochlorite exposure and is a small effect.
- There is an observable trend in the level of damage experienced relative to the location in the test tank, i.e., the more aggressive location from a corrosion perspective also provides for more damage from a coating perspective (see Figure 8.6).
- No accelerated failures were observed in any un-scribed coating system.

An analysis of variance of these data however, shows that at the 95% confidence level only the high hypochlorite level in the most aggressive location, i.e., 40 ppm exposure on the wheel could be said to exhibit significantly more damage.

While no quantifiable analysis is possible with respect to life expectancy from laboratory testing, the observation that damage is increased by the presence of chlorine is mitigated by the observation this increase can only be statistically verified in the highly aggressive environment. During the life of the ship, the period when tank structure is submerged and subject to repeated abrasion i.e. the splash zone of the tank, represents a fraction of its total life. This level of aggressivity is also only seen when the ship experiences some extraordinary motion when operating in the ballast condition or in the bottom of the tanks when residual ballast water is present.



**Figure 8.3: Coating Damage Comparison at Various Hypochlorite Dosages**



**Figure 8.4: Coating Damage Increase with Environment**

### 8.2.3 Steel Corrosion

Corrosion experiments were conducted in the simulated ballast tank conditions, four different environments to replicate conditions in a ballast tank, these being in order of aggressivity:

- (a) in the damp humid space replicating an empty ballast tank (HUMID);
- (b) fully submerged to replicate a full ballast tank (SUBMERGED) and
- (c) rotating on a wheel with cyclic immersion into the test solution to replicate the splash zone in the top of a partially full tank (WHEEL).

A final set was placed in an inert sand condition at the bottom of the test apparatus to simulate under sediment conditions. Experiments were conducted in fresh and salt water over time periods of 30, 60 and 90 day test period. Chlorine levels were monitored daily and adjustment made to ensure that TRC levels were maintained at near 10 ppm and 40 ppm in separate chambers. Fourteen fresh water and 10 salt water replicates were made in each condition; this number was governed by the capacity of the experimental apparatus.

This experiment was designed to examine the kinetics of the corrosion process and to establish a statistical rigorous data set.

### 8.2.4 Kinetics of Corrosion

Aqueous corrosion rates in steel typical of shipbuilding steels are known to vary with time. Initially corrosion is high as the entire surface of the metal is exposed to the electrolyte and there is a free connection and full availability of oxygen to establish the reaction. As corrosion products (rust) are produced, this free path and availability of oxygen is inhibited and corrosion rates diminish.

The objective of the tests is to establish whether there is any increase in corrosion due to the presence of hypochlorite in the concentrations likely to be found in a treated ballast tank and to resolve the kinetics of the corrosion process in a ballast tank.

Figure 8.7 displays the results of the experiments in terms of weight loss (grams) for both sea and fresh water environments.

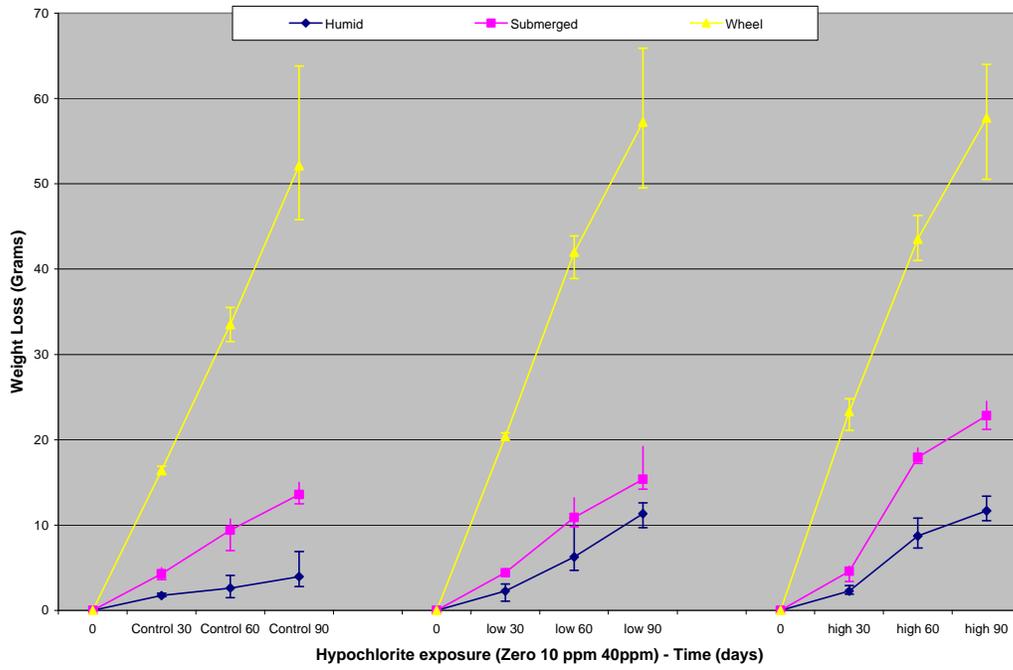


Figure 8.5: (a) Kinetic of Corrosion (Sea Water) (by Environment)

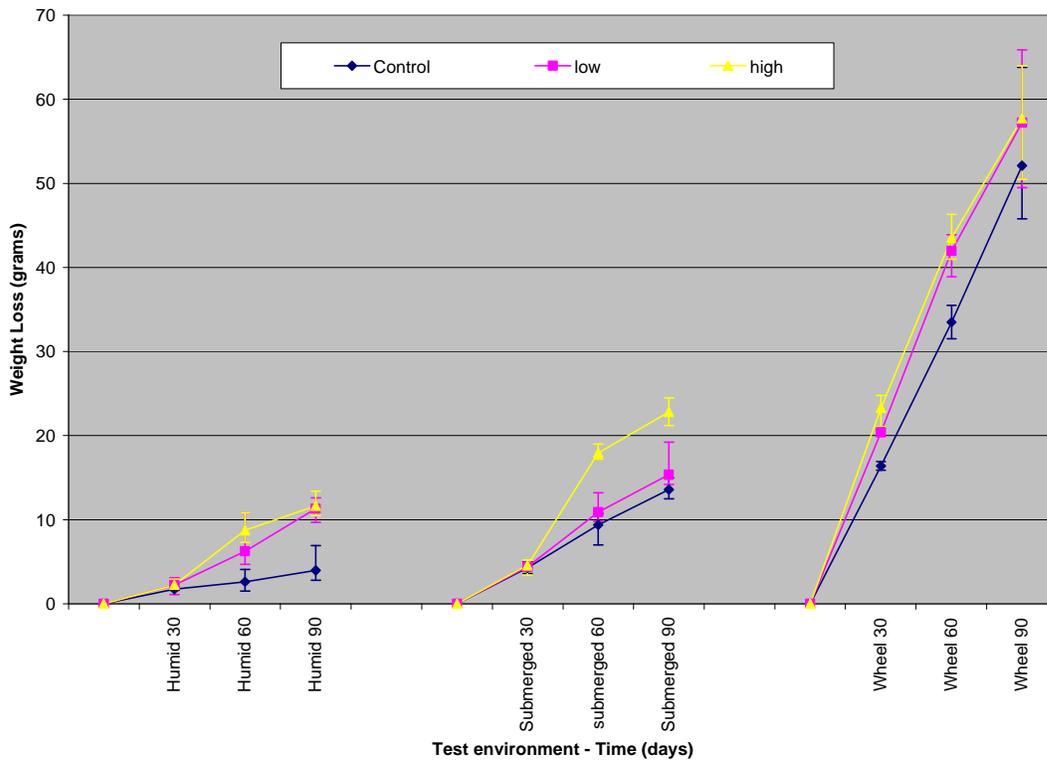
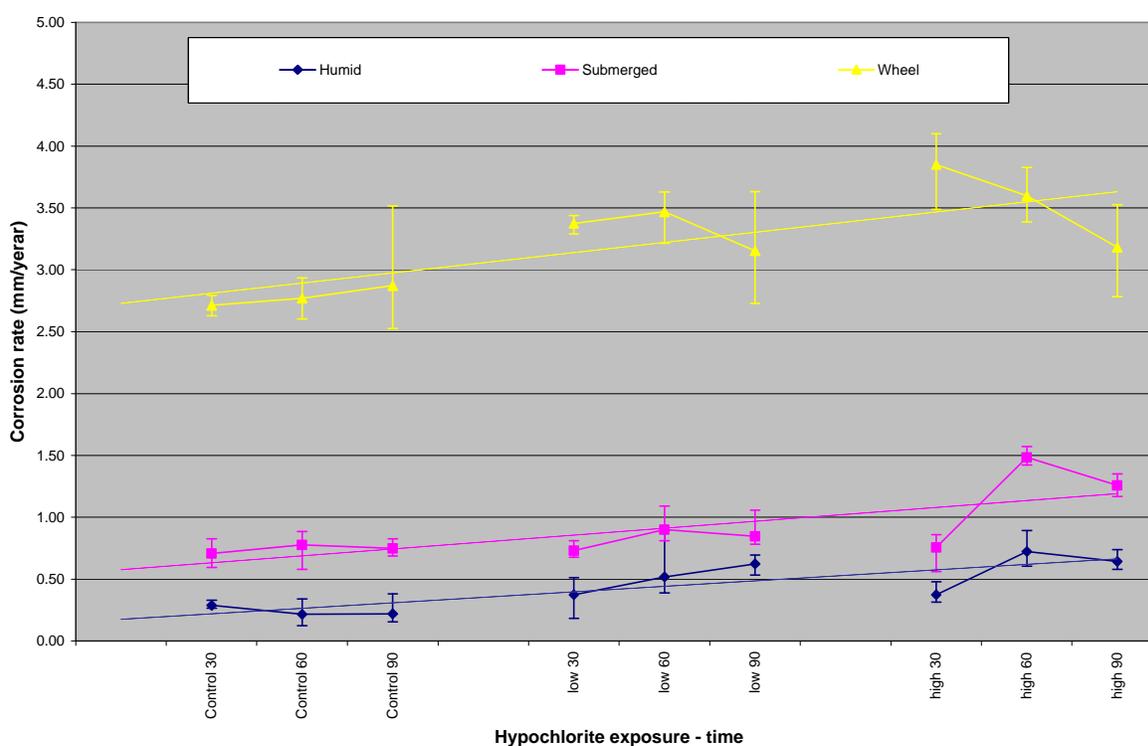


Figure 8.5: (b) Kinetic of Corrosion (Sea Water) (by Hypochlorite level)

The sea water experiment data displays the classical corrosion characteristics. The above figures show that in the less aggressive environments, the overall weight loss is significantly less and over time, the rate of loss reduces, this a classical parabolic kinetics of corrosion rate decay over time, i.e., the difference in weight loss due to corrosion is less in the last 30-day period than the previous periods. This is due to the build up of corrosion products partially insulating the metal surface to the test solution and over time retarding the corrosion. In the aggressive environment (wheel) a much steeper weight loss over time is evident. This is caused by the continual removal of corrosion products from the surface of the steel as the wheel rotates through the solution exposing the metal surface to contact with the solution.

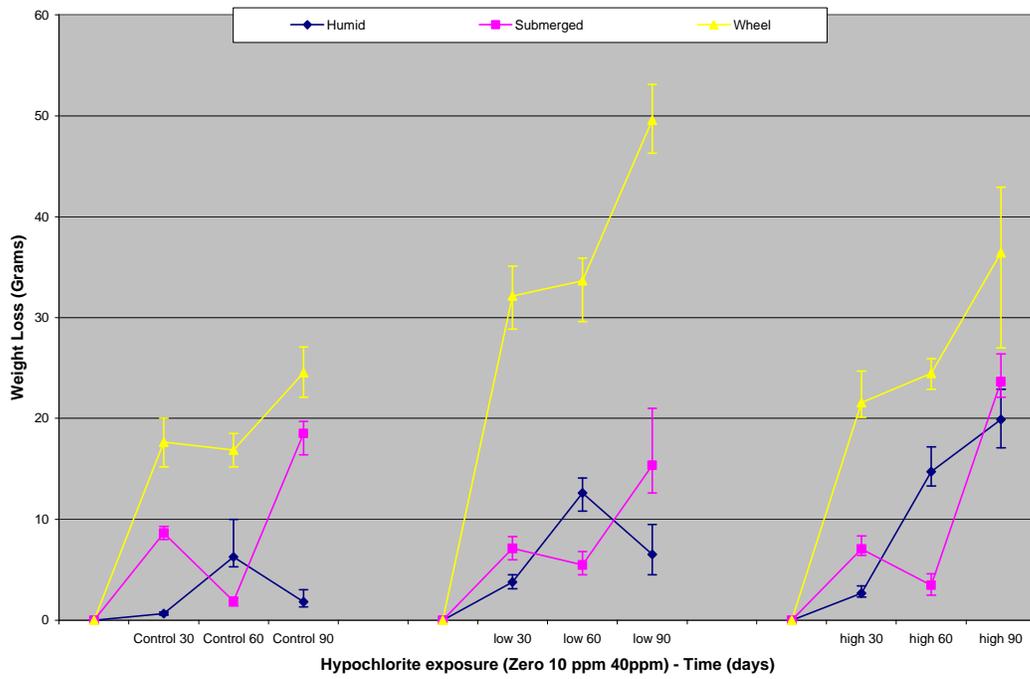
These data can be displayed as corrosion rates by equating the weight loss to steel thickness loss.



**Figure 8.6: Annualized Corrosion Rates Sea Water (mm/year)**

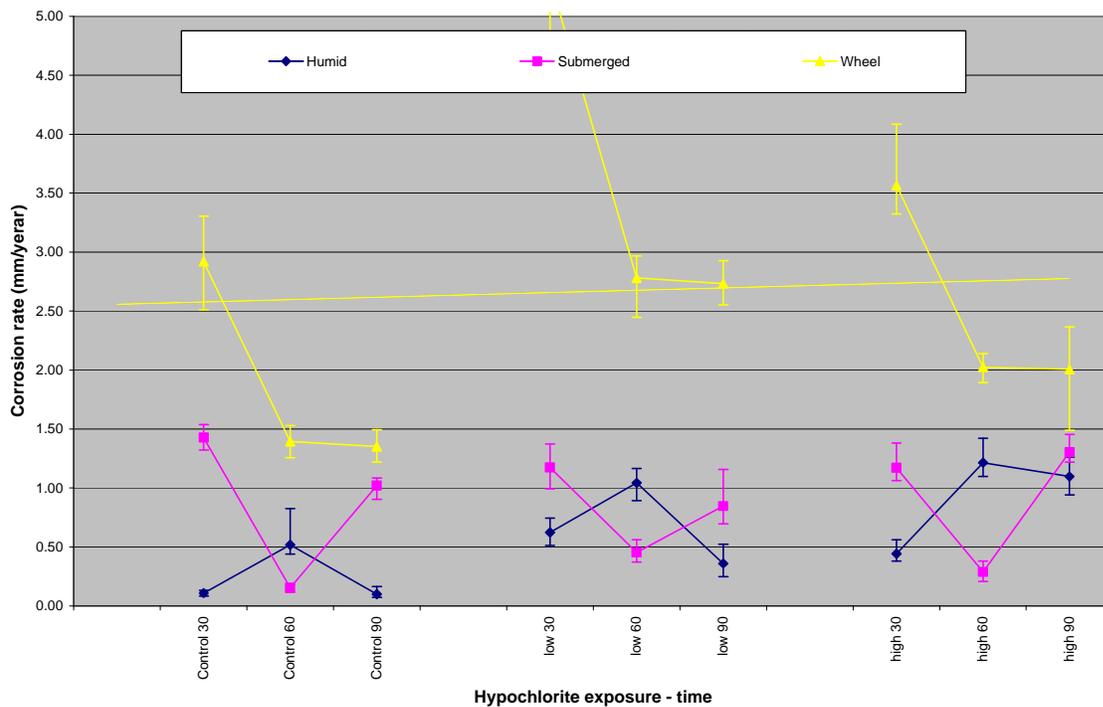
In this presentation, it can be seen that there is a trend to increasing corrosion as exposure to hypochlorite increases, i.e., the control data set is less than the low (10 ppm) which is less than the high (40 ppm) exposures. This visible trend is indicated by the rising line on the above figure but can only be supported to the 95% confidence level in the “wheel” environment, i.e., the more aggressive corrosion condition (Appendix E).

The fresh water experiment, in general, follows the same characteristics, i.e., the more aggressive the environment the more corrosion is experienced, however, there is somewhat more scatter in this data set. Furthermore, the most aggressive environment in the low dose experiment appears to be much higher than could be expected.



**Figure 8.7: Fresh Water Corrosion Weight Loss**

The fresh water corrosion data above is re-presented in terms of annual corrosion rates in the following figures and observation can be made as follows;



**Figure 8.8: Fresh Water Corrosion Rates**

### 8.2.5 Observations on corrosion experiments

Corrosion rates established in this experiment are generally in agreement with classically derived corrosion rates for mild steel in water. (From literature review, normal steady state corrosion rate is 1 mm per year (0.04 inches/year.) See submerged samples.

There is much more consistency in the results of sea water corrosion experiments than fresh water.

Corrosion rates significantly increase with the aggressivity of the environment, i.e., the tests on the wheel experience significantly more corrosion than in any other location in the test apparatus.

There is no significant increase in corrosion rate due to the addition of hypochlorite at either 10 or 40 ppm in the short exposure experiments.

In the longer exposure experiments and less aggressive conditions, mean corrosion rates increased but there is a low confidence in the difference of the statistical distribution of these data.

The addition of hypochlorite increases corrosion rates in aggressive environments, i.e., the tests on the wheel. This is tested by analysis of variance methods in Appendix E.

### 8.2.6 Ship Structures

The Tanker Structure Cooperative Forum [12] publish the most extensive publicly available database of “at ship” measured corrosion thickness diminution rates. In tanker ship ballast tanks designed solely for the carriage of ballast water (the tanks on all Great Lakes ships, bulk carriers and tankers, are designated solely for ballast), corrosion rates have been measured at between 0.1 mm/yr to 1.2 mm / y (0.047 inches). This order of magnitude difference is attributed to location in the tank. This reference also examines coating conditions and notes high levels of coating deterioration across all tank locations primarily related to age of coating and provides a measure as a percentage of coverage. All coating damage observed is attributed to localized disbonding and subsequent steel corrosion.

Paik [13] developed a time dependent corrosion wastage model for tankers and FPSO’s (Offshore Floating Production and Storage vessels) in which corrosion loss is calculated from the following equation:

$$t_r = C_1 (T - T_c - T_t)^{C_2}$$

where the thickness of the steel  $t_r$  at time  $T$  after construction is dependent on the time to coating break down  $T_c$  and a transition time  $T_t$  and coefficients  $C_1$  and  $C_2$ . Paik investigated 34 different components within the typical ship structure and completed a statistical review at ship of as found thickness over times of up to 32 years. He concluded that the variance in data was best approximated by setting  $C_2$  to 1 and that both  $T_c$  and  $T_t$  were indeterminable, however, a best fit to the data available was at around 7.5 years, i.e., the time to coating breakdown and corrosion to start is generally 7.5 years after construction and the rate of corrosion is linear but dependent on location within the tank. This model reflects mean corrosion rates in tanker structures at between

0.026 mm/year and 0.24 mm/year with maxima in the order of three times greater (0.08 mm/year to 0.7mm/year), again dependent on the environment in which the particular structural member resides. These rates are consistent with, but slightly lower than, the rates published by the tanker forum.

In the experiment reported above, designed to replicate condition in a ballast tank, corrosion rates are derived in the range 0.2mm/year (humid) to 3.8 mm/year (wheel). These rates double the tanker forum measured rates and are an order of magnitude greater than the mean values created by Paik. This can be explained by the life cycle exposure of the ballast tank structural members to various environments, i.e., tanks only spend a portion of time filled with ballast water.

### 8.2.7 Impact model

From the foregoing data, the most significant increase in paint deterioration and corrosion rates due to the addition of hypochlorite is in the most aggressive environment. Paint deterioration or acceleration of damaged locations in this environment will reduce the 7.5 years described in the Paik model, however, the reduction will be dependent on the level of defects already present in the coating.

Where corrosion rates are shown to increase from 2.75 mm/ year to 3.75mm/year (Figure 8.8, Sea Water Corrosion on the Wheel), this represents a 30% increase for full life time exposure to 40ppm hypochlorite, it does not relate to a similar increase at the ship where exposure to both the aggressive environment and hypochlorite is extremely limited. Therefore, to establish the impact on the ship over its life time an overall exposure model is needed.

On the basis of the operational scenario observed in the field trial on the *Federal Yukon*, it was assumed that the ship experienced a ballast water operation and thus treatment on a 30 day cycle and that during that cycle the structure was in ballast for six days. From investigation of typical operations of vessels which enter the Great Lakes, this exposure is probably high, i.e., 20% of the total time in ballast. Shippers try to minimize ballast carried and maximize the time their ships are carrying cargo to increase revenue generation.

A conservative estimate of potential increase in damage is thus proposed whereby given a range of time spent in ballast and a range of dose rates then an increase in the corrosion rate described in the Paik model can be calculated.

This effect when applied to the Paik type model and would indicate around a 3% increase in corrosion rates after the initial paint break down period of 7.5 years, for those structural components where heavy corrosion is predominant, i.e., splash zones in the tank. These areas are the only areas where accelerated coating damage and corrosion have been experimentally determined to increase.

The normal Classification Society rule for steel replacement is set at around 15% diminution dependent on several ship specific parameters. The potential for coating damage increase due to the added presence of hypochlorite in levels commensurate with ballast water treatment is seen as very small over the operational life cycle of the ballast tank. However, the most likely locations for coating damage acceleration also correspond to the highest areas of highest overall corrosion rate increase in areas of the ballast tank.

If steel repairs are normally seen after a 15 to 20-year life period due to corrosion (in ballast tanks) then assuming that paint break down occurs at 7 rather than 7.5 years in the presence of chlorine, the time for steel replacement is reduced by less than 5%. This model is shown in Table 8.2.

**Table 8.2: Life Cycle Impact on Structural Integrity Caused by Biocide**

	Aggressive corrosion	
	High	Low
Time in Ballast (%)	20	15
Ballast trips per year (n)	12	8
dose rate (ppm)	20	10
Days in ballast per dose	6.08	6.84
1/2 life (days)	2	1
Dose at discharge (ppm)	2.43	0.09
Average dose (ppm)	3.69	1.47
Corrosion increase rate increase per 10ppm	0.3	0.3
Life time corrosion rate increase (mm/year)	0.022	0.007
corrosion rate in PIAK (mm/year)	0.700	0.240
Increase over nominal corrosion rate (%)	3.2%	2.8%
<b>Time to paint breakdown (PIAK) (Years)</b>		
Time to paint breakdown (PIAK) (Years)	7.5	7.5
Time to replace steel due to corrosion (15%)	15	20
Rate (PIAK) (mm/year)	0.7	0.24
Increase corrosion rate (mm/year)	0.721	0.2472
Paint time to breakdown reduced to (Years)	7	7
Time to replace reduced by (Years)	0.72	0.86
Life reduction	4.8%	4.3%

## 9. DEVELOPMENT OF A SHIPBOARD DOSING SYSTEM

### 9.1 Introduction

The MESB review highlights the need for control of hypochlorite application and de-chlorination.

The Total Residual Chlorine (TRC) must be maintained at the biocidal level for a sufficient time at all locations in the tank to be considered effective, the application level depends on the water quality coming into the vessel. The TRC must be at or reduced to zero on discharge to avoid impacting the receiving environment, and thus measured to enable the correct application of sodium bisulphite as that water is discharged.

During water intake, the level of sodium hypochlorite to be administered is given by:

$$\text{Dose} = \text{Toxic biocide residual required} + \text{intake water demand} + \text{sediment re-suspension demand.}$$

During the water discharge the level of sodium bisulphite to be administered is given by:

$$\text{Dose} = \text{level to neutralize the Total Residual Chlorine (TRC).}$$

It is possible to measure the TRC in real time and this is done in other industries such as wastewater treatment and industrial cooling towers. However, the issue here is to develop an application from existing technology for TRC monitoring that can be utilized as a monitoring and control system suitable for the ship ballast tank environment.

The task of designing a shipboard chlorine dosing system presents several challenges which were addressed in the first report [1], foremost amongst these are issues related to storage and safe handling of chemicals, materials of equipment construction and specific spatial considerations related to bulk carrier type vessels.

The following discussion outlines the development of a shipboard system, engineered to control the application of chemicals, to provide to the ship owner/operator the most cost effective and reliable solution, to reduce life cycle costs in terms of consumable cost by minimizing chemical use and capital cost by optimizing component capacities and maintenance cost by ensuring reliability of components. In particular, the issue of control system design is addressed here.

### 9.2 Available Solutions

Given the biological considerations that demand environmentally-acceptable treatment and high killing rate, the engineering requirements for the dosing system are:

- must meet the demands of the shipboard environment. (be of marine construction quality);
- should minimize operational changes to the vessel's existing ballast management processes (not slow the ships operational ballast system);

- should fit within the existing operational procedures of shipboard personnel (not require extraordinary capabilities of a ships crew);
- must minimize initial capital and life cycle costs and optimize the use of consumable chemicals;
- must meet the existing safety standards of the industry, regulatory bodies, Classification Societies and the ship owner.

The central component of the shipboard system is the chlorine sensing mechanism. The level of TRC within the overall ballast water system will vary with time and location, per:

- Far away from the hypochlorite application point, the TRC will be at the dose level minus the intake demand, minus that portion of the sediment demand caused by re-suspension.
- Water borne sediment load. This can also be minimized by good ballast management practices but is a function of the water quality at the port of loading. It can be influenced further by the distance from the bottom of the ship intake to sediment on the harbour bottom, i.e., intake demand will vary with the changing draft of the ship, as the ballast operations take place lowering the intake closer to the bottom and changing the intake water characteristics.
- Sediment load already in the tank residual contents. This is a function of the cleanliness of the ballast tank and can be minimized by good management procedures (also important to minimize the possibility of sediment carrying invasive biota). This factor will increase demand when the tank is first filled and decrease as the water level rises into cleaner section of the tank, i.e., high levels in the tank will see much less sediment re-suspension than lower levels.
- The time of day may affect the intake level of biological activity in the water and the season of the year as it is causing blooms in the water are both major factors addressed by some of the IMO ballast water management guidelines.
- After time, the TRC level in the tank will drop as the chlorine naturally diffuses.

Other design function issues include;

- The ballast flow rates. This is a function of the static head in the ship ballast systems. Typically ballast pumps are centrifugal pumps which are influenced by the static head difference between intake and discharge. When the ship is filling the bottom tanks there is a positive static head caused by the outside water being higher than the empty tank and when filling the upper tanks the reverse is true.
- The system must also be reversible and be able to sense chlorine levels on the discharge of ballast water in order to control the addition of de-chlorination chemicals.
- The harsh shipboard environment, particularly within ship ballast tanks, is a concern with its range of motions and inaccessibility, i.e., tanks are normally closed systems with only infrequent access through man holes not deigned for rapid access. Components themselves have to be rugged and tolerant of vibrations and the relatively dirty operating condition. These are not typical conditions encountered with the land-based water treatment systems.

A number of possible solutions for monitoring were investigated. Two solutions, Tank-based Monitoring and Central-Monitoring System, are discussed. Component details are provided in Appendix F.

### 9.2.1 Tank-Based Monitoring

The most responsive solution for the control of a shipboard chlorine dosing system would be the placement of the chlorine sensors in the ship's ballast tanks. Routing cables through bulkheads is much easier than routing pipes, and the installation cost would most likely be lower. The downside is the higher number of sensors involved, their cost and their inaccessibility for maintenance. According to the chlorine sensor manufacturers, the equipment is designed to be permanently submerged which would not normally be the case with the tank-based sensors.

Furthermore, the lifespan of the average chlorine sensor is between six to twelve months, possibly less when installed in a ship's tank. This short lifespan would definitely impact the operating costs of the system.

### 9.2.2 Central Monitoring System

Another solution for treatment control is to have a central system with one or two (one per side) set(s) of sensors fed by a branched sampling piping system that draws water from each of the ballast tanks. Sensors would be easily accessible for inspection and cleaning at a convenient location within the engine room.

This system exhibits a time lag by virtue of the flow rate of ballast water to the tank being in the order of 700 m<sup>3</sup> / hour and the central monitoring station drawing sample water back through small pipes, however in the time taken to fill a given tank (say one hour) this is insignificant.

Sensor maintenance issues are much reduced but installation costs are higher and small pipelines in themselves induce some maintenance costs. This option was selected for further development.

### 9.2.3 Chlorine Sensors

Several types of sensors for the measurement of residual chlorine concentration are available. None was developed with the harsh marine environment in mind and they often employ thin membranes, glass cylinders and or fragile electrodes.

Free Chlorine (CLE) and Total Chlorine Sensors (CTE) offer good accuracy but are rather fragile and expensive. Their supplier projected lifespan is approximately six months and is based on continuous use. Although their intermittent use in a ballast system, several hundred hours per year, might lead to the conclusion that they could last longer this is unlikely as reactivation and "drying" out would shorten the overall life. The solids suspended in the ballast water and the ship's vibrations will further shorten the life of the sensors even if they are handled and stored properly.

Redox sensors are more rugged and offer the additional advantage of being able to detect the overdosing of neutralizing agents. Contradictory to the benefits are the calibration requirements that necessitate the use of highly corrosive and poisonous substances.

All sensors that are available require relatively frequent calibration that must be performed at times when the ship's crew is normally occupied with other routines. Redox sensors were considered to be more rugged and were selected for further development.

#### 9.2.4 Materials

Due to the aggressive nature of the chemicals used, pipes coming in contact with high-concentration solutions must be made of plastic or teflon-lined steel. Plastic pipes are rarely used onboard ship and their use is subject to special approval of Classification Societies, this should not pose a significant problem due to the small diameter required. The most effective material in terms of cost and chemical resistance would be PVC. Manufacturers' joining procedure should be carefully followed and the number of threaded joints, kept to a minimum.

Tanks for both chlorinating and de-chlorinating agents require special consideration. Due to corrosive nature of the chemicals, the usual shipbuilding material, steel, cannot be used. Plastic tanks are routinely used in the process industry ashore but these are not subject to severe motions that ships normally encounter in service. Therefore, tanks scantlings should be calculated to withstand the dynamic pressure of the sloshing liquid using the same approach as for other ship's tanks. The major difference would be in tank securing arrangements, i.e. the plastic tanks can not be welded to the surrounding steel structure.

Various materials have been found to be good candidates for storage tanks construction. There is a considerable experience in using these materials in wastewater treatment and other process plants and their properties are discussed below.

**FRP** (fiberglass reinforced plastic): This is by far the strongest of the tanks, albeit the cost is somewhat higher compared to other materials. A tank leak can be very difficult to trace in this type of tank because it can start with a small hole in the internal lining, and follow the filament winding of the tank wall until it escapes outside the tank at a location far from the internal defect. Epoxy coatings are recommended for both interior and exterior surfaces. FRP tanks are not proven to last any longer than the polyethylene tanks.

**FRP/PVC** (Dual Laminate): This is a good material for the tanks, combining strength and integrity and will provide the best life span. However, the lining significantly increases the price over a standard FRP tank.

**XLPE** (cross linked polyethylene): Cross linking of the PE transforms the resin from being a thermoplastic to a thermoset. This gives it the added strength, but takes away the ability to weld similar material to the tank.

**HDPE** (high density linear polyethylene): Tanks in this material are the most cost effective of the options, and have been proven to have a similar life span than the above tank materials (with the exception of PVC lined FRP). The major advantage of this material is the ability to weld fittings, which diminishes the chance of leakage.

Resin suppliers have confirmed that sodium hypochlorite has no direct effect on polyethylene. However, it is suspected that contaminated sodium hypochlorite does cause accelerated deterioration of polyethylene tanks when stored over a period of time. Contamination from such things as trace metals, e.g., iron, copper, etc., which may be generated from pumps, plumbing fittings, etc., or a poor quality (trace contamination) sodium hypochlorite shipment may cause brittleness and cracking of the polyethylene tanks.

According to Classification Society Rules, plastic storage tanks containing aggressive chemicals have to be placed in separated compartments with adequate ventilation. This means that an additional steel box has to be placed somewhere in the already crowded machinery spaces. Tank capacities for the ship used as an example in this report needed to store hypochlorite and bisulfite for one treatment cycle are 2.4 m<sup>3</sup> and 1 m<sup>3</sup> respectively. Space is limited in the engine room and these volumes are increased by the necessity to keep the two chemical separated in isolated compartments. Non-structural plastic tanks must be accessible for visual inspection so adequate clearance is required between the tanks and compartment sides, this could drive the larger compartment volume to more than 15 m<sup>3</sup>. Also, extensive monitoring equipment is required because of possible detrimental consequences of undetected leaks. Chlorine gas detectors should be placed in the compartment where the hypochlorite tank is located. Controlled venting and restricted gauging arrangements are also required by Classification Rules.

Fitting such a system into a new ship design would not pose significant difficulties; however for a retro-fit situation space available in machinery spaces of existing ships is rarely sufficient for separate compartments as discussed above.

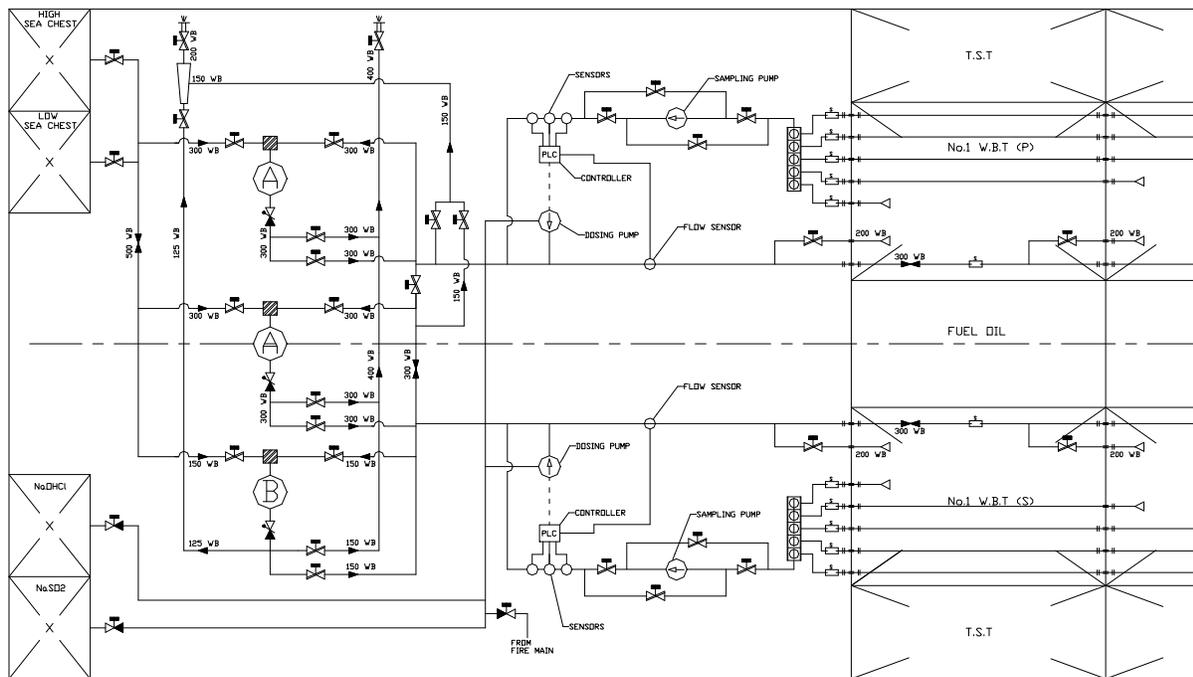
The solution for the existing ships would be to place the tanks at the main deck level, above the engine room. In such cases a dedicated enclosure is not needed for safety reasons because the natural ventilation is adequate. Some additional protection is needed as the hypochlorite can degrade quickly if exposed to solar radiation and heat. That additional protection can easily be achieved by adding UV inhibitors to tank material and a canopy over the tank. The freezing point of 15% solution of sodium hypochlorite is -17°C which is low enough for most ports. If the system is required to operate at lower temperatures, 12% solution with freezing point at -25°C can be used.

### **9.3 Monitoring System Description**

A conceptual design of a shipboard dosing system developed for a typical bulk carrier entering the Great Lakes is shown in schematic form at Figure 9.1. The system was designed to operate in two modes; ballasting when the tank content is being monitored through sampling pipes and deballasting when the discharge pipe content is driving the dosing rate.

### 9.3.1 Ballasting mode

The content of each ballast tank is sampled through a sampling piping that is installed and operated in parallel with the ship's ballast system. A small (1-litre/minute) pump is used to draw water from the ballast tanks to an in-line sensor holder. Signals from the sensors (pH, temperature and Redox potential) are fed to the microprocessor-based process monitor and controller. An additional signal is taken from a purposely installed flow meter to establish the rate of ballast water intake. Output from the controller is connected to the 500-litre/hour diaphragm metering pump with suction connected to a sodium hypochlorite tank that discharges to the ballast main.



**Figure 9.1: Dosing System Schematics**

Two tanks are usually ballasted at a time (port and starboard simultaneously to avoid heeling the ship) and two sets of sampling equipment have to be used to monitor all tanks in sequence. While it is technically possible to automate the process by having the sampling system that is a scaled-down version of ballast control system with all valves controlled in parallel, the cost of such a system would most likely be prohibitive in a retrofit condition. Therefore, a simple manual local control of all valves is proposed. This requires individual pipes for each tank, with valves in the engine room for accessibility. The pipe diameter is not critical and the smallest possible (1/4") is proposed. To keep the costs down, thick-walled steel pipes with no internal corrosion protection are used throughout, with the exception of pipes for the concentrated hypochlorite solution where plastic materials are required.

A time lag between detecting a change in the tank TRC level and correcting the dosing rate exists with this concept. This is unavoidable as samples must be taken from individual tanks and dosing is performed at the ballast main however over the time to fill one tank the lag will not affect total dosage.

Thorough mixing of hypochlorite with ballast water is essential. The injection point is downstream in reference to the best mixer in the system – the ballast pump. However, the turbulence induced by elbows and valves should provide sufficient mixing effect.

The amount of sodium hypochlorite required to achieve the prescribed chlorine dose is higher in the presence of sediment, as shown in Section 4 of the report. The effect of the sediment might not show instantly due to either slow chemical reactions or time lag in the dosing system loop. The feedback loop in the dosing system will compensate for the increased chlorine demand but if a significantly low concentration is detected at the end of the filling, the time remaining might not be sufficient for the set TRC level to be achieved. The mixing of ballast tank contents at the end of the filling process is also expected to be poor. The best strategy for solving such problems would be preventive as opposed to corrective behaviour of the system; since the controller is programmable it can be instructed to inject an excess amount of hypochlorite at the beginning when the resuspended concentration of sediment is at its maximum, then after that initial period, the target concentration of the residual chlorine would be set at the level required by biocidal efficacy (i.e., 10ppm).

### 9.3.2 Deballasting Mode

It is not necessary to monitor individual tank contents during discharge of the ballast water and therefore a much simpler flow path is required. Samples from the ballast main are continuously taken while the redox potential is being measured and the appropriate amount of reducing agent (sodium bisulphite) is being injected into the ballast main. In order to reduce the number of ballast main penetrations, sampled water from the sensors is pumped back into the ballast tank. The amount of water pumped back is insignificant as the sampling pump flow rate is 1 litre/minute. Because the sampling and injecting points are quite close in this phase, the response time of the system is expected to be very short.

Mixing of reducing agent with chlorinated ballast water will be good because the injection point is at the pump suction. As the chemical reaction is virtually instantaneous, discharged water is expected to be free of chlorine residual. The risk of improper dosing with the described system exists if the flow path between injecting and sampling points is too short. In such a case, the sampled water may not be a good representative of de-chlorinated ballast water. Therefore, it is necessary to confirm the system performance and possibly change the location of sampling and injecting points after developmental trials. Again, to reduce the risk of under dosing at the start, the control logic could be set to slightly overdose for a short initial period.

Flow sensors, ultrasonic (non-invasive) type are needed and are attached to each of the ballast mains. Their data are used to control dosing pumps through the feed back system control logic and to improve dosing system reaction time. They can also be logged to document the total quantity of discharged water and chemicals injected.

## 9.4 Storage Tanks Sizing

Estimates of the amount of chemicals needed per treatment are based on the typical voyages of the “Federal Yukon” bulk carrier. The maximum amount of ballast water to be treated is 20,000 tonnes. Although the maximum capacity is not always used, tanks should be sized to allow for the treatment of this amount of water. The recommended target NaOCl concentration is 10 parts per million (ppm).

Other assumptions are based on the results from Section 3 of this report (Sediment Effects). For the 100 ppm sediment concentration, the total amount of NaOCl needed to achieve the 10 ppm target concentration is 18.6 mg per liter of ballast water. Therefore, the quantity of chlorine needed per ballasting is estimated 371 kilograms (kg). It should be noted that the sediment concentration of 100 ppm is used as an average and this may vary between ports and ships.

A quantity of 371 kg per treatment is based on pure NaOCl, however commercially available trade concentrations contain between 15 and 37% of NaOCl. Chlorine tank volume and costs assume the lowest concentration as the worst case. Therefore, the maximum amount of 15% sodium hypochlorite needed for one full ship treatment would be 2480 kg, the volume of which is 2400 liters. Since the liquid hypochlorite decays if stored for long periods of time, storage capacity for just one treatment is assumed to be the maximum stored.

There must be sufficient capacity on board the ship to apply de-chlorination to the treated ballast water being discharged. This could be achieved by way of dosing with sodium bisulfite. It is assumed for the purposes of this concept design that 10 ppm would be the highest expected level of chlorine residual in the ballast tank during discharge. The nominal de-chlorination ratio for sodium bisulfite is 1:1.45 ppm (total residual chlorine:sodium bisulfite) thereby requiring a storage capacity of at least 0.83 tonnes of sodium bisulfite (given a 35% active ingredient solution).

## 9.5 Costs

The maximum ballast capacity of the example ship was used for chemical tanks sizing. Since the full volume is not usually used in great lakes operations, for cost calculations the average of 11000 tonnes per ballast operation is assumed. To treat 11,000 tonnes of ballast water at a dose of 18.6 ppm (to achieve 10 ppm) requires the purchase of 1311 liters of 15% liquid hypochlorite, and 455 liters of sodium bisulphite, for a per ballast material cost of \$756.

A life cycle cost model was developed based on nominal economic return parameters and an estimate of ship refit costs and is presented in Table 9.1. While the capital cost of this system is estimated to be in the order of \$125,000, this estimate does not consider the additional first cost associated with building and initiating the company-wide safety/training regimen necessary to handle this product. Nor does it estimate the first time approval costs associated with regulatory bodies and Classification Society approval processes, which could be significant for the first vessel. The estimated increase in shipping costs is presented using the same metric as above, and equals \$80 per day or an increase of 0.79%.

**Table 9.1: Life Cycle Cost Increment Storing Sodium Hypochlorite Onboard**

Item	
Capital cost	\$ 124,644
Refurbishment costs	\$ 10,000
Refurbishment Frequency	5
Ballast operations per year	12
Raw material costs	\$ 756
Vessel charter rate	\$ 10,000
Return rate	15%
Inflation rate	3%
Amortization period	15
Increase charter to maintain return	\$ 79.47
% Increase	0.79%

## 9.6 Long Term Estimates

The data used in this report on the number of ships entering the Great Lakes is the St. Lawrence Seaway Traffic Report data, based on the year 2002. Local traffic within the Great Lakes should be excluded so only data on ships transiting the Montreal - Lake Ontario section was used. According to the 2002 Seaway Report, a total of 30,000,000 tonnes was transported by ships transiting the Seaway.

The total volume of ballast water discharged into the Great Lakes from international ships is not recorded anywhere and can be estimated only. It is assumed, for the purpose of this study, that the average ship takes and discharges ballast once during its stay in the Great Lakes. The quantity of ballast water per one cycle is estimated to be half the weight of the payload. Since the ships transit the Seaway twice per visit, the total payload given in the Traffic Report should be divided by two. Therefore, an estimated quantity of ballast water discharged into the Great Lakes is 7,500,000 tonnes.

## 10. CONCLUSIONS

### 10.1 Temperature Impacts on Hypochlorite Toxicity

- A review of the available literature indicated that a definitive statement regarding the impact of temperature on the efficacy of sodium hypochlorite was not possible.
- Although an increase in temperature was generally accompanied by an increase in the toxicity of hypochlorite to the numerous species tested, it could not be determined whether the results were related to thermal stress or increased physiological requirements of the test organisms or to an increase in the chemical activity of hypochlorite as it relates to toxicity.

### 10.2 Sediment Impacts on Chlorine Toxicity

- Sediment concentration is a significant contributor to chlorine demand.
- TRC LC90s were generally similar regardless of sediment concentration when chlorine demand of the simulated ballast water was taken into account.
- LC90s ranged from > 10 ppm TRC after 30 minutes exposure to between 2.4 to 4.6 ppm TRC after 48 h.
- At a TRC concentration of 10 mg/l the LT90s were similar, ranging from 14.6 to 18.7 hr. This was true regardless of which sediments were used to prepare simulated ballast water.

### 10.3 Chlorination Byproducts

- The main by-products of treatment of simulated ballast water with sodium hypochlorite (to a TRC concentration of 10 mg/l) were chloroform, dichloroacetic acid, and trichloroacetic acid. The other trihalomethanes (THM) and halo-acetic acids (HAA) which were formed were less significant contributors to the total THM and HAA.
- The THM and HAA concentrations increased with increasing sediment concentrations, undoubtedly due to the increase in organic precursors in the added sediment.
- Acid extractible organics (e.g., phenol and o-cresol) and base neutral organics (e.g., naphthalene and pyrene) showed no evidence of being increased as a result of the chlorination process.
- Metals showed no evidence of any significant liberation from the sediments as a result of the chlorination process. Dissolved metals showed no significant increase with increasing sediment addition.
- Chloroform and other THM concentrations were within Michigan's theoretical permit effluent limits.
- HAA have not been previously regulated in Michigan surface water discharge permits. If permit effluent limits were of the same order of magnitude as for THM, the HAA would be within those theoretical limits.

- The amount of chlorinating chemicals needed to be used to treat all ballast water discharged in the Great Lakes (to the TRC concentration of 10 mg/l) would be small in relation to other uses of chlorinating chemicals in the Great Lakes Watershed.

#### **10.4 De-chlorination**

- De-chlorination is needed due to potential acute toxicity of chlorine residual in the ballast water discharge.
- No direct toxicity of bisulfite residual is expected, provided reasonable control of overdosing is maintained.
- Dissolved oxygen was not significantly affected by de-chlorination.
- De-chlorination reduced pH by about 0.5 units. This is not expected to cause problems in the receiving water.

#### **10.5 Structural Integrity**

- The addition of hypochlorite at the dose levels necessary to be biologically effective has no effect on the standard ship type coating system (paint permeability).
- There is no significant increase in the rate of ballast tank coating damage experienced by exposure to hypochlorite over a 90 day period.
- Corrosion rates of bare steel are increased by the presence of hypochlorite at the biologically effective dose rates under constant exposure conditions. However, the amount of increased corrosion is not considered significant over the life of a ship due to the relatively small amount of time that elevated hypochlorite concentrations would be present.
- Under the most aggressive corrosion conditions found in a ship ballast tank (splash zones) the life cycle for steelwork replacement to normal Classification Society standards is reduced by less than 5%.

#### **10.6 Shipboard Dosing System**

- A shipboard dosing/monitoring system is feasible and can be developed, however, there is no readily available automated system suitable for the shipboard working environment at this time.
- The cost to shippers using hypochlorite as a ballast tank biocide on ships typical of those trading internationally into the Great Lakes represents a 0.8% increase in daily charter rates (cost of shipping).
- The most important factor to ensure that hypochlorite is effectively and conservatively applied as a biocide is to ensure that sediment loads are minimized. Ship owners must adopt best management practices respecting ballast operations.

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APPENDIX A  
LITERATURE REVIEW

APPENDIX B

MATERIALS USED IN SAMPLING BALLAST WATER/SEDIMENTS

The materials that were used in the sampling of the ballast water/sediments are listed in Appendix B, Table B.1.

Table B.2 details the lab equipment that was used in the laboratory toxicity testing.

A description of the dosing apparatus provided by Prominent Controls Systems provided in Appendix B, Table B.3

APPENDIX C  
SUMMARY OF SEDIMENT TEST CONDITIONS

A summary of the sediment analysis and chlorination by-products is provided in Appendix C in the form of tables and test reports.

APPENDIX D  
SUMMARY OF THE TOXICITY TEST CONDITIONS

Control charts documenting this performance are provided in Appendix D-1.

Test reports for each sediment can be found in Appendix D-2.

The chlorine levels for each sediment over the 48 hr exposure period are found in the test reports (Appendix D-2). In all the exposure sediment levels, the chlorine levels decreased over the 48 hr period.

The amount of sodium hypochlorite required to achieve the prescribed chlorine dose in the presence of the various levels of sediment were monitored and are presented in the test reports in Appendix D-2.

APPENDIX E  
CORROSION EXPERIMENT RESULTS

A more detailed discussion of the corrosion and coating system experiments is provided in Appendix E, specifically corrosion rates (Appendix E-1), permeability (Appendix E-2) and paint (Appendix E-3).

APPENDIX F  
COMPONENTS OF SHIPBOARD DOSING SYSTEM