

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

FINAL REPORT

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Submitted to:

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FTL DOCUMENT QUALITY CONTROL DATA SHEET

REPORT/PROPOSAL: **Ballast Water Treatment Evaluation Using Copper and Sodium Hypochlorite as Ballast Water Biocides**

DATE: October 2002

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TABLE OF CONTENTS

1. ACKNOWLEDGEMENTS	1
1.1 Funding sources.....	1
1.2 Protocol Review	1
2. EXECUTIVE SUMMARY.....	2
3. INTRODUCTION.....	4
3.1 Background	4
3.2 Project Composition	5
3.2.1 Field Trials Onboard the M.V. <i>Federal Yukon</i>	5
3.2.2 Laboratory Toxicity Testing.....	5
3.2.3 Laboratory Corrosion Testing	6
4. METHODOLOGY	7
4.1 Test Protocols	7
4.2 Conduct of the Field trials onboard the M.V. <i>Federal Yukon</i>	7
4.3 Laboratory Toxicity Testing	10
4.4 Laboratory Corrosion Testing.....	10
5. SODIUM HYPOCHLORITE TREATMENT EVALUATION AND FINDINGS.....	12
5.1 The Efficacy of Sodium Hypochlorite in Killing Ballast-Borne Biota	12
5.1.1 Shipboard Testing.....	12
Laboratory Toxicity Testing	13
5.2 The Effect of Sediment on the Efficacy of Sodium Hypochlorite	15
5.2.1 Laboratory testing with sediment present	17
5.2.2 Sediment Chlorine Demand	17
5.3 The environmental considerations of discharge of sodium hypochlorite.....	20
5.3.1 Total Residual Chlorine Discharge Requirements.....	20
5.3.2 Ballast Water Discharge Byproducts	20
5.4 The Effects of Sodium Hypochlorite on Ballast Tanks	21
5.4.1 Corrosion rates	21
5.4.2 Coating Deterioration	24
5.5 The Economics of using Sodium Hypochlorite Onboard Ship	27
5.5.1 On-Board Chlorine Generation	27
5.5.2 Liquid Sodium Hypochlorite	29
5.5.3 Sodium Bisulfite Dechlorination	31
5.6 Handling Sodium Hypochlorite Onboard Ship.....	31
5.6.1 Handling and Storage of Liquid Hypochlorite.....	31
5.6.2 Sodium Bisulfite for Dechlorination	34
5.7 The Practical Considerations to using Sodium Hypochlorite.....	34
5.7.1 Gas generation	35
5.7.2 Ship Retrofitting	35
5.7.3 Operational Constraints and Opportunities.....	36
5.7.4 Monitoring / control mechanism	38
5.7.5 Establishing demand.....	39

6.	COPPER ION TREATMENT EVALUATION AND FINDINGS.....	41
6.1	The Efficacy of Copper in Killing Ballast-Borne Biota	41
6.1.1	Shipboard Testing.....	41
6.1.2	Laboratory Toxicity Testing.....	42
6.2	The Effects of Sediment on the Efficacy of Copper	44
6.3	The Environmental Considerations of Discharge of Copper	45
6.4	The Effects of Copper on Ballast Tanks.....	45
6.4.1	Corrosion Rates	46
6.4.2	Coating Deterioration	47
6.5	The Economics of Using a Copper Ion Generator Onboard Ship	48
6.6	Handling Copper Onboard Ship	49
6.7	The Practical Considerations to using Copper.....	49
6.7.1	Ship Retrofitting	50
6.7.2	Operational Constraints and Opportunities.....	50
7.	TEST PROTOCOL MANAGEMENT	51
7.1	Introduction	51
7.2	Quality Assurance/Quality Control Achieved	51
7.2.1	Shipboard Tests.....	51
7.2.2	Laboratory Tests	52
7.2.3	Corrosion Laboratory Tests	52
8.	SHIPBOARD TRIALS	53
8.1	Summary of Coastal Field Trials Conducted aboard the <i>Federal Yukon</i>	53
8.2	Summary of Great Lakes Field Trials Conducted aboard the <i>Federal Yukon</i>	54
	NOMENCLATURE	59
	REFERENCES.....	60
	APPENDIX A.....	1
	ITEM 1 – DISINFECTION BYPRODUCTS LEVELS IN HYPOCHLORITE TREATED BALLAST WATER AND SEDIMENT SAMPLES	2
	ITEM 2 – LETTER TO SHIP OWNER REGARDING DISCHARGE OF BIOCIDES IN BALLAST WATER TO SUPERIOR BAY	5
	APPENDIX B.....	1
	ITEM 1 – FRESH WATER TOXICITY TEST REPORTS	2
	ITEM 2 – SALT WATER TOXICITY TEST REPORTS	3
	ITEM 3 – MARINE AND FRESHWATER ALGAL TOXICITY TEST REPORTS.....	4
	APPENDIX C	1
	ITEM 1 – CORROSION TESTS DATA	2
	ITEM 2 – PLOTS OF PAINT DETERIORATION DATA (PHOTOGRAPHIC RECORD ON CD).....	3
	ITEM 3 – COATING SUPPLIERS SPECIFICATION DATA.....	4
	ITEM 4 – MSDS SODIUM HYPOCHLORITE	5
	ITEM 5 – GRANULATED SALT CHEMISTRY	6
	APPENDIX D	1
	ITEM 1 – EXPERIMENTAL PROTOCOL	2
	ITEM 2 – PROTOCOL AMENDMENTS ARISING DURING CONDUCT OF EXPERIMENTS	3
	ITEM 3 – ASTM STANDARD “TEST METHOD FOR EVALUATION OF PAINTED OR COATED SPECIMENS SUBJECTED TO CORROSIVE ENVIRONMENTS D 1654-92	4
	ITEM 4 – COMMENTS ON PROTOCOLS	5

LIST OF TABLES

Table 4.1: Coating System Supplied by Manufacturer.....	10
Table 5.1: Efficacy of Hypochlorite Treatment in Saltwater and Freshwater Trials.....	12
Table 5.2: Lethal Concentrations (LC99, IC99) of Hypochlorite for Selected Freshwater and Saltwater Biota.....	13
Table 5.3: Water Quality Characteristics of Laboratory and Ballast Waters.....	14
Table 5.4: Comparison of Sodium Hypochlorite Toxicity to <i>Lumbriculus Variegatus</i> and <i>Eohaustorius Estuarius</i> in Laboratory Waters versus Ballast Waters.....	14
Table 5.5: Toxicity of Sodium Hypochlorite to <i>Lumbriculus Variegatus</i> and <i>Cyprinus Carpio</i> with and without Sediment Present.....	17
Table 5.6: Impact of Sediment on TRC Demand in Laboratory Water and Ballast Water.....	19
Table 5.7: ASTM D 1654-92 Deterioration Rating.....	24
Table 5.8: Life Cycle Cost Increment for Onboard Generation of Sodium Hypochlorite.....	28
Table 5.9: Life Cycle Cost Increment Storing Sodium Hypochlorite Onboard.....	30
Table 5.10: Life Cycle Cost Increment when Sodium Hypochlorite is Supplied as Needed.....	30
Table 5.11: Health Effects Associated with Chlorine Gas Exposure.....	31
Table 5.12: List of Material Compatibility with Sodium Hypochlorite.....	32
Table 5.13: List of Material Reactions with Sodium Hypochlorite.....	33
Table 6.1: Efficacy of Copper Ion Treatment in Saltwater and Freshwater Shipboard Trials....	42
Table 6.2: Lethal Concentration Ranges (LC99/IC99) of Copper for Selected Freshwater Biota (Including Bacteria, Algae, Pelagic and Benthic Invertebrates and Fish).....	43
Table 6.3: Comparison of Copper Toxicity to <i>Lumbriculus Variegatus</i> and <i>Eohaustorius Estuarius</i> in Laboratory Waters versus Ballast Waters.....	43
Table 6.4: Toxicity of Copper to <i>Lumbriculus Variegatus</i> and <i>Cyprinus Carpio</i> with and without Sediment Present.....	44
Figure 6.2: Thickness loss through Corrosion in the presence of Copper.....	46
Figure 6.3: Coating System Damage increase with Added Copper.....	47
Figure 6.4: Coating System Defects Found after Exposure to Copper.....	48
Table 6.5: Life Cycle Cost Increase for Onboard Copper Ion Generation.....	49
Table 7.1: Summary of Standard Deviation Data for Replicated Analyses Conducted during the Shipboard Trials.....	51
Table 7.2: Summary of Physical/Chemical Water Quality Conditions during Coastal and Great Lakes Shipboard Experiments.....	52
Table 8.1: Type and Relative Abundance (% of total) of Zooplankton Organisms in Ballast Water at each Trial Location.....	55
Table 8.2: Organisms Recovered from Sediments Collected from Test Chambers following Saltwater Shipboard Trials (Presence/Absence).....	56
Table 8.3: Summary of Analytical Results for Sediments used in Field and Laboratory Studies.....	57
Table A.1: Disinfection Byproduct Levels in Control Hypochlorite Treated Ballast Water Samples.....	3

LIST OF FIGURES

Figure 4.1: M.V. <i>Federal Yukon</i> at Superior Wisconsin	8
Figure 4.2: Deck Layout of Test Chambers Onboard MV. <i>Federal Yukon</i> .	8
Figure 4.3: Loading Grain and covering access to bottom tanks	9
Figure 4.4: Accelerated Corrosion Testing Apparatus	11
Figure 5.1: Residual Ballast Water in Tanks of M.V. <i>Federal Yukon</i>	16
Figure 5.2: Average Total Residual Chlorine Levels in Saltwater Shipboard Trials	18
Figure 5.3: Average Total Residual Chlorine Levels in Freshwater Shipboard Trials	18
Figure 5.4: Thickness loss through Corrosion in the presence of Chlorine	23
Figure 5.5: Scribed Paint System Defects Found after Exposure	25
Figure 5.6: Paint Damage Increase with Added Chlorine	25
Figure 5.7: Paint Damage Increase with Environment	26
Figure 5.8: Conceptual Sodium Hypochlorite Control System Diagrammatic	39
Figure 6.1: Copper Ion Generator in Engine Room of M.V. <i>Federal Yukon</i>	41
Figure 6.2: Thickness loss through Corrosion in the presence of Chlorine	46
Figure 6.3: Scribed Paint System Defects Found after Exposure to Copper	47
Figure 6.4: Paint Damage increase with Added Copper	48
Figure 8.1: Chlorine Decay in Laboratory Saltwater Containing Various Levels of Sediment	58
Figure 8.2: Chlorine Decay in Laboratory Freshwater Containing Various Levels of Sediment	58

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In particular, we would like to thank the officers and crew of the M.V. *Federal Yukon* for their assistance in gaining access to the ballast tanks, and in providing laboratory space, accommodation and hospitality to the investigators.

The project team wishes to acknowledge the input provided to this project by the management of Fednav Limited. In addition, the project team would like to thank Fednav Limited for making the ship available for the conduct of the field trials, and in their investment in the purchase and installation of the prototype Wilson Taylor Biomatic copper ion generator.

Further acknowledgement is due the paint manufacturers, Jotun A/S Norway and Akzo Nobel Coatings Limited (International Paints) who supplied samples of paint for this project.

1.1 Funding sources

This project was funded by the following agencies:

- Michigan Great Lakes Protection Fund
- Office of the Great Lakes, Michigan Department of Environmental Quality
- U.S. Fish and Wildlife Service

In addition to the work conducted for this project, a supplemental project was initiated to examine the effects of copper ion treatment on ballast tank structures (steel corrosion) and coatings (paint). This effort was funded by Transport Canada Marine Safety Branch and will be supplied as an addendum to this report.

1.2 Protocol Review

The project schedule called for the development, review and implementation of a novel experimental protocol in a very short time period. The project team wishes to acknowledge the following persons and organizations kind enough to review the draft protocol and provide input in a timely manner.

- Allegra Cangelosi, Northeast Midwest Institute;
- William Boytim, Sea River Maritime;
- Peter Landrum, Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration;
- Jennifer Nalbone, Great Lakes United;
- Hugh McIsaac, University of Windsor; and
- Richard Harkins, Lakes Carriers Association.

2. EXECUTIVE SUMMARY

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

The biocidal properties of sodium hypochlorite and copper as they relate to ballast water treatment were evaluated in shipboard trials aboard the MV *Federal Yukon*, and in laboratory toxicity tests. Additionally, the potential detrimental effects of routine application of the biocides in ballast tanks were explored using accelerated corrosion experiments in the laboratory.

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

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

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

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

- The removal of bottom sediment from ballast tanks and suspended sediment in incoming ballast water would likely have additional treatment benefits for both biocides
- Appropriate dosing and monitoring and distribution equipment will be required to ensure accurate biocide levels have been reached.
- There are un-addressed safety issues surrounding the use of hypochlorite on ships, and classification societies and regulatory bodies would require special consideration of any on-board facility.

- There are environmental discharge concerns associated with using copper.
- The ranges of water qualities, particularly amount of sediment that can be expected to require treatment have yet to be identified.
- Sodium hypochlorite is readily available throughout the Great Lakes ports or can be generated on board.
- Copper ion generators are capable of supplying copper ions to the ballast water intake.

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

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

3. INTRODUCTION

BMT Fleet Technology Limited (FTL), in conjunction with its partner, ESG International, is pleased to submit this report at the completion of the contract number 07B1001669, dated July 15, 2001 and titled, "WATER STUDY RESEARCH SERVICES – CONDUCT A SHIP-BOARD STUDY TO EVALUATE THE EFFICACY AND PRACTICALITY OF USING HYPOCHLORITE AND COPPER (CUPRIC) ION AS BALLAST WATER BIOCIDES".

3.1 Background

This project was initiated in response to recommendations from Michigan's Ballast Water Work Group (BWWG). The BWWG is a group of technical experts assembled by the Michigan Department of Environmental Quality (MDEQ) to find the best way currently available to minimize the introduction of Aquatic Nuisance Species (ANS) into the Great Lakes via ships' ballast water. The BWWG concluded that:

- Management practices and biocides are the only two methods currently available to deal with this problem.
- Hypochlorite and copper ion are potentially currently available ballast water biocides.
- On-board field testing of these two biocides should be carried out as soon as possible.

In addition, results from this project will help the MDEQ fulfill its statutory obligation under Michigan Public Act 114 of 2001, to determine whether there are any treatment methods that could be used by oceangoing vessels to prevent the introduction of ANS into the Great Lakes.

The project is not designed to determine whether specific standards for biocidal efficacy are achieved because such standards do not now exist. However, the question remains, can copper ion and/or hypochlorite be recommended for general application as ballast water biocides? This led the MDEQ to pose the following more detailed questions relating to whether the two biocides are practical means of minimizing ANS in ballast water and in particular, ships entering the lakes with no ballast on board (NOBOB).

- Are they effective in killing a broad range of ballast-borne biota?
- Can they be safely handled?
- Are the ultimate discharge concentrations environmentally acceptable to regulatory agencies?
- Do they damage ballast tanks?
- Do they work with sediment present?
- Are they economical and readily available?
- Are there any other practical considerations regarding their use?

This project is designed to help the DEQ answer these questions.

3.2 Project Composition

The project is comprised of three parts:

1. A field demonstration on-board the MV *Federal Yukon*,
2. Toxicology testing in the biological laboratory, and
3. Corrosion testing in the material laboratory.

3.2.1 Field Trials Onboard the M.V. *Federal Yukon*

This part of the project is characterized as a field trial, rather than a research project. The purpose of this part was to examine the shipboard application of biocides and assess the efficacy of treatment on a single typical voyage and to further determine whether the application of biocides adversely affects the real-life operations of the ship.

The project work was not allowed to interfere with the commercial operations of the ship and certain on-site modifications to the experimental plan were necessary to accommodate the local biological conditions and engineering difficulties encountered.

The tests were conducted on the deck of the ship using 55 gallon plastic barrels as test chambers. Additionally, the deck mounted decant tank (a metal deck tank typically reserved for capturing cargo wash water prior to discharge) was modified and coated with paint used in the ballast tanks for additional hypochlorite tests.

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

Port #1 (“Coastal Port #1”): An ocean port in a saltwater environment. Cargo was off-loaded, and ballast water taken on.

Port #2 (“Coastal Port #2”): An ocean port where cargo was taken on, and ballast water discharged, creating a NOBOB condition.

Port #3 (“Great Lakes Port #1”): A Great Lakes, fresh water port. Cargo was off-loaded, and ballast water taken on.

Port #4 (“Great Lakes Port 2”): A Great Lakes port where cargo was taken on and ballast water discharged.

3.2.2 Laboratory Toxicity Testing

The ship is an operational platform and its voyage plans may take it anywhere in the world. Given the variability of ballast water characteristics that this entails, shipboard trials are not as well controlled as laboratory experiments. For example, given where and when ballast water is taken on, it may not contain high numbers of specific organisms of concern, and it may not contain high levels of sediment. Therefore, a series of laboratory toxicity tests were conducted at ESG International’s Ecotoxicity Laboratory (Guelph, Ontario) to complement the shipboard testing of biocide efficacy.

The purpose of this part of the project was to quantify the efficacy of the biocides as it relates to the treatment of organisms of concern in ballast water. The toxicity testing was conducted on freshwater and saltwater fish, invertebrates, algae and bacteria. In addition, the toxicity of the biocides to selected resting stages was evaluated. The organisms were selected to represent the range of pelagic and benthic organisms and the various lifestages that may be found in ballast water. In general, and where possible, organisms/lifestages that tend to be more resistant to chemical treatment were selected over more sensitive organisms. In certain instances, the toxicity of the biocides was tested in both laboratory water and ballast water collected from the ship. A limited number of tests were conducted with and without the presence of a clean, control sediment for characterizing the effect of sediment on biocide efficacy. Appendix D contains the laboratory for laboratory protocol addenda.

3.2.3 Laboratory Corrosion Testing

Likewise, the relatively short shipboard trial could not reveal the true corrosion or tank coating damage potential of the biocides. Thus, complementary laboratory studies of the potential for biocide-induced damage were undertaken at the Fleet Technology Limited Material Laboratories (Kanata, Ontario).

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

4. METHODOLOGY

4.1 Test Protocols

The experimental protocols for the three components were developed in house based on the proposal document and modified in accordance with the literature review.

These protocols were issued to invite peer review and comment on the applicability and validity of the experiments. The following persons responded to that request:

- Allegra Cangelosi, Northeast Midwest Institute;
- William Boytim, Sea River Maritime;
- Peter Landrum, Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration;
- Jennifer Nalbone, Great Lakes United;
- Hugh Mclsaac, University of Windsor; and
- Richard Harkins, Lakes Carriers Association.

The project team and the Michigan technical authority reviewed these comments. The experimental protocols were revised in accordance with those comments which were deemed to enhance the conduct of the project and which were practical within the project objectives, schedule and budget. See Appendix D for a detailed copy of the test protocols used in this study. Included in Appendix D is a list of addenda to the original protocol document and comments provided by reviewers.

In addition, the three major Classification Societies, Det Norske Veritas, American Beaureau of Shipping, and Lloyd's Register of Shipping were also solicited for comments on the protocols, however no responses were received.

4.2 Conduct of the Field trials onboard the M.V. *Federal Yukon*.

The field trials were conducted on-board the M.V. *Federal Yukon*. This vessel is typical of the modern bulk carrier trading into the Great Lakes for all parts of the world. The design of the vessel is optimized for this trade and is built to the maximum dimension of the seaway lock system. Figure 4.1 shows the vessel loading grain in Superior Wisconsin after discharging the ballast previously loaded in Burns Harbor Indiana.

Tests were conducted on the deck of the ship using eight polyethylene 55 gallon drums, and the decant tank (modified to include 3 internal sections). The decant tank was used to test hypochlorite efficacy (one control and replicated treatments). The decant tank is part of the ship structure located at the aft of the ship and normally used to settle out solids from cargo hold washing water prior to discharge over board. Two plastic barrels were also used as test chambers for hypochlorite studies. Four plastic barrels were used for testing copper efficacy, two barrels per ballast tank that was treated. Two plastic barrels were used as control barrels. Barrel treatments and controls were placed in the Bosun's store at the fore of the ship during the trials. Figure 4.2 shows the overall layout of the experimental test chambers.



Figure 4.1: M.V. *Federal Yukon* at Superior Wisconsin

During saltwater trials, bottom sediment was collected from ballast tank 3 and added to test chambers at 1% v/v. In freshwater trials, sediment was collected from ballast tank 5 for inclusion in tests. The ballast tanks are constructed as individual port and starboard tanks comprising lower or double bottom tanks and upper or wing tanks connected by pipes at the forward and after ends of each cargo hold. These pipes drain the upper tanks to the lower. During ballast operations, ballast water is pumped into the lower tank and the piping supply and suction lines are all in the lower tanks. The lower tanks are entered through access holes on the inner bottom (cargo hold deck) and can only be reached after cargo has been removed. Figure 4.3 shows the tank layout on board the *Federal Yukon*.

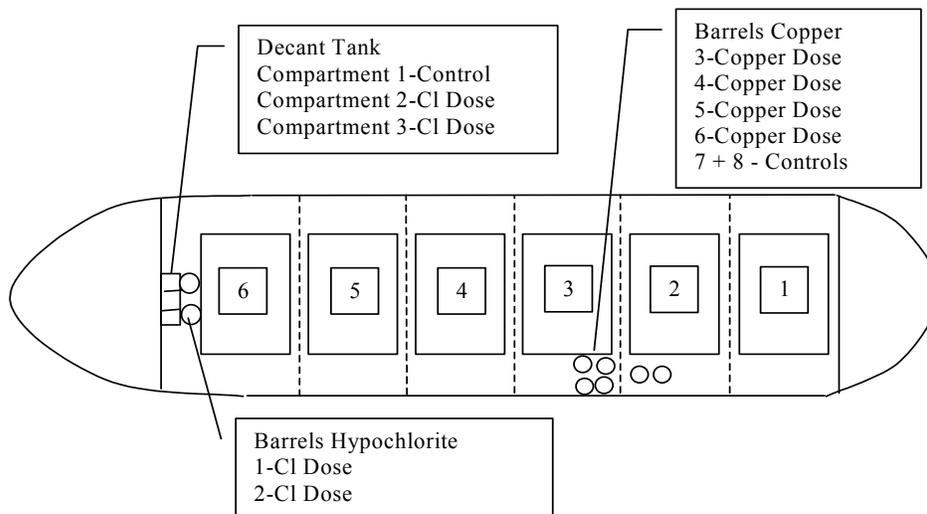


Figure 4.2: Deck Layout of Test Chambers Onboard MV. *Federal Yukon*.

Water from the ballast main was collected from the fire-hose for use as hypochlorite and control test water. The hypochlorite test chambers were dosed sodium hypochlorite to a residual of 10 ppm TRC. Two different ballast tanks (previously untreated) were dosed using the copper ion generator at approximately 0.2 ppm, and the dosed ballast water was pumped into the plastic barrels containing sediment.

Shipboard trials were conducted using ballast water collected from the location of ballasting. At each location organisms were collected in the area, filtered (at 60µm) to increase densities, and added to test chambers.

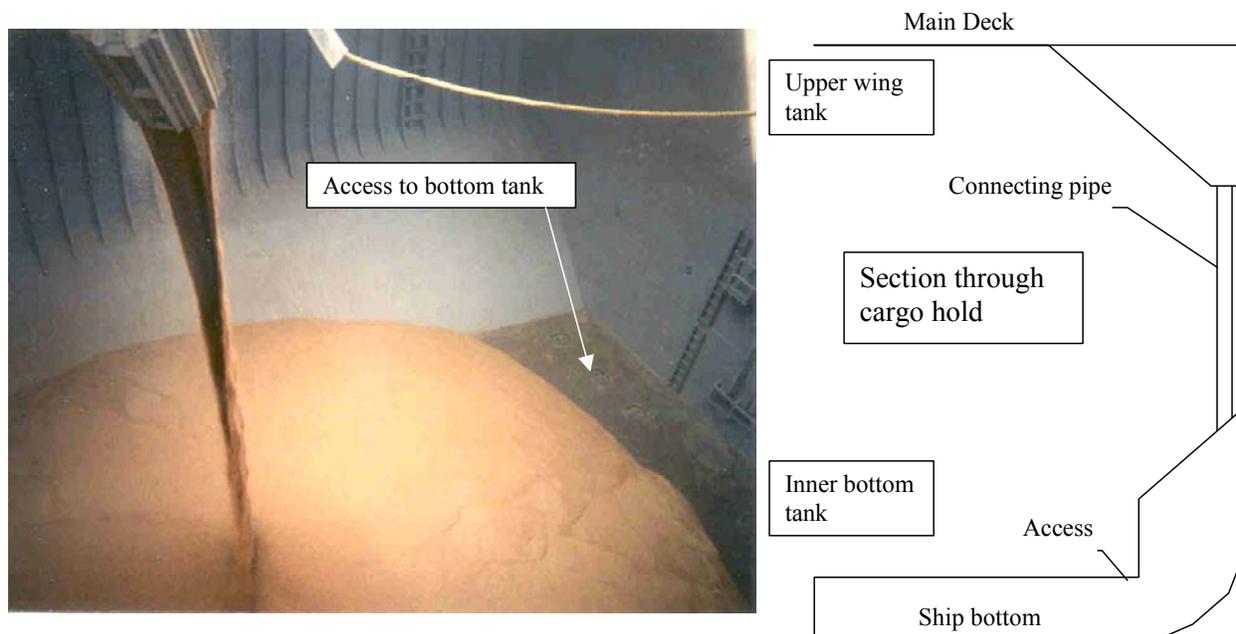


Figure 4.3: Loading Grain and covering access to bottom tanks

Overlying water from test chambers was removed and organisms previously collected were added to 20 L sub-samples for a two-hour exposure. Live/dead and total culturable bacteria analyses were performed on organisms recovered from the test chambers. Temperature, pH, dissolved oxygen, and salinity/conductivity were measured in test chambers and ballast tanks during the voyage. TRC was measured in hypochlorite tests for the duration of the voyage and samples were collected from copper test chambers for total copper analysis.

Sediment was collected from test chambers for chemical and biological analysis in the laboratory. Samples of ballast water organisms were collected and preserved (5% formaldehyde/boric acid) for examination in the laboratory.

4.3 Laboratory Toxicity Testing

Acute toxicity tests ranging from as little as 15 minutes (e.g., Microtox® test) to 48 hours (e.g., algae, aquatic invertebrates excluding resting stages and fish) were conducted in freshwater and saltwater using sodium hypochlorite (12.5% trade solution) and copper (as copper sulfate). Tests were run at 15°C for 48 hours in the absence of light to simulate conditions in ballast tanks during a short voyage. Range-finding tests were conducted to establish appropriate concentration series for the definitive tests used to estimate the LC99 (i.e., the concentration estimated to cause 99% mortality of the test organisms within a specified period of time) or other specified effect (i.e., EC99 in the case of algae). All definitive tests involved replication of test vessels and included a negative control (i.e., clean, uncontaminated laboratory dilution water). For select organisms, range-finding tests were conducted with and without sediment (1%), and in ballast water and lab water. Organisms tested included fish, aquatic invertebrates (including resistant life stages), algae, and bacteria (including a spore former). Tests were dosed nominally using stock concentrations of both toxicants, and samples of test solutions were analyzed to verify dose. A summary of the general test methods is provided in the Appendices.

Samples of ballast water and sediment collected from the ballast tanks during shipboard trials were chlorinated in a similar fashion to what was conducted in test chambers on the ship. These samples were dechlorinated (using sodium bisulfite) and shipped along with an untreated (control) sample to the MDEQ laboratory in Lansing, Michigan for disinfection byproduct (DBP) analysis.

Chlorine decay experiments were conducted by dosing 4L test solutions of lab water (saltwater and freshwater) containing varying levels of sediment with hypochlorite. TRC levels in these test solutions were monitored over 48 hours.

4.4 Laboratory Corrosion Testing

Accelerated corrosion testing and coating integrity testing was conducted in fresh water and simulated sea water (addition of 3.5% sodium chloride) using sodium hypochlorite (5.25 % bleach solution) and copper (as copper sulfate). Test coupons of bare metal (mild steel) were tested to measure corrosion. Test coupons of metal coated with zinc based pre-weld primer and epoxy based marine paints from two manufacturers were tested to examine coating integrity. Table 4.1 lists the paint systems used in the tests.

Table 4.1: Coating System Supplied by Manufacturer

Material	Trade name	Particulars
Primer	Interzinc 22	Inorganic Zinc-Rich Silicate
International 1	Intertuf 702	Coal Tar epoxy
International 2	Intergard 432	Tar free epoxy
Jotun 1	Jotamastic 87	2 pack high solids epoxy
Jotun 2	Balloxy HB light	2 pack modified epoxy

Test coupons coated and then scribed to simulated damage were tested to examine the acceleration of coating edge “creepage” in accordance with ASTM Standard “Test Method for evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D 1654-92”.

Test coupons were placed in the test solution, directly above the test solution (in the damp air space) buried under inert sand (aquarium quality) in the bottom test tank, and on a wheel constantly rotating to simulate periodic immersion.

Air was constantly “bubbled” through the test solution to ensure saturation of dissolved oxygen. All test coupons were electrically isolated to remove galvanic interaction.

Tests were conducted over a 15-day cycle with complete changes of the test solution every 24 hours.

Figure 4.4 shows the test tanks set up with test coupons at the start of a test.



Figure 4.4: Accelerated Corrosion Testing Apparatus

5. SODIUM HYPOCHLORITE TREATMENT EVALUATION AND FINDINGS

5.1 The Efficacy of Sodium Hypochlorite in Killing Ballast-Borne Biota

5.1.1 Shipboard Testing

During saltwater trials, zooplankton mortalities of 96.6% and 96.2% relative to controls were achieved after a two-hour exposure to 9.6 and 8.9 ppm total residual chlorine (TRC) respectively. Similar zooplankton mortalities were observed in freshwater trials with 94.9% and 90.3% zooplankton mortality after a two-hour exposure to 10.0 ppm and 9.2 ppm TRC respectively. In both saltwater and freshwater trials, zooplankton mortalities in treated ballast water were significantly different from the controls ($p < 0.05$). Additionally, no significant differences in zooplankton mortalities were observed between the decant tank and barrel treatments ($p < 0.05$) or between decant tank and barrel controls ($p < 0.05$). Low numbers of worms, mussel larvae, and a few large copepods survived the 2-hour treatments, but were not observed in samples at the end of the trials. Significant numbers of organisms could not be recovered from the overlying water in test containers at the end of the trials. It is possible that during the trial dead and moribund organisms settled out of the overlying water into bottom sediments. Recovery of organisms was also hampered by the presence of the large quantities of suspended sediment.

Results from bacterial tests indicate that the hypochlorite treatment levels in shipboard trials were capable of reducing total culturable bacteria levels from 93.2% to 99.9% relative to the controls after a 2-hour treatment. During freshwater trials, analyses of the water in the decant tanks revealed a regrowth (101.3%) of bacteria relative to the control. It is not clear at this point the cause of the elevated bacterial level for this sampling time, however, overlying water in the decant tanks was visibly more turbid than that of the barrels, and bacteria associated with high levels of suspended sediment may be the cause. Table 5.1 below summarizes the biological data collected during shipboard trials.

Table 5.1: Efficacy of Hypochlorite Treatment in Saltwater and Freshwater Trials

Location	Mean Dose ¹ (ppm)	Zooplankton ²	Total Culturable Bacteria ³	Total Culturable Bacteria ³
Saltwater Trial			T= 2 hours	T=8 days
Decant Tanks	9.48	-96.6 ± 2.08	-99.9	-80.7
Barrels	7.85	-96.2 ± 3.17	-98.0	-99.98
Freshwater Trial			T= 2 hours	T= 5 days
Decant Tanks	9.60	-94.9 ± 3.19	-93.2	101.3
Barrels	8.90	-90.3 ± 5.81	-95.9	-96.71

1. Measured TRC after ½ hour.

2. Reduction in percent live vs dead relative to controls after 2 hour exposure.

3. Percent change relative to control (positive value indicates growth).

Table 8.1 (Section 8) summarizes the zooplankton organisms identified in ballast water samples collected during the saltwater and freshwater trials. In both trials the numbers and diversity of organisms found in the ballast water was low. For this reason, organisms were collected to add to the test systems. In saltwater trials, organisms were concentrated from water collected through the fire hose (off the ballast main). In freshwater trials, organism densities in the immediate ballasting area were very low, and organisms had to be collected beyond the harbour breakwater using a plankton tow (60µm mesh).

Chlorophyll-a samples were collected and processed according to the protocol. However, processing of these samples was confounded by the presence of high levels suspended sediment. Additionally, chlorophyll-a levels in analyzed untreated controls were low (i.e., near or below the detection limit) and statistical comparisons between treated and untreated samples could not be performed.

Laboratory Toxicity Testing

Testing was conducted in the laboratory using hardness adjusted well water (hardness 125 ± 5 mg/L as CaCO_3) and reconstituted salt water (Instant Ocean™) to simulate ballast water. Range-finding tests were conducted with each species to establish the range of concentrations required for definitive tests. Numerous range-finding tests were conducted in the presence of sediment, however significant technical difficulties were encountered. Subsequent range-finding tests and definitive laboratory toxicity tests did not include sediment. Most testing was conducted using a 48-hour exposure. *A. salina* cysts and *D. polymorpha* veligers were exposed for 24 hours (cysts hatch in 24-36 hours). Additionally, the Microtox® assay (i.e., *V. fischeri*) includes a 15 minute exposure time limitation.

Table 5.2 lists the range of lethal total residual chlorine concentrations for the freshwater and marine species tested in the laboratory. For both freshwater and marine species, the range between the least and most tolerant organism was significant (i.e., several orders of magnitude). Detailed test reports for all toxicity tests are provided in Appendix B.

Table 5.2. Lethal Concentrations (LC99, IC99) of Hypochlorite for Selected Freshwater and Saltwater Biota

Lethal Concentration Range TRC (ppm)	Freshwater	Salt water
< 1	Alga - <i>S. capricornutum</i> (48 hr) Alga - <i>Nanochloris sp.</i> (48 hr) Alga - <i>S. obliquus</i> (48 hr) Invertebrate - <i>D. magna</i> (neonate) (48 hr)	Bacteria - <i>V. fischeri</i> (15 min) Alga - <i>S. costatum</i> (48 hr)
1 to 10	Bacteria - <i>Bacillus subtilis</i> (spore) (48 hr) Mollusc - <i>D. polymorpha</i> (veliger) (24 hr) Benthic invertebrate - <i>L. variegates</i> (48 hr) Fish - <i>C. carpio</i> (48 hr)	Amphipod - <i>E. estuarius</i> (48 hr) Fish - <i>C. variegatus</i> (48 hr)
10 to 100	Invertebrate - <i>D. magna</i> (ephippia) (48 hr)	
100 to 1000		Invertebrate - <i>A. salina</i> (cyst) (24 hr)

Within the freshwater species, algae (including *S. capricornutum*, *S. obliquus*, and *Nanochloris sp.*) exhibited the lowest tolerance to sodium hypochlorite ($\text{IC}_{99}\text{s} \leq 0.1$ ppm), followed by *D. magna* ($\text{LC}_{99} = 0.2$ ppm based on exposure of neonates (< 24-h old)). The most tolerant species, based on exposure of the resting egg or “ephippia”, was *D. magna* ($\text{IC}_{99} = 76.3$ ppm). Lethal effect levels for all other species were in between this range with LC_{99}s below 10 ppm.

For the saltwater species, the bacterium, (*Vibrio fischeri*) and the alga (*S. costatum*) exhibited the lowest tolerance to sodium hypochlorite with IC99's estimated to be 0.15 and 0.20 ppm, respectively. The most tolerant species was the brine shrimp (*A. salina*), based on exposure of the cyst (IC99 \approx 486 ppm). All other species were in between this range with IC/LC99s below 10 ppm.

Table 5.3 summarizes water quality of lab water and ballast water used in toxicity evaluations.

Table 5.3: Water Quality Characteristics of Laboratory and Ballast Waters

Parameter	pH	Hardness (ppm as CaCO ₃)	Conductivity (μ S/cm)	Salinity (ppt)
Freshwater Laboratory Water	8.0 – 8.2	125 \pm 5	265 \pm 15	-
Freshwater Ballast Water	7.9 – 8.1	220 \pm 5	635 \pm 15	-
Laboratory Saltwater	8.1 – 8.2	-	-	30 \pm 0.5
Saltwater Ballast Water	7.6 – 7.7	-	-	34 \pm 0.5

From Table 5.3, it can be seen that freshwater laboratory and ballast water were similar in terms of pH, but ballast water was higher in water hardness and conductivity than the laboratory water. Marine ballast water was characterized by a slightly lower pH (0.5 pH unit) and higher salinity relative to the laboratory saltwater.

Toxicity tests using selected organisms were conducted to assess the relative toxicity of sodium hypochlorite in laboratory dilution water versus ballast water. The results of the toxicity tests are presented in Table 5.4.

Table 5.4: Comparison of Sodium Hypochlorite Toxicity to *Lumbriculus Variegatus* and *Eohaustorius Estuarius* in Laboratory Waters versus Ballast Waters

Species	Freshwater (48 hr)		Saltwater (48 hr)	
	Laboratory Water LC99 (TRC ppm)	Ballast Water LC99 (TRC ppm)	Laboratory Water LC99 (TRC ppm)	Ballast Water LC99 (TRC ppm)
<i>L. variegatus</i>	1.485 (1.410-1.508)	0.743 (0.743-0.743)	-	-
<i>E. estuarius</i>	-	-	6.998 (3.728-7.245)	7.448 (7.448-7.448)

Tests conducted with the *L. variegatus* suggested that sodium hypochlorite was more toxic in ballast water (LC99 (0.743 ppm)) relative to the laboratory water (LC99 (1.485 ppm)). However, in tests with *E. estuarius*, results indicate hypochlorite is slightly more toxic in lab water than ballast water.

Detailed test reports for all toxicity tests are provided in Appendix B.

5.2 The Effect of Sediment on the Efficacy of Sodium Hypochlorite

During any given ballast operation, solid material will settle out of suspension from the overlying ballast water forming bottom sediments. As ballast tanks cannot be completely emptied during deballasting, and due to the myriad of structural components within ballast tanks, there are natural traps where the bottom sediment accumulates. During the field trials onboard the *Federal Yukon*, bottom sediments were recovered from ballast tanks for use in the test systems. During the examination of the tanks there was approximately 5 cm of water present in the after part of the tank, and the depth of the bottom sediment throughout the tank was not significant. As a result, the field crew had to travel through the tanks for some distance to gather the required volume of bottom sediments.

The primary impact of sediment on sodium hypochlorite treatment is an increase in chlorine demand relative to the amount of sediment present in the water. Sediment can also build up over time in the bottom of ballast tanks, offering a protective refuge for certain organisms. With this in mind, and for the purposes of this study, sediment is further defined as bottom sediment or suspended sediment. Bottom sediment is solid material that has previously settled out of the ballast water, forming a layer of solid material on the bottom of the ballast tank. Suspended sediment is the solid material suspended in ballast water as it is being brought on board. As ballast water is taken onboard, it is possible for bottom sediment to be lifted into the water column in the ballast tank as resuspended sediment. Figure 5.1 shows the overlying water and bottom sediment in the ballast tanks of the *Federal Yukon* that constitute the residual ballast water “un-pumpable” from the tanks.

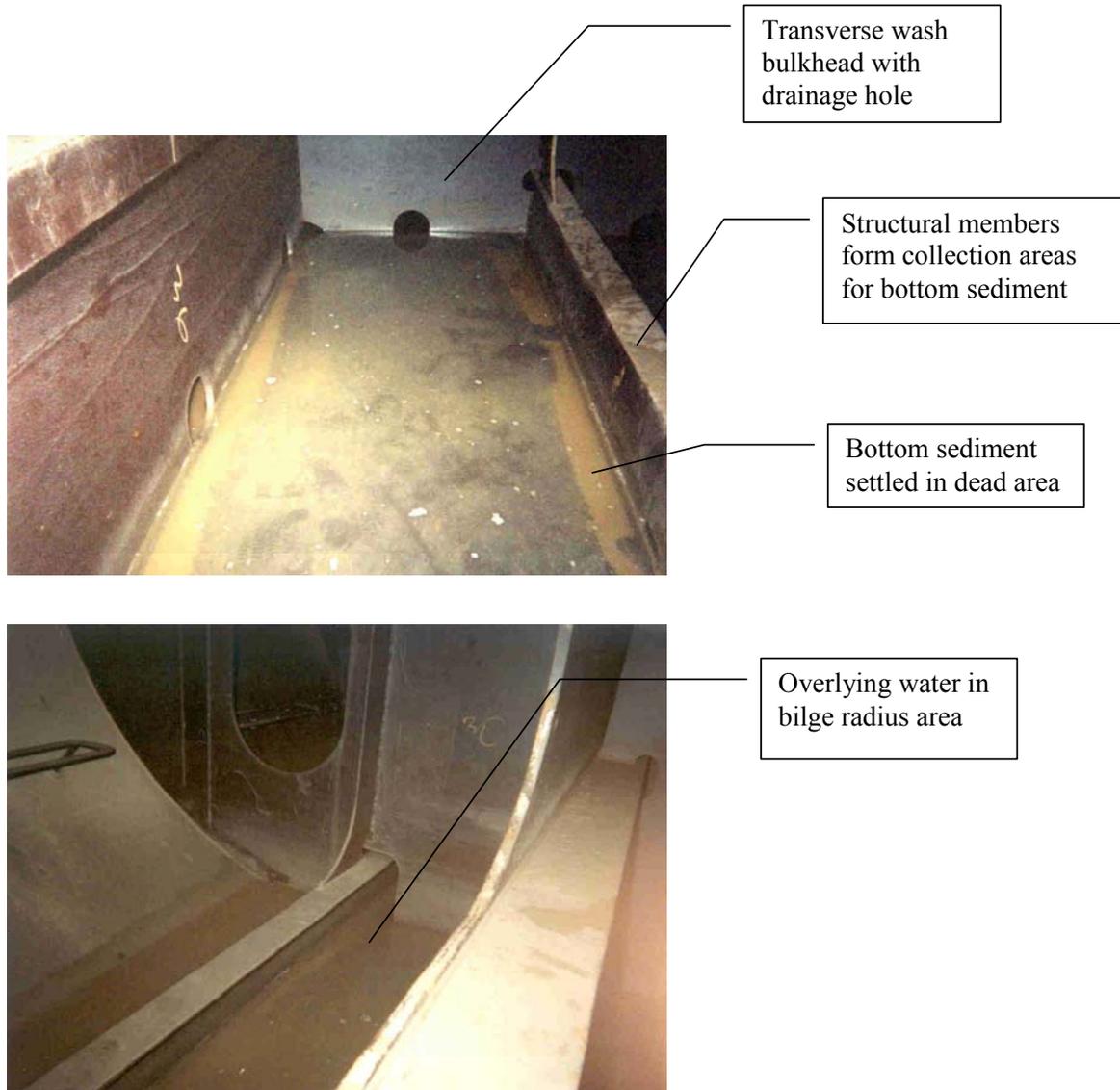


Figure 5.1: Residual Ballast Water in Tanks of M.V. *Federal Yukon*

The presence of large amounts of bottom sediment will have numerous impacts on sodium hypochlorite treatment. The sediment can act as a physical barrier to treatment, protecting organisms already present in bottom sediment in the tank. The result is that when treating residual ballast water during a NOBOB condition, some target organisms and resting stages may not receive effective treatment. Similarly, bottom sediment can act as a refuge for organisms being treated during ballasting. Organisms that have the capability may enter the existing bottom sediment layer as they are being brought in, avoiding treatment. Finally, bottom sediments that are resuspended during ballasting may increase chlorine demand of the overlying water, reducing treatment effectiveness.

5.2.1 Laboratory testing with sediment present

Bottom sediment samples were collected at the end of each trial and sent to the laboratory for study. Examination of sediments recovered from the bottom of the test chambers after the saltwater shipboard evaluation revealed that numerous viable organisms were present in the sediment after treatment. Live invertebrates, protozoa, and diatoms were recovered from all sediment samples. Of particular interest is the presence of nematodes in all treated sediment samples. As nematodes were only recovered in a few of the samples of ballast water, it is likely that they entered the test systems in the sediment, and were able to avoid treatment.

It is not clear at this point what depth of sediment protects organisms from treatment. In shipboard test chambers, sediment depth varied from a millimeter or less in some areas of the decant tanks to approximately 1.0 cm in barrels. Organisms identified in sediment samples collected during coastal trials are provided in Table 8.2 (section 8).

Toxicity testing was conducted in the laboratory to attempt to quantify the impact of sediment on the efficacy of sodium hypochlorite. The results of range-finding tests performed on selected species with and without a one percent sediment load are summarized below in Table 5.5.

Table 5.5: Toxicity of Sodium Hypochlorite to *Lumbriculus Variegatus* and *Cyprinus Carpio* with and without Sediment Present

Species	With Sediment (48 hr)		Without Sediment (48 hr)	
	Laboratory Water Lethal Range TRC (ppm)	Ballast Water Lethal Range TRC (ppm)	Laboratory Water Lethal Range TRC (ppm)	Ballast Water Lethal Range TRC (ppm)
<i>L. variegatus</i>	1.0 - 10	1.0 - 10	0.1 - 1.0	0.1 - 1.0
<i>C. carpio</i>	>6.25	-	0.75 - 7.5	-

Sediment had a significant impact on the toxicity of sodium hypochlorite to *Lumbriculus*, resulting in a 10-fold increase in the ranged nominal concentration to achieve 100% mortality. In range-finding tests with juvenile common carp (*C. carpio*), 100% mortality was not achieved at up to 6.25 ppm in the presence of sediment. Complete mortality was achieved between 0.75-7.5 ppm without sediment.

Table 8.3 (Section 8) summarizes the inorganic composition, organic carbon content, and solids of sediments used in shipboard and laboratory studies. Aluminum, zinc and copper levels were all elevated in sediments collected from the ship relative to the laboratory control sediment, however the survival of numerous organisms in the sediment samples recovered from test containers suggest that it is likely the metal levels in these sediments were not toxic.

5.2.2 Sediment Chlorine Demand

To achieve effective treatment using sodium hypochlorite, the chlorine demand of the suspended sediment in the ballast water must be overcome. This presents numerous challenges, primarily because sediment content of the ballast water will change with harbour water conditions at the time of ballasting and with proximity of the ballast water intakes to the bottom of the harbour.

An analysis of water samples taken from ballast tanks of ships entering the Great Lakes by Whitby *et al* (2000) revealed total suspended solids levels up to 6,024 ppm (i.e., 0.6 percent). For this study, one percent sediment in ballast water was selected as a worst case scenario. In shipboard trials, test chambers containing 1% sediment were dosed with sodium hypochlorite until a total residual chlorine (TRC) of approximately 10 ppm was achieved. The half hour chlorine demand of the ballast water and sediment was between 20.27 – 20.97 ppm in saltwater trials and between 21.25 - 25.30 ppm in freshwater trials. After the half-hour chlorine demand of the sediment and ballast water was met, TRC levels in test containers continued to decline over the duration of the trial. Figures 5.2 and 5.3 below illustrate changes in the TRC levels in test containers during the shipboard trials.

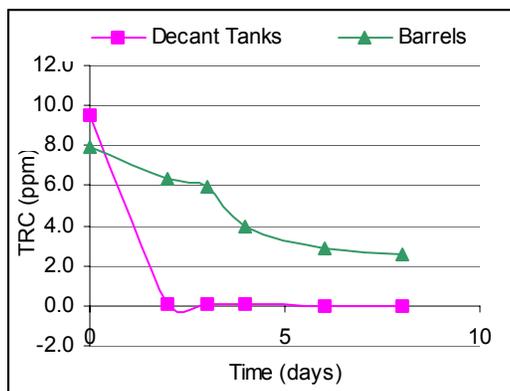


Figure 5.2: Average Total Residual Chlorine Levels in Saltwater Shipboard Trials

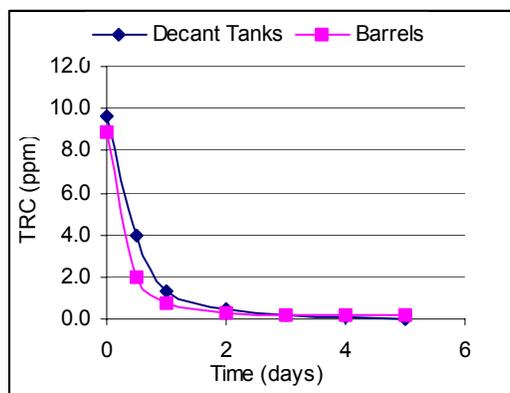


Figure 5.3: Average Total Residual Chlorine Levels in Freshwater Shipboard Trials

In instances where TRC levels dropped to near zero within the duration of the trials, considerable turbidity was visible in the overlying water. In saltwater trials, the overlying water in barrel tests was visibly clearer than the waters the decant tank. It is possible that the differences in decay rates of TRC in the treatments are due in part to the varying amount of re-suspended sediment in the water column during the tests. Every effort was made during shipboard trials to maintain consistent levels of re-suspended sediment in the overlying water in test containers. However, variations in ship movement caused by sea conditions during each trial, and differences in test chamber shape (i.e., barrels compared to decant tanks) may have impacted re-suspended sediment levels.

Laboratory experiments attempted to model the effect of sediment load on chlorine demand using sediment collected from the Great Lakes. In addition, experiments were conducted to examine the chlorine demand of ballast water (no sediment addition) obtained from control tanks during the shipboard trials. Table 5.6 below summarizes data collected from laboratory chlorine demand experiments.

Table 5.6: Impact of Sediment on TRC Demand in Laboratory Water and Ballast Water

Water Type	% Sediment (v/v)	TRC (nominal) (ppm)	1/2hr demand (ppm)	48hr demand (ppm)
Laboratory Freshwater	0	50	0.5	4.0
	0.05	50	6.5	26.5
	0.1	50	8.0	35.0
	0.5	50	17.0	48.5
	1.0	50	20.0	49.2
Laboratory Saltwater	0	50	3.5	16.5
	0.05	50	11.0	34.5
	0.1	50	12.0	48.4
	0.5	50	21.5	49.5
	1.0	50	23.5	~50.0
Freshwater Ballast Water	0	10	2.3	7.0
Saltwater Ballast Water	0	10	3.2	7.6

Data from chlorine demand experiments indicate a higher TRC demand (7 times higher at ½ hour and 4 times higher after 48 hours) in saltwater than in freshwater without sediment present. This higher TRC demand may be a result of an increased decay of the hypochlorous acid molecule caused by high ion levels present in saltwater. In the presence of sediment, TRC demand in saltwater is still higher than that of freshwater, however, as the sediment load accounts for the majority of the chlorine demand, these differences are less dramatic. The TRC demand in both fresh and saltwater increased with an increase in sediment content. The immediate chlorine demand was high during the first half hour of the tests accounting for nearly half the total TRC demand in 1% sediment tests, and nearly a quarter of total TRC demand in 0.01% sediment tests. After the immediate TRC demand was met, TRC decay rates in saltwater was similar across treatments regardless of sediment content. This trend was also observed in decay experiments in freshwater, with the exception of the control, where considerably less decay occurred relative to solutions with sediment. The freshwater ballast water (without sediment addition) had a half hour TRC demand of 2.3 ppm and a TSS of 14.8 ppm. The saltwater ballast water (without sediment addition) had a half hour TRC demand of 3.2 ppm and TSS of 8.6 ppm. Figures 8.1 and 8.2 (Section 8) provide further details of TRC decay experiments.

It should be noted that during these experiments a majority of the sediment settled to the bottom of test containers during the test period. During shipboard trials settling of sediment was less apparent, and more variable, resulting in differences in TRC demand in some test containers during shipboard trials.

5.3 The environmental considerations of discharge of sodium hypochlorite

5.3.1 Total Residual Chlorine Discharge Requirements

Ballast water discharge requirements for TRC were solicited by the MDEQ from all Great Lakes jurisdictions prior to the biocide study. Based on the information received from responding Great Lakes states, theoretical TRC discharge limits for a ballast water discharge, specific to this short-term study, range from 19 µg/l to 38 µg/l. The current Ontario water quality objective for TRC is 2 µg/l in the receiving water. However, the 2 µg/l TRC level is below the detection limit of most analytical methods.

The general permit for short duration discharges was obtained from the State of Wisconsin to discharge ballast water containing a small residual of TRC into Lake Superior near the Port of Duluth/Superior. The ultimate ballast water discharge into Lake Superior from the *Federal Yukon* was in compliance with the 38 µg/l discharge limitation for TRC required in the permit. TRC was neutralized with sodium bisulfite prior to discharge and the TRC monitoring data were submitted to the Wisconsin Department of Natural Resources as required. The TRC data collected prior to the Lake Superior discharge are available in Appendix A Item 2.

The effectiveness of the dechlorination agent sodium bisulfite at neutralizing chlorine was evaluated at the ESG International laboratory through TRC measurements of ballast water test solutions before and after chlorination/dechlorination. These data indicate that, when sodium bisulfite is properly added and mixed with chlorinated ballast water, all theoretical TRC discharge requirements for Great Lakes waters can be met. Also, the effectiveness of sodium bisulfite (and other chemicals) as dechlorination agents is well-documented in the literature and by wastewater treatment plants throughout the Great Lakes region.

The equipment requirements associated with shipboard chlorination and dechlorination are discussed later in Section 5.7.

5.3.2 Ballast Water Discharge Byproducts

A laboratory simulation of ballast water chlorination was used to assess potential formation of organic chemicals and related ballast water discharge acceptability issues. Laboratory simulation was necessary because the intended shipboard experiment sampling effort failed due to sample bottle breakage that occurred during transport to the MDEQ Environmental Laboratory in Lansing.

At the ESG International laboratory pre- and post-chlorinated ballast water samples were collected for subsequent organic chemical analyses for pollutants using gas chromatography/mass spectrometry (Appendix A item 1). The analytical results were compared to Michigan Water Quality Standards applicable for a typical, short-term or intermittent discharge. The key highlights of these analytical data are listed below:

- The only organic chemicals detected in the chlorinated ballast water samples were acetone, chloroform, bromodichloromethane and tetrahydrofuran. None of the organic chemicals tested were detected in the pre-chlorinated ballast water sample.
- Addition of chlorine to the simulated ballast water appeared to produce small quantities of the trihalomethanes, chloroform and bromodichloromethane. The presence of tetrahydrofuran and acetone in the chlorinated ballast water samples is probably not attributable to chlorine addition.

- No organic chemicals were detected in the chlorinated ballast water samples at levels that would exceed Michigan Water Quality Standards applicable for a short-term point source discharge scenario. The four organic chemicals measured in the chlorinated ballast water samples were found at concentrations several orders of magnitude below applicable Michigan Water Quality Standards for a typical short-term or intermittent discharge.

5.4 The Effects of Sodium Hypochlorite on Ballast Tanks

The effects of sodium hypochlorite on ballast tank structure were investigated in the Accelerated Corrosion testing facility. This work examined both the corrosivity on bare steel and coating system failure in both simulated seawater and freshwater. The experiment and results are presented in Appendix C.

Visual inspections of each decant tank section before and after shipboard trials with sodium hypochlorite treated ballast water did not reveal any visible corrosion to the interior surfaces. No obvious visible differences between treated and untreated decant tank sections were observed.

5.4.1 Corrosion rates

Corrosion rates in ship structures are dependent on the several factors. These include the galvanic dissimilarity of steel and weld metals or other components, the salinity or electrolytic capacity of the water, the aggressivity of the environment experienced by the structure thus disturbing the corrosion products, the availability of oxygen and the temperature. The Tanker Structure Cooperative Forum (reference n) 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 similar to those on bulk carrier cargo ships like the M.V. *Federal Yukon*, corrosion rates have been measured at between 0.1 millimeters per year (0.0039 inches or 4 thou) to 1.2 mm / y (0.047 inches).

Corrosion cannot take place until the coating has been removed, damaged, or in the presence of application defects (known as holidays in the paint) and while all modern ships are coated at construction, coating systems do break down and defects are present. In most cases, when ships are constructed the steel is first coated with a weldable primer, which is rich in its zinc content in order to aid in the fabrication welding processes. A topcoat is added after fabrication and this is normally an epoxy based paint system.

It is known that the largest cause of corrosion activity in ships is by galvanic attack from the presence of dissimilar metals and that in ship structures corrosion, the rate of steel diminution in sea water is several times that in fresh water. The objective of these tests was, however, to examine the influence of adding biocides. Thus in the experimental apparatus, each test coupon was electrically isolated. This was done to remove galvanic corrosion activity caused by dissimilar metals used in the test apparatus and thus establish the corrosion characteristics from oxygen availability only.

This was also done to ensure the experiment captured any increase in coating damage that may be incurred by galvanic action associated with the zinc based pre-weld primer.

The corrosion rate increase in the presence of hypochlorite was investigated with un-coated test coupons. Tests were conducted by dosing test water with 10ppm and 40ppm sodium hypochlorite. In fresh water, the low dose (i.e., 10 ppm) was seen to decrease to a TRC content of around 1ppm within 2 hours and remained near that level (dropping slowly) over a 24-hour period, at which time the system was re-dosed. In order to ensure that there was a representative TRC equivalent to what would be encountered in the ship's ballast tanks, the level of chlorine in the high dosage water was increased to account for the initial demand. The high dosage (i.e. dose at 40 ppm) was seen to decrease to around 15ppm after 2 hours and then to around 5ppm over the 24 hours before re-dosing, providing on average a 10ppm exposure. In the salt water (simulated marine water by adding 3.5% sodium chloride) the same effects were observed but TRC decay was more rapid and the high level dose reduced to less than 2ppm over the 24-hour period.

In each experiment, the highest corrosion rates were in those test coupons mounted on the wheel, followed by those continually submerged under water, then those in the damp atmosphere and finally the lowest corrosion rates were experienced by test coupons in the buried samples. This result demonstrates that:

The removal of corrosion products through more aggressive water splashing increases corrosion, i.e., the wheel provides the highest corrosion,

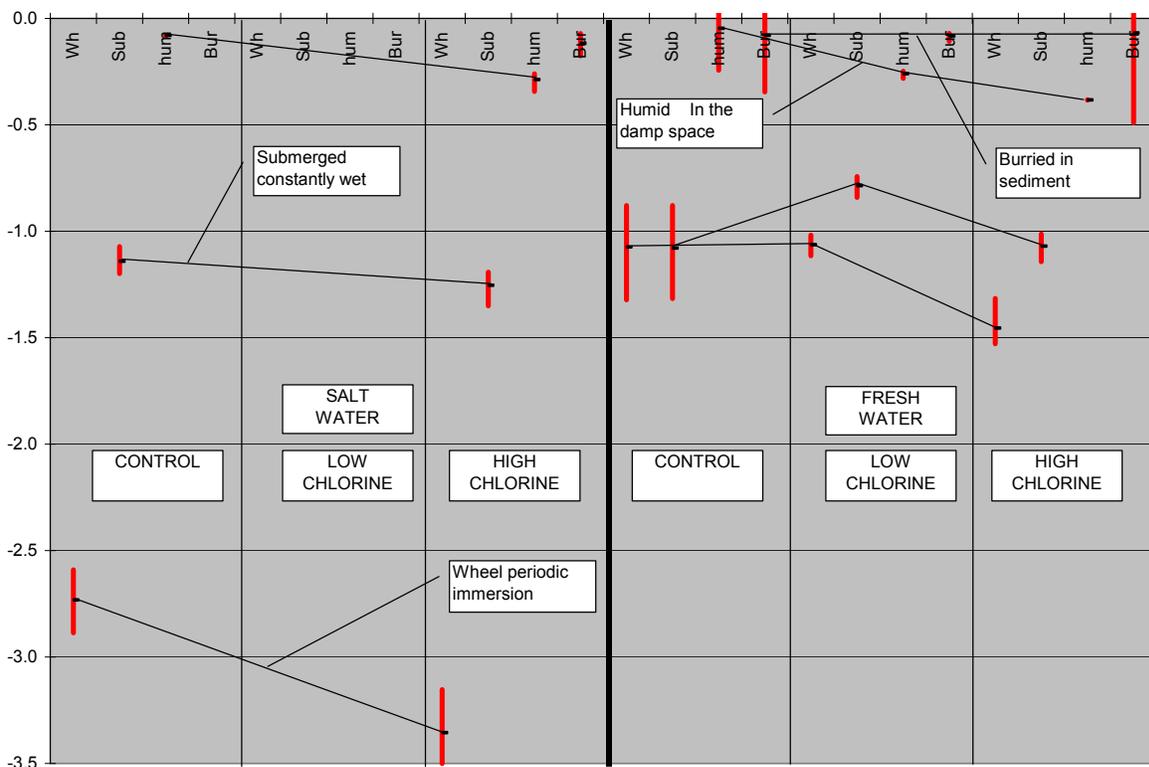
The availability of oxygen limits corrosion, i.e., the buried samples exhibited least corrosion,

The equivalent annual corrosion rates when adjusted from the measured thickness loss incurred by the samples in the test apparatus are between 0.1mm/y in the buried/humid test coupons to 3 mm/y in the salt water test coupons on the wheel. During the operational life time of any given ballast tank structure there is a range of exposures to ballast water immersion, humid conditions and washing through splashing, that is dependent on the location in the tank and the operational profile of the ship. The experimental conditions replicate each of these separately and remove the galvanic attack component. Direct comparison of in service corrosion rates and test apparatus rates is, therefore, not possible, however an exposure scenario can be developed based on the field experiment performed on the *Federal Yukon*. For example, during the field trial, the total time for a round trip (Europe to the Great Lakes and back to Europe) covered some 69 days, during which time the ballast tanks were filled and emptied twice. This potentially exposed the steel to biocide for 14 days (approximately 20% of the time). Such a scenario would result in a corrosion rate based on the tests of 0.68mm/y ($3 \times 20\% + 0.1 \times 80\%$). Given the absence of galvanic attack, this value fits within the range of the Tanker Forum in service data.

In those samples designed to replicate the most harsh ballast tank environment of periodic immersion of steel with the corrosion product being removed by washing, i.e. on the wheel, an increase in corrosion rate over the control levels was measured in the high chlorine dosage for both the saltwater and fresh water experiments. This increase in corrosion rate represents approximately 20% increase in annual thickness diminution. For the submerged samples, the increase in corrosion rate was undetectable in fresh water and was marginal in salt water.

In those samples designed to replicate the humid or damp spaces of a ballast tank, i.e., the samples suspended just above the water surface, the increase in corrosion was from 0.1mm/y to 0.3mm/y. This appears to be a dramatic increase but is derived from small absolute rates and while statistically the mean result is a three-fold increase the variation in experimental data is such that the increase can not be precisely derived. It would however suggest that there is increased corrosion which correlates to the deterioration of chlorine whereby chlorine related gas resulting from decomposition is prevalent in the humid environment. No significant increase in corrosion was observed in the samples buried in sediment where oxygen availability is relatively limited and constant.

Figure 5.4 shows the experimental results in terms of annual diminution rates from the accelerated corrosion tests on bare steel coupons in salt and fresh water. It should be noted that the groups of tests labeled “High Chlorine” and “Low Chlorine” refer to the application of 40 ppm and 10 ppm dosing levels of sodium hypochlorite respectively.



Note: Labels refer to location of test coupons in the test tank, e.g. wheel refers to periodic immersion, etc. Units are annualized millimeters thickness diminution (millimeters / year)

Figure 5.4: Thickness loss through Corrosion in the presence of Sodium Hypochlorite

On the basis of the operational scenario previously developed from the field trial on the *Federal Yukon*. It is assumed that a ship will be subject to ballast water treatment on a 30 day cycle and that during that cycle the structure will be exposed to 2 days of high sodium hypochlorite dose and 4 days at a low dose given in the experiment (20% of total time) decomposing chlorine reducing the levels to zero over time. Under this assumption, the effective corrosion rate of bare exposed steel (after removal or damage to the coating system) in the ballast tank would be increased by 1% and its serviceable life reduced accordingly.

5.4.2 Coating Deterioration

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”. In this standard, coated samples are scribed down to bare metal and exposed to the corrosive environment. Coating deterioration (i.e., creepage) for a distance away from this scribe line is rated in accordance with Table 5.7

Table 5.7: ASTM D 1654-92 Deterioration Rating

Representative Mean Creepage from Scribe	
Millimeters	Rating
Zero	10
0 to 0.5	9
0.5 to 1	8
1 to 2	7
2 to 3	6
3 to 5	5
5 to 7	4
7 to 10	3
10 to 13	2
13 to 16	1
Over 16	0

This rating system was used to rate the damage arising from exposure to two levels of hypochlorite exposure for four different coating systems using identical triplicate test coupons.

One coating system broke down completely in 1 control coupon, 2 low chlorine coupons fresh water, 1 high chlorine coupon fresh water and 2 low chlorine coupons salt water. Microscopic examination of this failure indicated that the bond between primer and steel was lost and that the zinc-based primer to paint coating bond remained intact as the primer was attached to the coating. All of these failures occurred in the submerged condition and on those test coupons that were scribed to simulate damage. This result distorted the overall trends that could be derived from the comparison necessary to test with and without biocide. Therefore, this particular coating system was removed from the data set. Figure 5.5 shows a comparative measure of coating loss over all 4 coating systems highlighting the coating 3 failure which was therefore removed from the data set for the development of trends (average etc). Note that again in all the following figures, “High” and “Low” Chlorine refer to tests where hypochlorite was applied at 40 and 10 ppm respectively and FW and SW refers to fresh and salt water.

The experiment results are described in full in Appendix C. Examination of the ASTM rating score for the three coating systems reveals the following;

- (a) Samples exposed to hypochlorite tend to experience slightly more damage than the control samples; however, this is a small effect and is not quantifiable in terms of life expectancy from this analysis. The saltwater low hypochlorite exposure showed no difference in damage to that experienced by the control exposure (see Figure 5.6).
- (b) 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 5.7).

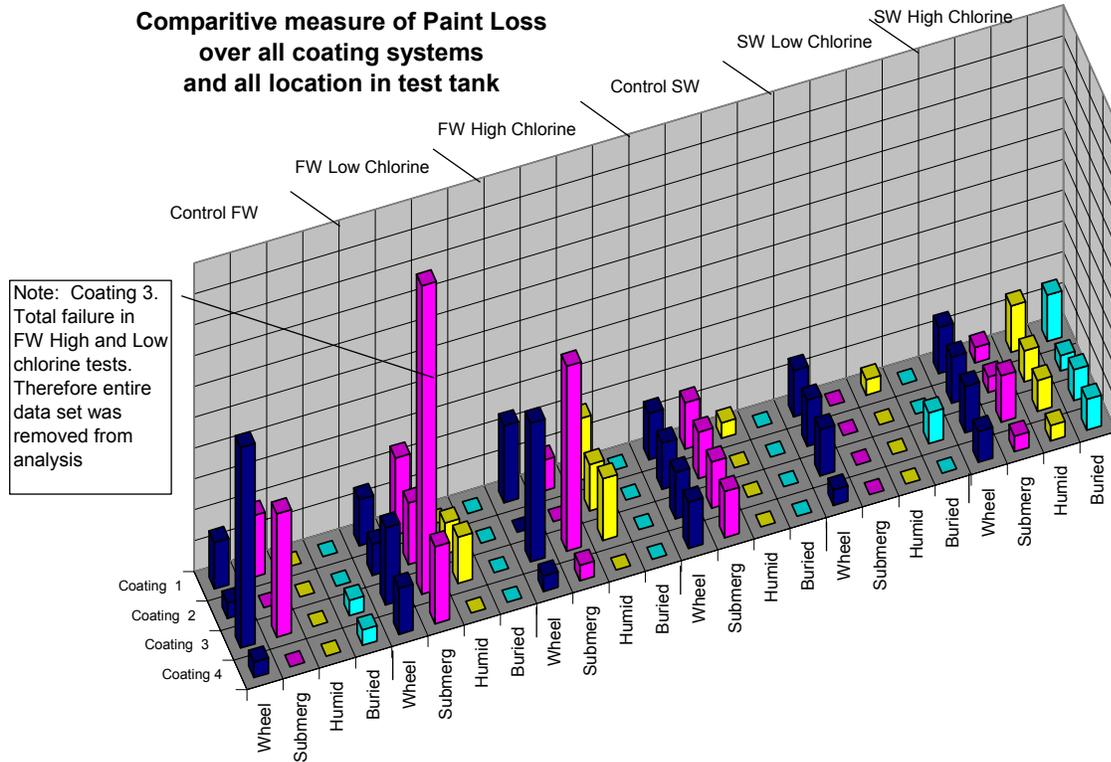


Figure 5.5: Scribed Coating System Defects Found after Hypochlorite Exposure (Why system 3 was discarded)

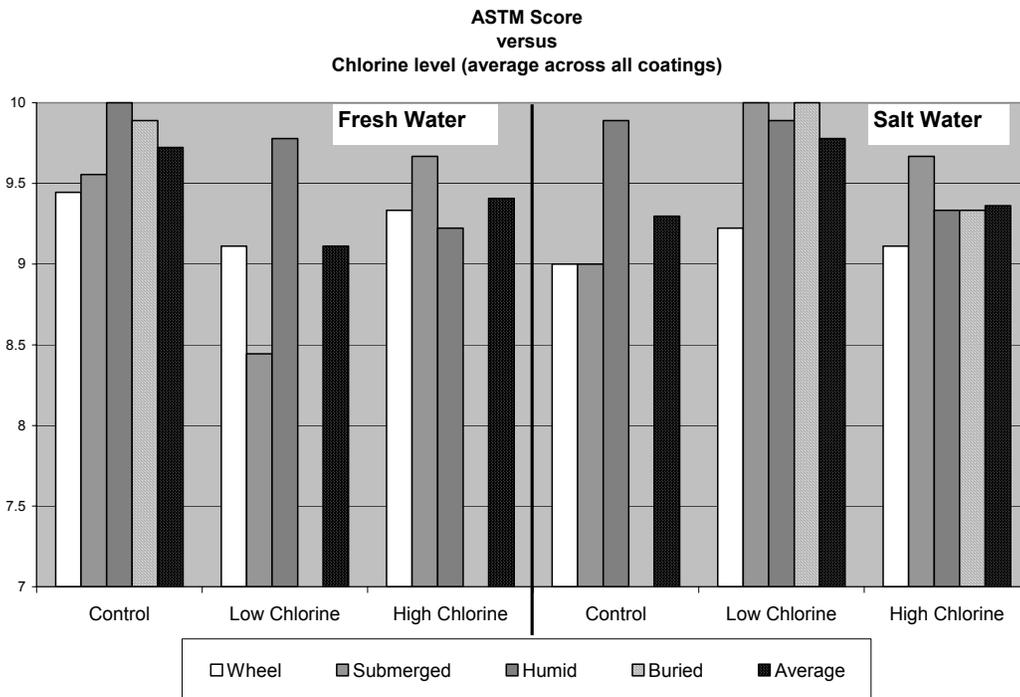


Figure 5.6: Coating Damage comparison at various Hypochlorite Dosages

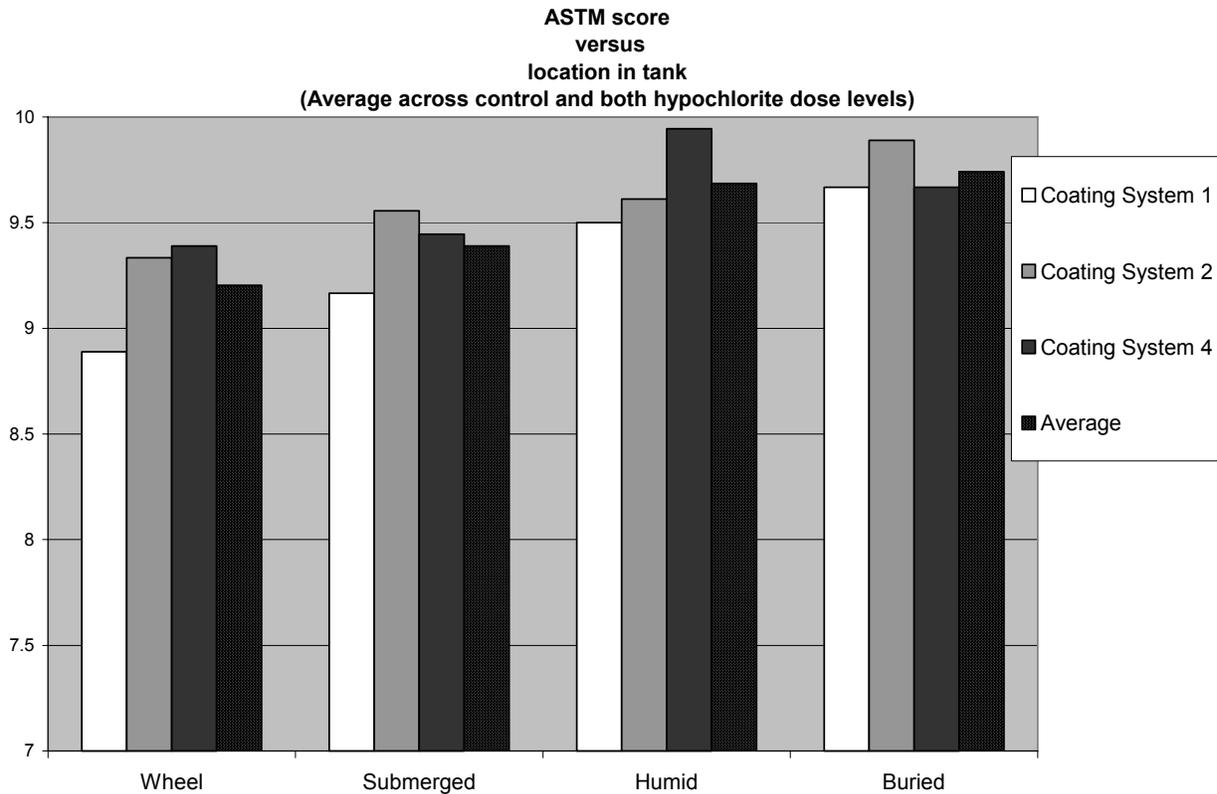


Figure 5.7: Coating Damage Increase with Environment

While no quantifiable analysis is possible with respect to life expectancy, the observation (a) that damage is increased by the presence of chlorine, is mitigated by observation (b), i.e., that during the life of the ship, the period when tank structure is submerged represents a fraction of its total life and increased damage occurs primarily when submerged. Using the example from the field trial again, the exposure to ballast water was in the order of 20% of the time, thus the accelerated damage to coatings that was observed in the experiment should be pro-rated accordingly.

No accelerated failures were observed in any un-scribed coating system.

There was no detectable decrease in the thickness of coating applied.

In other tests drawn from the open literature, there was some pigment color change in coatings subject to hypochlorite exposure. During this study, high quantities of iron oxides in the corrosion products being washed off the test coupons engrained the coating with a rust color. The removal of this rust color was not possible without chemically or mechanically degrading the coating thickness.

The potential for coating damage increase due to the presence of hypochlorite is seen as small over the operational life cycle of the ballast tank when subject to the biocide levels described in the trial. 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.

5.5 The Economics of using Sodium Hypochlorite Onboard Ship

Sodium hypochlorite can be purchased as a liquid in concentration of 15% sodium hypochlorite, or it can be generated onboard a ship using a sodium hypochlorite generator. Either option requires appropriate storage, handling and dosing and metering systems. In addition, any chlorine-based system will also need a de-chlorination capacity to render discharge environmentally acceptable. This system will also require control and monitoring of pumps and storage facilities.

5.5.1 On-Board Hypochlorite Generation

Onboard a ship, sodium hypochlorite can be generated electrically from seawater or brine systems. The principal advantages of generating sodium hypochlorite on board are the operational flexibility afforded to the ballasting schedule of the ship, its independence from shore base facilities and suppliers and a greatly reduced safety concern by virtue of its weak concentration. Generated solution is only 0.8% concentration versus the commercial concentration of 12% to 15% (household bleach is typically 5.25%). The draw back is cost.

Seawater varies in composition between 30 to 36 parts per thousand (ppt) total salinity. This makes on site generation of hypochlorite particularly efficient where saline water is present. However, sodium hypochlorite generated from seawater is not very stable (decays at 2-3% per hour), due to the presence of heavy metals, and seawater systems can only produce in low concentrations (i.e., 2000 ppm (0.2%)). This instability would limit the storage of previously generated hypochlorite for future use when ballasting in a freshwater environment. It is also unclear as to the time available for ships to use seawater. In the field trial, the *Federal Yukon* took on ballast in both seaboard harbor waters and Great Lakes ports and was, during the 69 day round trip, in freshwater or less than full saltwater conditions 44% of the time.

Brine systems can produce hypochlorite in a similar fashion to seawater systems, however this necessitates the carrying of salt (with fewer impurities than sea salt) as a raw material. Brine systems can produce higher concentration of hypochlorite solutions (i.e., 8000 ppm (0.8%)) that are very stable and can be stored for extended periods. Any water source can be used provided it is pre-filtered (200 micron) to prevent element blockage. Also care should be taken to respect the content of fluorides, manganese, iron, calcium, and magnesium, which can shorten element life.

With either method of generation, there is considerable addition of sodium (as NaCl) to the process stream. From brine systems, this addition is estimated at 2.3 parts sodium per part chloride, and with seawater systems, this addition is estimated at 13 parts sodium for each part chloride.

The relationship of raw components required in the generation process is;

3.5 kg salt + 125 litres water + 5.5 kWh (AC) = 1 kg Hypochlorite

(3.5 lbs salt + 14.89 gallons water + 3.3 Hp (h) (AC) = 1 lbs Hypochlorite)

For the purposes of this study, and to act as a baseline for determining cost and sizing models, a nominal chlorine residual of 10 ppm was selected as the level to be dosed to the ballast tanks. Therefore, to treat a typical ballast load (*Federal Yukon* capacity) of 11,000 tonnes of ballast water at a dose rate of 10ppm, 110 kg (242 lbs) of hypochlorite would be required. This would entail the generation of 13.75 tonnes of 8000ppm (3487 US gals at 0.8%) hypochlorite solution using 375 Kg (825lbs) of salt and 600 kWh of power.

Capital cost for onboard generation systems vary in proportion to their output. A system designed to generate sodium hypochlorite at a rate compatible to the ballast pumping and distribution system characteristics of the *Federal Yukon*, i.e., nominal capacity to ballast 11,000 tonnes in 8 hours, will require a 300 kg/day system. The estimated capital purchase component cost \$200,000 however installation of the extensive piping, pumping and control systems would double this cost.

Given that power generation onboard ship requires in the order of 200 grams of fuel per kWh, with a typical fuel cost of \$200/tonne, and including a salt price of \$0.25 / kg, the material cost required to achieve a 10ppm dose is \$318.

A life cycle cost model was developed based on the economic return parameters and estimates of ship refit costs and are presented in Table 5.8. The metric used to demonstrate the cost implications is the estimated increase necessary in daily charter rate to maintain a desired profitability over an amortization period of 15 years. This metric includes the capital cost, the per-ballast operational cost and the annual maintenance and refit cost. This increase for the onboard generation system equals \$207 per day or an increase of 2.31% in the daily charter rate.

Table 5.8: Life Cycle Cost Increment for Onboard Generation of Sodium Hypochlorite

Item	330 kg (725lbs) per day 0.8%
Capital cost	\$ 437,710
Element replacement cost	\$ 50,000
Element replacement frequency	5 Years
Ballast operations per year	12
Raw material costs	\$ 318
Vessel charter rate	\$ 9,000
Return rate	15%
Inflation rate	3%
Amortization period	15 years
Increase charter to maintain return	\$ 207.73
%increase	2.31%

Chlorine demand from re-suspended sediment and intake water suspended sediment would likely increase the treatment dose that would be required in certain locations of the Great Lakes and during certain time periods. As a measure of sensitivity, and to illustrate the impact of assuming the best-case treatment scenario (i.e., 10ppm sodium hypochlorite), the model was exercised over a range of treatment rates. The cost relationship is essentially linear at the area of interest and represents approximately a \$9.1 dollar increase for each part per million increase in treatment (i.e., 10ppm = \$207 \Rightarrow 20ppm = \$298).

5.5.2 Liquid Sodium Hypochlorite

Although it tends to be more costly than calcium hypochlorite, sodium hypochlorite is easier to handle and presents less maintenance problems during general usage. It is generally available at all ports around the Great Lakes and at most industrialized ports of the world.

The primary concern with carrying liquid hypochlorite over extended periods is decay. Typically, the higher the concentration of a sodium hypochlorite solution, the higher the decay rate. To illustrate this, the half-life of a 15% trade solution of liquid hypochlorite is around 120 days, i.e. it can be expected to lose nearly half of its available chlorine in 4 months, whereas a 10% solution loses approximately 30% available chlorine during the same period. Increased temperature also has a similar effect on available chlorine, and a 10% solution has an expected half-life of approximately 220 days at 77°F compared to 800 days at 59°F. To minimize storage requirements (space and weight) higher concentration are advantageous, to avoid excessive decay, storage times need to be minimized. Thus frequent loadings of smaller quantities of higher concentration sodium hypochlorite solutions would be more cost effective, e.g. the Federal Yukon made 2 complete ballast loading operations during a 69 day round trip voyage consequently capacity to store 15% hypochlorite sufficient for 2 full operations is assumed in the following assessments.

To treat 11,000 tonnes of ballast water at a dose of 10ppm requires the purchase of 763 liters (200 US gals) of liquid hypochlorite, for a per ballast material cost of \$505.

A life cycle cost model was developed based on the economic return parameters and an estimate of ship refit costs and is presented in Table 5.9. While the capital cost of this system is estimated to be in the order of \$207,000, 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 societies 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 \$104 per day or an increase of 1.16%.

As a measure of sensitivity and to illustrate the impact of assuming the best-case treatment scenario (i.e., 10ppm sodium hypochlorite) the model was exercised over a range of increased treatment levels. The cost relationship is essentially linear at the area of interest and represents approximately \$2.16 per part per million increase in treatment level (10ppm = \$104 \Rightarrow 20ppm = \$125).

Table 5.9: Life Cycle Cost Increment Storing Sodium Hypochlorite Onboard

Item	Buy and store onboard
Capital cost	\$ 207,025
Refurbishment costs	\$ 10,000
Refurbishment Frequency	5
Ballast operations per year	12
Raw material costs	\$ 504
Vessel charter rate	\$ 9,000
Return rate	15%
Inflation rate	3%
Amortization period	15
Increase charter to maintain return	\$ 104.03
% Increase	1.16%

A second version of this model was developed to illustrate the cost effects of not having sodium hypochlorite stored onboard, but simply delivered to the ship on an as required basis. While this option would reduce the infrastructure associated with an onboard tank and the safety precautions necessary to house bulk chemicals, it would not alleviate the necessity to install dosing equipment and train on-board crew on its use. It would also require the supplier to stand-by the vessel as it ballasts, and this could be a lengthy process where cargo operations are slowed. Consequently, while the capital cost is reduced, the per-operations cost is increased.

Table 5.10: Life Cycle Cost Increment when Sodium Hypochlorite is Supplied as Needed

Item	Deliver to the ship as required
Capital cost	\$ 77,318
Refurbishment costs	\$ 10,000
Refurbishment Frequency	5
Ballast operations per year	12
Raw material costs	\$ 756
Vessel charter rate	\$ 9,000
Return rate	15%
Inflation rate	3%
Amortization period	15
Increase charter to maintain return	\$ 60.54
% Increase	0.67%

In this case, the sensitivity of increasing the dose rate is driven directly by the cost of delivery of sodium hypochlorite to the ship and results in a slightly higher increase rate of \$2.52 per ppm increase in the daily charter rate.

5.5.3 Sodium Bisulfite Dechlorination

There must be sufficient capacity on board the ship to apply dechlorination 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 cost model, 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 (chlorine:sodium bisulfite), thereby requiring a storage capacity of 0.5 tonnes of sodium bisulfite, given a 35% active ingredient solution.

The installation of this tank is also considerably simpler than that of the sodium hypochlorite and the product is essentially safe to handle. It should be noted however that explosions may result from the contact of sodium bisulfite with sodium hypochlorite. This and the resulting generation of chlorine gas are serious dangers associated with these chemicals. Safety considerations therefore dictate that installations must be made to isolate each storage and dispensing system so that Hypochlorite and Sodium Bisulphite do not come into contact at any time.

5.6 Handling Sodium Hypochlorite Onboard Ship

5.6.1 Handling and Storage of Liquid Hypochlorite

Anyone working with sodium hypochlorite must be made aware of the precautions necessary for its safe handling, storage and use. All direct contact with solutions must be avoided, as it is an irritant to the skin, eyes, and mucous membranes.

A Material Safety Data Sheet for sodium hypochlorite is appended to this report and identifies equipment required for the handling of the chemical. These include;

- Coveralls
- Heavy duty gloves
- Goggles
- Face shield
- Positive pressure full face respirators
- Emergency eye wash and shower stations
-

Of greatest concern when storing and handling liquid hypochlorite are leaks that may inadvertently mix with acid solutions. Any mixing of hypochlorite with acidic solutions will result in the immediate formation of chlorine (Cl₂) gas. It is imperative that hypochlorite solutions be kept isolated from contact with acidic solutions, as exposure to chlorine gas can be fatal. Table 5.11 outlines some of the health effects associated with exposure to chlorine gas.

Table 5.11: Health Effects Associated with Chlorine Gas Exposure

Chlorine Level ppm (v/v)	Effect	Notes
1.0	Slight symptoms	
3.5	Odor threshold	
4.0	No serious effects	One hour maximum exposure
5.0	Breathing difficulty	Few minutes exposure
15.1	Throat irritation	
30.2	Causes coughing	
40-60	Dangerous	30 minutes to an hour
1000	Lethal	Lethal to most animals

In all cases sodium hypochlorite solutions will decompose. The material safety data sheet refers to the decomposition products as gases containing chlorine compounds. Hypochlorous acid and chlorine monoxide are the predominant chlorine species in the vapor phase above hypochlorite solutions under normal conditions. The decomposition rate is affected by many factors including: the initial concentration, contact with catalyzing metallic impurities, the pH of the solution, the temperature of the solution, exposure to light sources and contact with organic impurities.

Gases containing chlorine compounds are detrimental to combustion machinery causing the production of toxic and corrosive compounds through the combustion process and must therefore be kept away from machinery intake ventilation systems. While not an immediate health problem, combustion products will produce deleterious engine stack emissions and may cause severe internal engine damage.

Liquid hypochlorite has a long history of use in the water treatment industry, and can be safely handled provided appropriate storage precautions are taken. Table 5.12 rates the compatibility of sodium hypochlorite with various other materials.

Table 5.12: List of Material Compatibility with Sodium Hypochlorite

Material	Compatibility	Material	Compatibility
304 stainless steel	C- Fair	Hypalon®	A- Excellent
316 stainless steel	C- Fair	Hytrel®	A- Excellent
ABS plastic	B- Good	Kel-F®	A- Excellent
Acetal (Delrin®)	D- Severe Effect	LDPE	A- Excellent
Aluminum	D- Severe Effect	Natural rubber	C- Fair
Brass	D- Severe Effect	Neoprene	C- Fair
Bronze	C- Fair	NORYL®	A- Excellent
Buna N (Nitrile)	B- Good	Nylon	D- Severe Effect
Carbon graphite	B- Good	Polycarbonate	C- Fair
Carpenter 20	D- Severe Effect	Polypropylene	A- Excellent
Cast iron	D- Severe Effect	PPS (Ryton®)	A- Excellent
Ceramic Al2O3	A- Excellent	PTFE (Teflon®)	A- Excellent
Ceramic magnet	A- Excellent	PVC	A- Excellent
Copper	N/A	PVDF (Kynar®)	A- Excellent
CPVC	A- Excellent	Silicone	B- Good
EPDM	B- Good	Titanium	C- Fair
Epoxy	C- Fair	Tygon®	C- Fair
Hastelloy-C®	A- Excellent	Viton®	A1- Excellent

Hypochlorite storage tanks are normally constructed of rubber-lined steel, fiber reinforced plastic (with suitable considerations of UV light effects), or high density polyethylene. Materials used in the transfer system components, (i.e., pipes, valves, pumps, etc.) must also be selected to be compatible to the concentration levels of hypochlorite solutions. In general, steel components normally used in ship construction are not compatible with sodium hypochlorite and some plastic material may not be permissible for inclusion in machinery spaces in accordance with a vessels structural fire protection requirements.

Table 5.13 outlines the hazards that may occur when sodium hypochlorite is mixed with other material.

Table 5.13: List of Material Reactions with Sodium Hypochlorite

Incompatible Material	Mixing May Result In
Acids, Acidic Compounds and Acid Based Cleaning Compounds such as: - Alum (Aluminum Sulfate) - Hydrochloric Acid (HCl) - Aluminum Chloride - Sulfuric Acid - Ferrous or Ferric chloride - Hydrofluoric Acid - Ferrous or Ferric Sulfate - Fluorosilicic Acid - Chlorinated Solutions of - Phosphoric Acid Ferrous Sulfate - Brick and Concrete Cleaners	- Release of chlorine gas, may occur violently.
Chemicals and Cleaning Compounds containing ammonia such as: - Ammonium Hydroxide - Ammonium Sulfate - Ammonium Chloride - Quaternary Ammonium - Ammonium Silicofluoride Salts (Quats)	- Formation of explosive compounds. - Release of chlorine or other noxious gases.
Organic Chemicals and Chemical Compounds such as: - Solvents and Solvent - Propane Based Cleaning - Organic Polymers Compounds - Ethylene Glycol - Fuels and Fuel Oils - Insecticides - Amines - Methanol	- Formation of chlorinated organic compounds. - Formation of explosive compounds. - Release of chlorine gas, may occur violently.
Metals such as: - Copper - Cobalt - Nickel - Iron	- Release of oxygen gas, generally does not occur violently. Could cause overpressure/rupture of a closed system.
Avoid piping and material handling equipment containing stainless steel, aluminum, carbon steel or other common metals.	
Hydrogen Peroxide	- Release of oxygen gas, may occur violently.
Reducing agents such as: - Sodium Sulfite - Sodium Hydrosulfite - Sodium Bisulfite - Sodium Thiosulfate	- Evolution of heat, may cause splashing or boiling.

Onboard ship it is common to find the general cleaning products listed above and some of the paints, solvents, etc. The biggest risk, however, comes from contact with fuel oils. The hypochlorite dispensing system will by necessity need to be located in the machinery room close to the bilge system and thus where fuel and lubricants are common, and where oily bilge lies in the engine room bottom. Therefore system must be installed such that any spill or leakage of sodium hypochlorite would be contained by physical barriers (spill trays, double piping etc) to avoid the possibility of hypochlorite contact with bilge oil.

An emergency plan for spills and fires will likely be required. The fighting of a fire within the area of the sodium hypochlorite storage tanks will require the use of positive pressure, full-face respirators. The Chlorine Institute recommends the use of water as the fire-fighting agent and also recommends against the use of foams and dry agents. It is also recommended that local fire agencies are contacted and informed of the presence of sodium hypochlorite at the installation. This is not an immediate consideration for a vessel, however, information should be readily available and form part of the company ISM plan and be available to shore based emergency system.

The level of additional fire fighting and response system necessarily integrated into the overall ship emergency systems and plans will be dependent on the concentration of solution carried, and the location of the storage system. Any additional systems and procedures will require approval from the ship flag state, the jurisdiction where the product is procured and handled etc., and also the classification society that provides the notation to the vessel.

Companies in North America involved in the handling of hazardous materials (including commercial concentrations of sodium hypochlorite) are required to provide standard operating procedures and training to personnel. In the United States, The Department of Transportation administers regulations under the Hazardous Materials Transportation Act (HMTA). Title 49 of the Code of Federal Regulations (CFR) deals with the transportation loading and unloading of hazardous materials and sections 171 through 178 describe the requirements for documentation, labels, emergency response, training and packaging. In Canada, a similar regimen is present under the Canadian Transportation of Dangerous Goods Regulations. It is unclear as to the extent of direct applicability of these regulations to international shipping, however 49 CFR section 176 contains descriptions of additional requirements for carriage by vessels and it is probable that the regulatory agencies and classification societies would invoke all of the above requirements in their assessment of on-board facilities and procedures. In both jurisdictions there are also requirements for Occupational Health and Safety (29 CFR).

5.6.2 Sodium Bisulfite for Dechlorination

Sodium bisulfite is commonly used in the wastewater treatment industry as a method for dechlorinating effluents prior to discharge to receiving waters. Sodium bisulfite is non carcinogenic or mutagenic however, it is known to cause skin, eye and respiratory tract irritation, and is harmful if swallowed or inhaled. Additionally, sodium bisulfite is known to be highly corrosive, and appropriate storage and metering equipment is required to reduce the potential for leaks. Separation between sodium hypochlorite and sodium bisulfite storage and distribution systems would be required to avoid accidental mixing of concentrated solutions. Like sodium hypochlorite, sodium bisulfite dechlorination systems have been used successfully in the wastewater treatment industry.

5.7 The Practical Considerations to using Sodium Hypochlorite

It is likely that sodium hypochlorite would be added to the ballast water during intake to ensure adequate mixing within the tank. Control systems must be adequate to ensure that appropriate concentrations are delivered in accordance with demand. Further onboard monitoring capacity is essential to ensure discharge levels are within environmental standards.

There are significant health and safety issues surrounding the storage of industrial trade strength concentrations of sodium hypochlorite, and although no specific regulatory requirements are in-place to deal with shipboard installations of this type, due consideration will have to be made to safety standards.

5.7.1 Gas generation

During the treatment of ballast tanks with sodium hypochlorite, the creation of some degree of gases containing chlorine compounds is expected. The amount of gas formed in the headspace of the ballast tanks will be dependant upon treatment dose (residual), temperature, and agitation of the ballast water in the tanks.

It is not clear at this point what levels or type of treatment related gases would be generated during the chlorination of ballast water. In shipboard experiments, hypochlorite tests were covered, but ventilated, during treatment. During the first few days of treatment, and in test containers with measurable residual chlorine, a typical “bleach” odor could be easily detected in the air near the water surface. During a ships ballast operations the entire tank is filled and emptied thereby making one complete air exchange though the tank. The ballast water is discharged from the tank rapidly bringing clean air into the tank, and as such it is unlikely that the chlorine residual level in a NOBOB condition will cause dangerous levels of gases to be present in the tank. However, as a precautionary measure, appropriate ventilation of tank spaces would be required and ballast tank access would need to be restricted after treatment until monitoring indicates the airspace has been cleared of dangerous gases.

5.7.2 Ship Retrofitting

The international regulations respecting carriage of chemicals as cargo onboard ship are not applicable to sodium hypochlorite, and there are no directly applicable marine regulations that deal with its carriage on this type of vessel. However, the IMO Resolution A.673(16) *Guidelines for the Transport and Handling of Limited Amounts of Hazardous and Noxious Liquid Substances in Bulk on Offshore Support Vessels*, will most likely describe the requirements of the regulatory inspection agencies (US Coast Guard and Transport Canada Marine Safety Branch). These requirements would only be applicable to the carriage of commercial sodium hypochlorite concentrations, and not the low concentration (i.e., 0.8%) solutions generated on board. Some of the most relevant considerations contained therein are;

Section 3.1 – Cargo tanks should be segregated from machinery spaces, shaft tunnels, accommodation, drinking water and stores for human consumption by a cofferdam, or void space. On deck stowage of independent tanks or installation of an independent tank in a void meets this criteria. As well, piping systems for the tank must be separate and not pass though other tanks unless they are encased in a tunnel. The cargo system must also have its own venting system.

Section 3.2 – Accommodation, control stations and service spaces should not be located within the cargo area. Due consideration should be given to the location of air intakes and openings into accommodation, control stations, service and machinery spaces with regard to the cargo piping and venting system.

Section 3.4.3 – Except for connections to pump rooms, all cargo openings and connections will be located on the top of the tank. The openings in the tank should be located above the weather deck.

Section 3.5 – Materials of construction should be in accordance with chapter 6 of the Bulk Chemical Code, as applicable.

Section 3.10 – Floors and decks underneath acid storage tanks and piping systems must be lined with a corrosion resistant material extending up to a minimum height of 500mm on the bounding bulkheads and coamings. Where this is not practical, a lesser height may be required. Spray shields should cover flanges and other detachable pipe connections. Drip trays should be installed under loading manifolds. Deck spills should be kept away from accommodation areas by permanent coamings of an acceptable height. Drainage should be provided for the tanks and piping system and the drainage should also be lined or made of corrosion resistant materials.

Section 3.12.1 – Vapor detection for the cargo carried should be provided in accordance with the requirements in the International Bulk Chemical Code.

Section 3.12.4 – At least two portable instruments suitable for measuring the concentration of oxygen in atmospheric air should be provided

Section 3.15 – Each cargo tank should have a level gauging system acceptable to the administration. At a minimum the system should meet relevant requirements of the International Bulk Chemical Code.

These requirements when applied to the typical bulk carrier of the *Federal Yukon* concept will require careful integration with the current ship layout. The machinery spaces are located aft and directly above these are the galley, stores, and crew accommodation. All air intakes for the accommodations and machinery intakes are also positioned in this block.

Storage containers must be made with a non-reactive material, UV filtered and opaque material, or a steel tank lined with a non-reactive material. They should be placed in a well-ventilated area, away from any air intakes or exhaust. A containment system must also be installed around any storage containers(s) on the deck.

This essentially means that the storage container should be in a separate compartment or be of a double walled type to accommodate any spillage and ship motions, and be located away from the accommodation block aft.

As with the storage container, all pipes, valves and pumps used in the distribution system must be selected taking into consideration the compatibility of the construction material with sodium hypochlorite. Other design considerations would include avoiding the creation of areas in the treatment system that allows the sodium hypochlorite to stand. For example, stagnant sodium hypochlorite in the recesses of ball valves, U-bends in piping, etc., will cause crystalline formations that, over a period of time, may freeze moving parts and clog pipes. In certain instances, the creation of gases in distributions can contribute to localized pressure buildup resulting in pipe or valve failure. Pumps must also be made of, or lined with, compatible materials.

5.7.3 Operational Constraints and Opportunities

Hypochlorite Decay

The problems associated with hypochlorite decay will more than likely limit the storage time of concentrated solutions, and trade-offs regarding concentration, decay, and availability will need to be evaluated further.

Variable Water Quality

It is anticipated that during ballasting operations, water quality characteristics (i.e., sediment load) of water being brought on for ballast will change depending on the port. It is also possible that water quality characteristics of water being brought on for ballast may change during ballasting due to proximity of the ballast water intake to sediments in the harbour bottom. As a result, the chlorine demand of water being brought on for ballast would need to be monitored continually to ensure target residual chlorine levels are being reached.

Variable Pump Rates

The rate at which ballast water is brought onboard varies with the level of liquid in the tanks and the draft of the ship. At commencement of ballasting operations the ship is light and high in the water while the bottom tanks are well below the water line resulting in a large static pressure head forcing the water onboard. When the ballast operations are filling the upper tanks then there is pressure head requirement to pump the water above the ship's waterline. In the field trials it was seen that the flow rates at the commencement of ballasting were twice the nominal pumping rate. Consequently any injection / monitoring system for biocide input must be able to compensate for the flow rate automatically.

Re-suspension of Bottom Sediments

Additionally, it is not clear to what extent sediment in the bottom of the ballast tanks is resuspended in the overlying water during ballasting operations. The field trials and laboratory testing indicate that suspended sediment has considerable chlorine demand. Real time TRC measurement would be required in ballast tanks to make sure an effective chlorine residual is being achieved.

Bottom Sediments

It is likely that hypochlorite treatment effectiveness could be increased by removal of sediment from the bottom of ballast tanks. The removal of bottom sediment from the ballast tanks would have numerous positive effects on treatment. Firstly, a thorough cleaning of the ballast tanks would provide a clean, organism free environment as a starting point for treatment, allowing treatment effectiveness to be monitored with better accuracy. Secondly, the potential for increased chlorine demand caused by bottom sediments being re-suspended in incoming ballast water would be reduced. Thirdly, sediment organisms and resting stages in incoming ballast water would no longer have a refuge to avoid treatment. Finally, it is known that the sediment builds up over time and as ballast tanks are used. If water is treated at every ballast operation throughout the vessel life it is likely that a cumulative effect would render the sediment less prone to housing and containing viable biota of any form.

Furthermore, the arrangement of tanks and the structural support therein in the typical bulk carrier means that there is a preponderance of sediment in the bottom of the double bottom tanks and very little in the upper wing tanks. It is unlikely that there is much mixing of water already in the bottom tanks when the upper tanks are being filled, therefore a higher dose level may be more appropriate during the commencement of ballast operations than during the final stages.

Availability

Sodium hypochlorite is a common chemical used throughout the industrialized world where chemical production and general manufacturing capacity exists. It is therefore available for bulk delivery to virtually all ports in North America and Europe. Availability may be an issue in other more isolated locations where bulk cargoes are sometimes loaded (i.e., South America).

Sodium chloride suitable for use in onboard Hypochlorite generation systems is also generally available to the shipping industry but could also be stored onboard in capacities sufficient to generate Sodium Hypochlorite for more than one ballasting if necessary (in the order of 0.5 tonnes per ballast operation).

Application Method

A treatment application technique and an application regimen using biocides have yet to be determined. One option would be to treat incoming ballast water each time it is loaded or when a known transit to the Great Lakes or other sensitive areas occurs. Alternatively, the treatment of residual ballast water in the NOBOB condition is possible, and this could be done prior to ballasting in the Great Lakes, during the NOBOB voyage, or immediately after achieving a NOBOB condition.

The efficacy, economics, and logistics of possible application methods need to be evaluated further.

5.7.4 Monitoring / control mechanism

From the forgoing discussion, it is clear that there is a need to monitor ballast water flow rate, intake water quality, and sediment load during the filling of tanks. Also identified is a need to measure TRC content during and after filling, and preferably at different locations in the tank (upper and lower). These data can then be used to control the dose rates ensuring that the desired level of biocide is applied, and that environmental limits are observed without excessive dechlorination. Figure 5.8 outlines a conceptual diagrammatic layout of the control system. The principal components for the system are available in the current water treatment industry but have yet to be developed in the marine industry for this type of application. This figure serves to illustrate the complexity of a control system necessary to ensure that hypochlorite is applied in an effective, efficient and economic manner. Such a system has not been integrated into any marine environment.

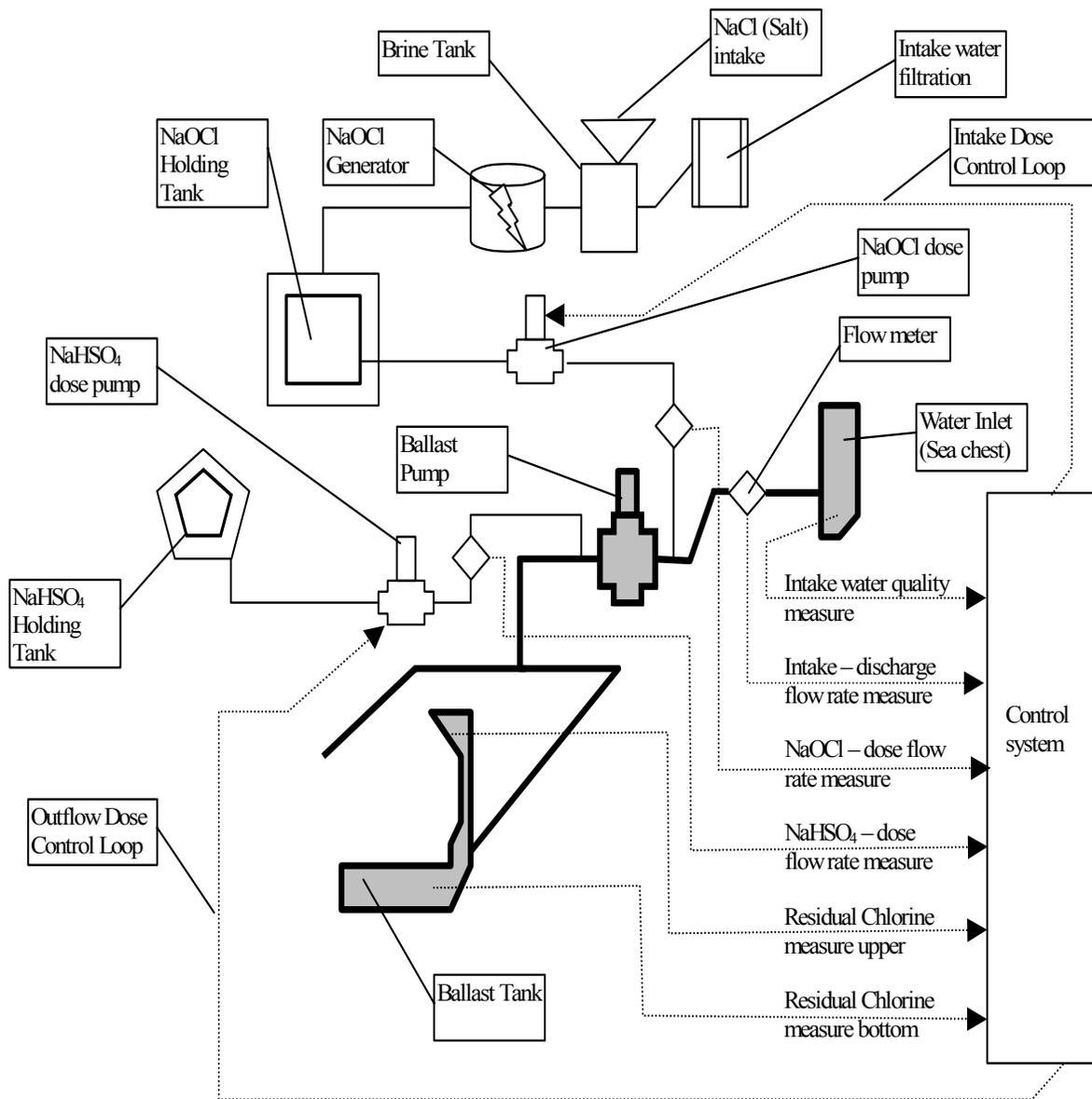


Figure 5.8: Conceptual Sodium Hypochlorite Control System Diagrammatic

5.7.5 Establishing demand

The ultimate derivation of a dose rate for application of sodium hypochlorite to treat ballast water effectively has three components and can be expressed as:

$$\text{Dose} = \text{Desired residual} + \text{Intake water demand} + \text{Onboard sediment demand}$$

For the purposes of estimating, this study assumes that the desired residual is in the order of 10 ppm.

The intake water demand is un-quantified and it will vary with the harbour water quality characteristics, the ship's position (proximity of intake to the bottom), and seasonal variations in port water quality.

The already on-board bottom sediment demand is also un-quantified as it depends on the management practices used on board the ship. This demand could vary from very high levels where there is a large residual or build up of sediment to near zero where the tanks are clean.

This study indicates that it is possible, assuming a worst case sediment load in the incoming ballast water of 1%, that ballast water may need to be dosed to as high as 20 to 30 ppm sodium hypochlorite to overcome chlorine demand. This sediment demand dose will be considerably less for a clean ship taking on ballast in a clear cold-water harbor. To further explore the range of dose requirements that may be required for a hypochlorite treatment system, a more complete data set, including seasonal and geographic variations in intake water quality in ports of concern, would be required. Additionally, knowledge of the sediment conditions in ballast tanks would be beneficial in determining the impact of bottom sediment on chlorine demand.

6. COPPER ION TREATMENT EVALUATION AND FINDINGS

The M.V. *Federal Yukon* was retrofitted with a copper ion generator. Figure 6.1 shows the installation in the Engine room.

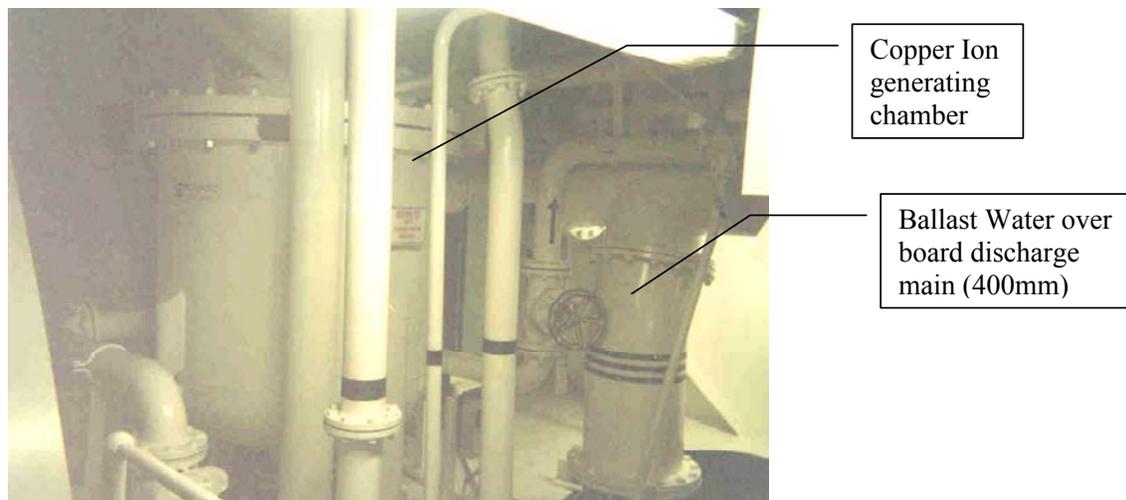


Figure 6.1: Copper Ion Generator in Engine Room of M.V. *Federal Yukon*

6.1 The Efficacy of Copper in Killing Ballast-Borne Biota

6.1.1 Shipboard Testing

During freshwater trials, an increase in zooplankton mortalities of 33.0% and 32.4% relative to the controls were achieved after a two-hour exposure to 167 and 145 ppb total copper respectively. Additionally zooplankton mortalities in treated ballast water were significantly different from the controls ($p < 0.05$). High levels of suspended sediment and low organism densities hampered recovery of organisms from test containers at the end of each trial. At the end of both trials live copepods, mussel larvae, and crustaceans were observed in ballast water samples, however, recovery of low numbers of individuals prevented statistical comparisons.

Results from the saltwater trials indicate copper ion treatment was capable of reducing bacterial levels by just over 70% when compared to controls. However, results from freshwater trials indicate the copper ion treatment, for the most part, was not effective at reducing bacteria levels. It is likely that re-suspension of sediment into the water column in these test chambers during the freshwater trials resulted in an increase in the total culturable bacteria levels. These results also suggest that sediment in the water column may be impacting total culturable bacteria results to a point where the changes in bacterial levels relative to the control may not be representative of the treatment.

Table 6.1: Efficacy of Copper Ion Treatment in Saltwater and Freshwater Shipboard Trials

Location	Mean Dose ¹ (ppb)	Zooplankton ²	Total Culturable Bacteria ³	Total Culturable Bacteria ³
Saltwater Trial			T= 2 hours	T= 8 days
Test 1	<100 (68.2) ⁴	ND	-72.4	-68.2
Test 2	<100 (68.2) ⁴	ND	-74.5	-43.3
Freshwater Trial			T= 2 hours	T= 5 days
Test 1	167	-33.0 ± 9.97	102.8	-54.3
Test 2	145	-32.4 ± 11.76	232.7	305.5

1. Mean total copper.

2. Mean percent reduction live vs dead relative to controls after 2 hour exposure

3. Mean percent change relative to control (positive value indicates growth)

4. Theoretical dose based on power/pump rates

ND = No Data

Chlorophyll-a samples were collected and processed according to the protocol. Chlorophyll-a levels in samples that were analyzed were low (i.e., near or below the detection limit) and statistical comparisons between treated and untreated samples could not be performed. Additionally, large quantities of sediment in samples negatively impacted recovery.

Table 8.1 (Section 8) summarizes the zooplankton organisms identified in ballast water samples collected during the saltwater and freshwater trials. In both trials, the numbers and diversity of organisms found in the ballast water was low. For this reason, organisms were collected to add to the test systems. In saltwater trials, organisms were concentrated from water collected through the firehose (off the ballast main). In freshwater trials, organism densities in the immediate ballasting area were very low, and organisms had to be collected beyond the harbour breakwater using a plankton tow (60µm mesh).

6.1.2 Laboratory Toxicity Testing

Table 6.2 lists the range of lethal total copper concentrations for the freshwater and saltwater species tested in the laboratory. As with sodium hypochlorite, the range between the least and most tolerant organism was also large (i.e., several orders of magnitude). For the freshwater species, *D. magna* (neonate) and the algae exhibited the lowest tolerance to copper with LC99/IC99s at or below 0.2 ppm. The bacterium (*B. subtilis*) was the most tolerant of the freshwater species showing little or no reduction in spore viability at total copper concentrations up to 1,000 ppm. *D. magna* were the next most tolerant species to copper, based on exposure of ehippia (IC99 > 100 ppm). Invertebrate species, *D. polymorpha* (zebra mussel) and *L. variegatus* (oligochate worm) had LC99s in the 2 to 20 ppm range.

For the marine species, bacteria (*Vibrio fischeri*) and algae (*S. costatum*) exhibited the lowest tolerance to copper with IC99's estimated to be 1.218 and 2.393 ppm, respectively. The most tolerant species was the brine shrimp (*A. salina*), based on exposure of the cyst (IC99 >1000 ppm). The sheepshead minnow and the amphipod, *E. estuarius* were intermediate in their tolerance to copper with LC99s of ≈20 and ≈100 ppm, respectively.

Copper toxicity was compared in ballast and lab waters on selected organisms. The differences in water quality for each water type are discussed previously in section 5.3. From Table 6.3, it can be seen that for the species tested, there was little difference in LC99s for copper whether the tests were conducted in laboratory waters or in the ballast water. For example, tests with *L. variegatus* yielded LC99s for copper in laboratory water and ballast water of 2.798 and 2.865 ppm, respectively. Endpoints generated in tests using *E. estuaries* were also similar (LC99 73.3 – 75 ppm).

Table 6.2. Lethal Concentration Ranges (LC99/IC99) of Copper for Selected Freshwater Biota (Including Bacteria, Algae, Pelagic and Benthic Invertebrates and Fish)

Lethal Concentration Range (ppm)	Freshwater	Marine
< 0.2	Invertebrate - <i>D. magna</i> (neonate)(48 hr) Alga - <i>S. capricornutum</i> (48 hr) Alga - <i>Nanochloris sp.</i> (48 hr)	
0.2 to 2.0	Alga - <i>S. obliquus</i> (48 hr) Fish - <i>C. carpio</i> (48 hr)	Bacteria - <i>V. fischeri</i> (15 min)
2.0 to 20	Mollusc - <i>D. polymorpha</i> (24 hr) Benthic invertebrate - <i>L. variegatus</i> (48 hr)	Alga - <i>S. costatum</i> (48 hr)
20 – 200	Invertebrate - <i>D. magna</i> (ephippia) (48 hr)	Amphipod - <i>E. estuarius</i> (48 hr) Fish - <i>C. variegates</i>
> 1000	Bacteria - <i>Bacillus subtilis</i> (spore) (48 hr)	Invertebrate <i>A. salina</i> (cyst) (24 hr)

Table 6.3. Comparison of Copper Toxicity to *Lumbriculus Variegatus* and *Eohaustorius Estuarius* in Laboratory Waters versus Ballast Waters

Species	Freshwater		Marine	
	Laboratory Water 48 hr LC99 (ppm)	Ballast Water 48 hr LC99 (ppm)	Artificial Seawater 48 hr LC99 (ppm)	Ballast Water 48 hr LC99 (ppm)
<i>L. variegatus</i>	2.798 (0.202-3.218)	2.865 (2.610-3.000)	-	-
<i>E. estuarius</i>	-	-	75	73.29 (73.29-73.29)

6.2 The Effects of Sediment on the Efficacy of Copper

Bottom sediment samples were collected from each test chamber at the end of each trial for laboratory study. Examination of sediments recovered from the bottom of the test chambers after the saltwater shipboard evaluation reveals that numerous viable organisms were present in the sediment after treatment. Live invertebrates, protozoa, and diatoms were recovered from most sediment samples.

In shipboard test chambers, sediment depth was approximately 1.0 cm in barrels. The depth of sediment that protects organisms from treatment has yet to be investigated. Organisms identified in sediment samples collected during saltwater trials are provided in Table 8.2 (Section 8).

Live invertebrates, protozoa, and diatoms were recovered from most samples suggesting that the copper ion treatment has a limited impact on the survival organisms contained in sediments. Only dead diatoms (frustules) were recovered in sediments treated with ballast water during one test, while numerous live diatoms were found in sediment treated with ballast water from a different tank. Why these differences exist is not clear as the source sediment is from the same location and the two barrels were treated with similar copper doses. A list of organisms identified in sediment samples collected from saltwater trials is provided in Table 8.3, (Section 8).

Having to achieve discharge limits with the dilution method restricted the amount of copper that could be added to the ballast tank. Consequently, organisms potentially suspended above the dosed ballast water are not exposed to the higher levels of copper.

Additionally, toxicity testing was conducted in the laboratory to attempt to quantify the impact of sediment on the efficacy of copper. The results of range-finding tests performed on selected species with and without a one percent sediment load are summarized below in Table 6.4.

Table 6.4. Toxicity of Copper to *Lumbriculus Variegatus* and *Cyprinus Carpio* with and without Sediment Present

Species	With Sediment (48 hr)		Without Sediment (48 hr)	
	Laboratory Water Lethal Range (ppm)	Ballast Water Lethal Range (ppm)	Laboratory Water Lethal Range (ppm)	Ballast Water Lethal Range (ppm)
<i>L. variegatus</i>	1.0 – 10	1.0 – 10	0.1 - 1.0	1.0 – 10
<i>C. carpio</i>	1.0 – 10	-	0.1 - 1.0	-

From Table 6.4, it can be seen that the presence of sediment reduced the toxicity of copper to *Lumbriculus* and common carp (*C. carpio*) when tested in laboratory water. For tests conducted in ballast water, the presence of sediment had less of an effect on copper toxicity to *Lumbriculus*.

6.3 The Environmental Considerations of Discharge of Copper

Discharge requirements for ballast water containing small residuals of copper were solicited by the MDEQ from all Great Lakes jurisdictions prior to the biocide study. Based on the information received from responding Great Lakes states, theoretical copper discharge limits for a ballast water discharge, specific to this short-term study, range from 2 µg/l to 48 µg/l. Because the toxicity of copper is affected by water quality characteristics (e.g., dissolved organic carbon and hardness), the discharge limitations for copper will vary from port to port throughout the Great Lakes. The current provincial water quality objective in Ontario waters for total copper discharges is 2 µg/l. It is likely however that while permission was granted by Ontario to conduct this experiment, some additional work demonstrating environmental impact of repeated discharge would be required.

The general permit for short duration discharges was obtained from the State of Wisconsin to discharge ballast water containing a small residual of copper into Lake Superior near the Port of Duluth/Superior. The ultimate ballast water discharge into Lake Superior from the *Federal Yukon* was in compliance with the 46 µg/l limitation for total copper required in the permit. The copper monitoring data were submitted to the Wisconsin Department of Natural Resources as required. The total copper data collected prior to the Lake Superior discharge are available in Appendix A, Item 2.

Because copper cannot be neutralized or easily removed from ballast water, the method used to achieve the discharge concentration limit for the shipboard study was dilution of the treated ballast water prior to discharge. In the shipboard study, only the bottom portion of the NOBOB tank was dosed with elevated levels of copper ion. Then, after an exposure time estimated to result in effective kill in the bottom water, un-dosed ballast water was added to dilute the copper and fill the ballast tank.

6.4 The Effects of Copper on Ballast Tanks

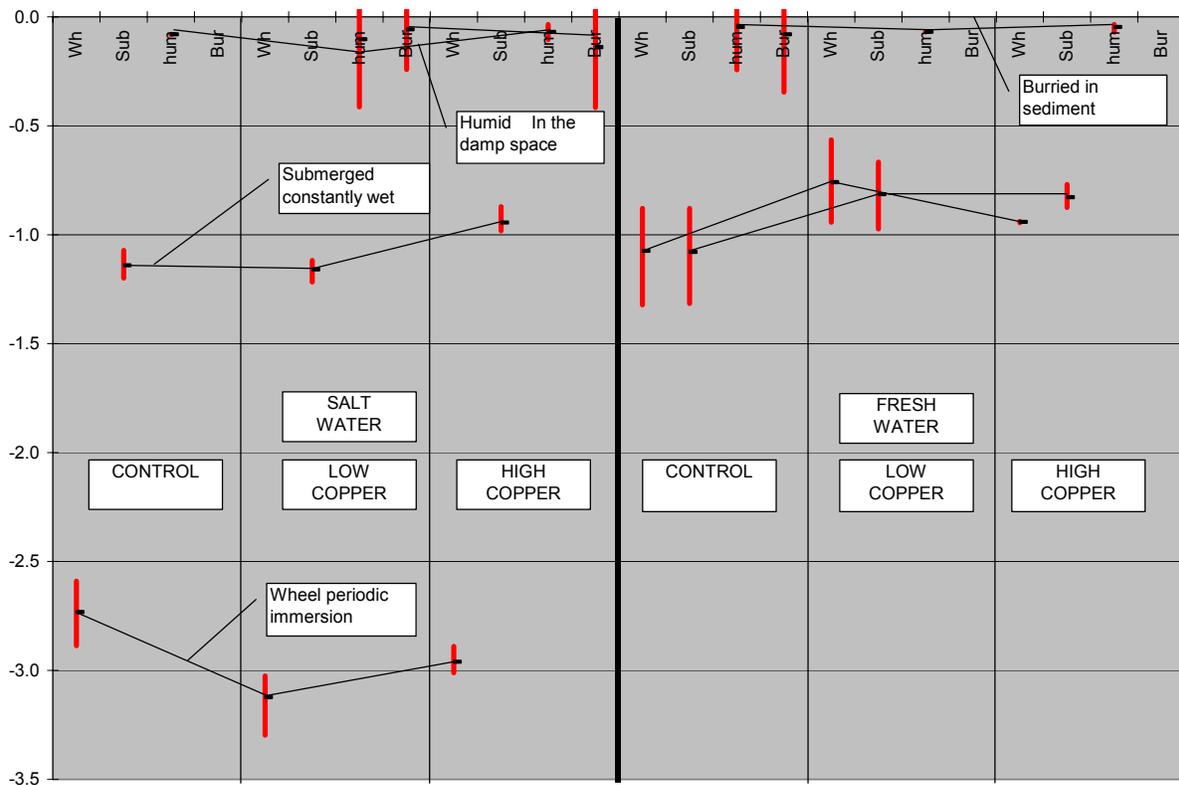
The project initially required the corrosion study be limited to the effects of sodium hypochlorite. It was however deemed also relevant, to the copper ion biocide, although in this instance, the problem is much more complex. It can be expected that the copper ions will be reduced to copper by iron and a surface plating of copper will be produced wherever bare steel is in contact with the electrolyte (ballast water). Iron will, in turn, go into the solution and corrosion will be accelerated. The effect of copper ion on tank coatings and zinc based substrates is not so predictable, hence the project was expanded to examine, in the corrosion testing facility, the effects of copper ion on the coating systems and steelwork.

The effects of copper on ballast tank structure were investigated in the Accelerated Corrosion testing facility. This work replicated that previously conducted in the sodium hypochlorite experiments (Section 5.4) and again examined both the corrosivity on bare steel and coating system failure in both simulated seawater and fresh water. The experiment and results are presented in Appendix C.

6.4.1 Corrosion Rates

The corrosion rate increase in the presence of copper was investigated with un-coated test coupons. Tests were conducted by dosing test water with 1 ppm and 2 ppm copper, added as copper sulfate. In both fresh water and seawater, the total copper content was seen to deteriorate to around 10% of the dose rate over the 24 hour re-dose period. This deterioration rate was essentially linear.

The results of the corrosion tests showed that there is an increase in corrosion for those test coupons positioned on the rotating wheel in seawater. All other locations and water type displayed little effect and could not be differentiated from the control conditions. Given that the copper content is diminishing over time it is probable that it is plating out on the bare steel and that this effect is highest on the wheel where constant washing removes the protective oxide corrosion product thus revealing more bare steel. Thereafter, the corrosion effects are enhanced through the galvanic attack, which is greatest in saltwater, between the copper plated on the wheel test coupons and adjacent bare metal. The overall effect is, however, small and is exaggerated in the test facility by virtue of constant replenishment of copper at 2 ppm, an order of magnitude greater than in the field trial dosing system. Figure 6.2 shows the annualize thickness diminution rates from the test.



Note Labels refer to location of test coupons in the test tank, e.g. wheel refers to periodic immersion, etc. Units are annualized millimeters thickness diminution (millimeters / year)

Figure 6.2: Thickness loss through Corrosion in the presence of Copper

6.4.2 Coating Deterioration

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” and the rating system described in Table 5.7 was used to quantify the effects.

No increase in coating damage was observed in the presence of copper in any location in the tank. Figure 6.3 shows the ASTM rating scores for different levels of copper.

Increases to coating damage were observed in the harsher environments of submerged and period immersion over the less aggressive humid and buried locations in the tank. Figure 6.4. shows the ASTM rating scores for different locations in the tank as measured on the scribed coating samples.

No accelerated failures were observed in any un-scribed coating system. Coating System Damage increase with Added Copper

There was no detectable decrease in the thickness of coating applied.

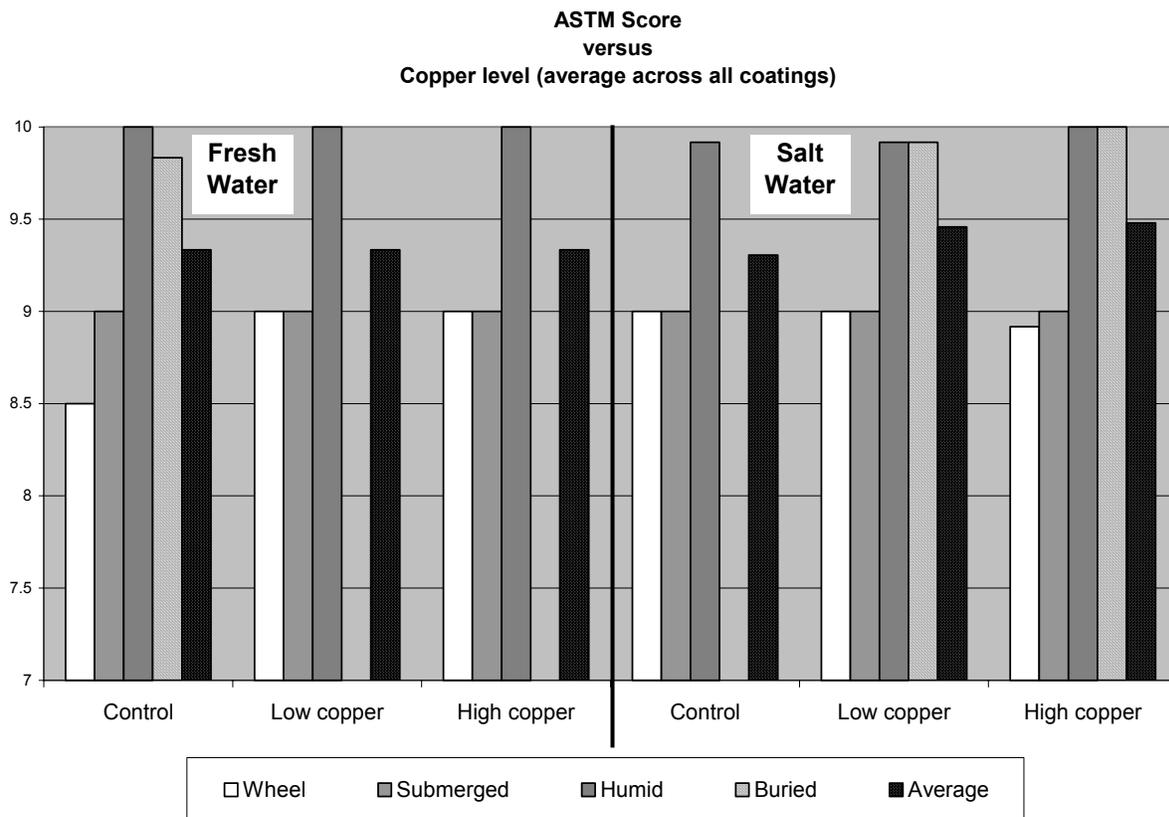


Figure 6.3: Coating System Damage increase with Added Copper

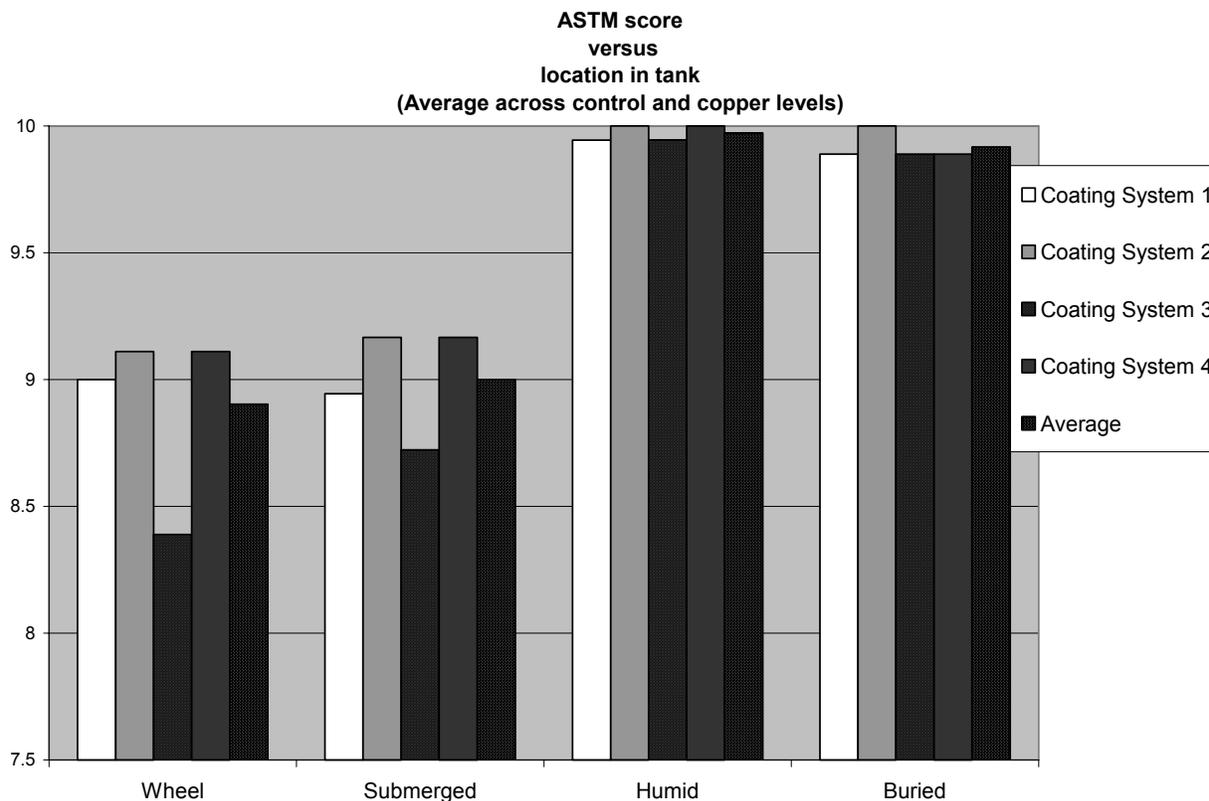


Figure 6.4: Coating System Defects Found after Exposure to Copper

6.5 The Economics of Using a Copper Ion Generator Onboard Ship

The system as fitted on the M.V. *Federal Yukon* demonstrated that the use of a copper ion generator is economical both in terms of capital cost and operational cost.

This system installed is, however, a prototype and needs to be re-engineered to enable it to be fully automatic in its application of copper ions to the intake water.

The life cycle cost of a copper generating system as fitted to the *Federal Yukon*, with the inclusion of a re-engineered application pumping system, would represent in the order of a 0.5% necessary increase to the daily charter rate, i.e., a capital cost of \$105,000 and a small per ballast operation material cost.

The power requirement to generate copper sufficient to dose the first 40 to 50 tonnes of ballast entering each tank is in the order of 2.4 Kwh per ballast operation.

A life cycle cost model was developed to show the cost impact on shipping and the results are shown in Table 6.5

Table 6.5: Life Cycle Cost Increase for Onboard Copper Ion Generation

Item	0.2 ppm on 50 tonnes
Capital cost	\$ 104,696
Element replacement cost	\$ 18,750
Element replacement frequency	5
Ballast operations per year	12
Raw material costs	\$ 0.09
Vessel charter rate	\$ 9,000
Return rate	15%
Inflation rate	3%
Amortization period	20
Increase charter to maintain return	\$ 48.08
%increase	0.53%

To increase the dosage rate would simply require the application of more power to the generator and or a slowing of the flow rate, this would have virtually no effect on the economics of running the system.

6.6 Handling Copper Onboard Ship

There are no known hazards associated with handling copper, as developed in this example, for installation onboard the trial ship. There is virtually no mechanism for human contact with the ballast water during normal operations with a copper ion generator.

At the dosage levels applied during the conduct of the experiment, entry into tanks previously treated with the copper ion generator would not present any hazard nor require change to confined space entry procedures already in place.

6.7 The Practical Considerations to using Copper

The single biggest consideration to using copper is the environmental acceptability of the discharge of treated ballast water.

In the field trial conducted, the methodology used was to apply copper at a high concentration for the first 50 tonnes of ballast and after some time period to complete the tank filling and thereby dilute the copper concentration in the tank to acceptable discharge levels. The determination of the ratios of copper concentration to volume initially filled and the efficacy thereof was not investigated in this trial.

Any system needs to be engineered to the operating parameters of the vessel and appropriate control mechanism integrated.

6.7.1 Ship Retrofitting

The prototypical system integration as installed on the M.V. *Federal Yukon* for this trial did not meet the performance standard as described by the dosing requirements. Although a specific “work around” was developed by the trials team at the ship for the second set of trials in the Great Lakes, it is not a solution that could be relied on for a permanent installation.

The as-fitted system relies on there being a negative pressure differential before and after the ballast pump to “bleed off” a known percentage of intake water and apply a dose rate based on power across the generator plates. Such a system as-fitted would be totally passive and require no pumps or flow controls. However, at the commencement of ballast operations, the water is filling the ballast tank by gravity in excess of the pump capacity, therefore no differential head is developed, consequently there is no bleed off and no copper is applied. During the trial, the ballast water was re-directed to flow through the generator only and copper was applied to the entire intake water, this was effective but slow as the nominal 300 mm intake pipe was reduce to the 100 mm generator supply pipe. In order to correct this, the concept of passive bleed off will need to be replaced and the system will require modification to incorporate an active pumping and control component.

6.7.2 Operational Constraints and Opportunities

The methodology proposed for the copper dosing system is to apply a high level of copper to the initial ballast water intake in the NOBOB condition thereby treating the tank residuals. This high level of biocide is then diluted to achieve an acceptable discharge level. This methodology as applied during the shipboard trials does not permit a sufficient dosage to be effective.

An alternative, therefore, might be to dose at an even higher level during the open ocean tank washing operations and discharge at sea.

There is no known technology that can remove the copper from the discharge waters at the rates necessary to be effective for ship ballast tank applications.

It is likely that given the strict environmental standards to which copper discharge must comply at ports throughout the world, there will be a requirement for verification that discharge levels are appropriate. For example, when the vessel visited the European port of Antwerp, the port authority required that the ballast water be analyzed for total copper content before discharge would be permitted. There is no known copper monitoring capacity developed for the shipboard environment and such tests must be performed in a shore based laboratory. These are not costly but require some time and will add an operational constraint to the vessels cargo operations.

It is likely that, should the copper ion solution be adopted in the long term, Environment Canada will require an environmental assessment of the impact of frequent discharges at the ports of concern.

Copper discharge rates from a system such as the one used in this field trial are unlikely to meet environmental regulatory standards if applied at biologically effective dosages.

7. TEST PROTOCOL MANAGEMENT

7.1 Introduction

The experimental protocols for the three components of the project were developed in house based on the proposal document and modified in accordance with the literature review.

These protocols were issued to invited peer review and comment on the applicability and validity of the experiments.

The project team and the Michigan technical authority reviewed these comments. The experimental protocols were revised in accordance with those comments deemed to enhance the conduct of the project and which were practical within the project objectives, schedule and budget. See Appendix D for a detailed copy of the test protocols used in this study. Included in Appendix D (Item 2) is a list of addendum to the original protocol document and comments provided by reviewers.

7.2 Quality Assurance/Quality Control Achieved

7.2.1 Shipboard Tests

Where possible, replicate testing for TRC, total copper and bacteria were conducted to quantify method error. For bacterial and TRC tests, one sample was analyzed in triplicate during each sampling period. Numerous total copper samples were collected and analyzed in duplicate. Table 7.1 below summarizes standard deviation data for replicated tests.

Table 7.1: Summary of Standard Deviation Data for Replicated Analyses Conducted during the Shipboard Trials

Analysis	Mean SD (%)	Low (%)	High (%)
Live/Dead	5.21	1.4	11.5
Bacteria	23.3	14.0	30.8
Total residual chlorine	2.4	0.8	4.9

In addition to replicate tests, chlorine analyses was conducted using standardized ampoules to determine method accuracy. The reference standards of 68.1ppm TRC were measured at 72.3 ± 0.58 ppm and 70.7 ± 0.58 ppm.

Table 7.2 summarizes water quality data collected during the shipboard trials. During saltwater and freshwater trials the average dissolved oxygen levels in test containers were not significantly different ($p > 0.01$, and $p > 0.05$, respectively) than those observed in the control ballast tank. Similarly, the average temperatures in test containers did not differ significantly ($p > 0.05$, and $p > 0.05$, respectively) from the control ballast tank. During the saltwater trials the pH of the decant control was significantly different ($p < 0.0001$) from the control ballast tank, as was the case with the pH in decant chlorine treatments during freshwater trials ($p = 0.007$). These data suggest that the water quality conditions in the treatments were similar to what could be expected in the ballast tanks during the trials.

Table 7.2: Summary of Physical/Chemical Water Quality Conditions during Coastal and Great Lakes Shipboard Experiments

Location	PH	Dissolved Oxygen (ppm)	Temperature (°C)	Salinity (%)
Saltwater Trial				
Decant Tanks	7.85 ± 0.11	8.1 ± 1.2	20.2 ± 2.2	32.5 ± 0.41
Test Barrels	8.03 ± 0.12	8.7 ± 0.5	19.8 ± 2.1	32.7 ± 0.67
Ballast Tanks	8.08 ± 0.14	8.1 ± 1.0	18.9 ± 1.9	32.4 ± 0.51
Freshwater Trial				Conductivity (µs/cm)
Decant Tanks	8.09 ± 0.36	10.7 ± 1.3	11.6 ± 1.8	656 ± 141
Test Barrels	8.35 ± 0.15	10.5 ± 0.5	12.5 ± 1.6	930 ± 603
Ballast Tanks	8.55 ± 0.30	10.1 ± 0.4	12.8 ± 2.8	323

7.2.2 Laboratory Tests

Toxicity tests were conducted in ESG's Ecotoxicity laboratory under strict test conditions and laboratory procedures. Although certain test conditions outlined in the standard test procedures (where they exist) were modified to suit this study, all data was collected and documented in accordance with ESG's quality management system.

ESG International's Ecotoxicity Laboratory (Speciality Chemicals) is recognized for full OECD GLP compliance by the Standards Council of Canada (SCC)/Pest Management Regulatory Agency's (PMRA) GLP recognition program. Moreover, the laboratory is also currently a candidate in Environment Canada's provisional Good Laboratory Practice (GLP) program. ESG International Inc.'s Ecotoxicity Laboratory (Environmental Division) is accredited/certified in Canada by the Canadian Association for Environmental Analytical Laboratories (CAEAL) and the Standards Council of Canada (SCC) for a number of specific tests. This means that ESG complies with Canadian standards for laboratory practice and the requirements of ISO/IEC Guide 25. The culturing and holding facilities meet criteria set by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA). ESG is also internationally recognized by the National Institute for Standards Development and the American Association for Laboratory Accreditation (A2LA).

7.2.3 Corrosion Laboratory Tests

All corrosion and coatings deterioration tests were conducted in the materials laboratory under strict test conditions and laboratory procedures. The tests conducted are non-standard tests, however, the procedures followed enable repeatability and all tests were conducted and recorded in accordance with BMT - FTL's quality management system.

The evaluation of coating deterioration was done using ASTM Standard "Test Method for evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D 1654-92". A copy is included in Appendix D, Item 3.

8. SHIPBOARD TRIALS

Shipboard trials using copper ion and sodium hypochlorite were conducted in a saltwater environment in Europe, and in a freshwater environment in the Great Lakes. Trials were conducted between October and December, 2001. The following describes the conduct of those trials and the basic data sets of recovered organisms and associated data.

8.1 Summary of Coastal Field Trials Conducted aboard the *Federal Yukon*

The following summarizes the field trials conducted aboard the M.V. *Federal Yukon* as the ship transited from Lisbon, Portugal (cargo unloading and ballast water loading) through to Bilbao, Spain (partial cargo loading, no ballast water discharge) and finally to Antwerp, Belgium (cargo pick up and ballast water discharge). Relevant dates and events for the coastal shipboard trials conducted in the saltwater port are as follows:

October 23, 2001 – Cargo unloading operations. Ballasting #5 port and starboard (P/S). Preliminary testing. Determined ballast water chlorine demand, and ballast water biological characteristics (bacteria levels and organism density).

October 24, 2001 – Cargo unloading operations. Test set up. Collected sediment (60L) from #3 P/S. Sediment loaded into test chambers. Filled decant tanks and barrels with ballast water for hypochlorite and controls tests. P/S #1 and #3 tanks filled with 100 tonnes, 68ppb (max dose) copper ion (theoretical). Buckets (20L) filled with copper ion treated water from P tanks #1 and #3. Biological analyses and sampling.

October 25, 2001 – Cargo Unloading operations. P/S #1 and #3 ballasted fully to maintain ship trim during unloading. Buckets filled with diluted copper ion water. Hypochlorite dosing and test initiation. Biological and chemical sampling and testing of hypochlorite tests.

October 26, 2001 – Unloading operations complete. Samples shipped to laboratory. Depart to Bilbao. Chemical/Physical testing and monitoring.

October 27, 2001 – Transit to Bilbao. Chemical/Physical testing and monitoring.

October 28, 2001 – Arrive Bilbao. Chemical Physical testing and monitoring.

October 29, 30, 2001 – Cargo loading operations. Chemical/Physical monitoring and testing.

October 31, 2001 – Depart to Antwerp. Chemical/Physical monitoring and testing.

November 01, 2001 – Transit to Antwerp. Chemical/Physical monitoring and testing.

November 02, 2001 – Transit to Antwerp. Chemical/Physical monitoring and testing. Biological monitoring.

November 03, 2001 – Transit to Antwerp, arrive pm. Complete biological monitoring. Sampling of ballast water and sediment. Prepare and ship samples to laboratory. Test termination, clean up, and equipment packing and stowage.

November 04, 2001 – Depart Ship.

8.2 Summary of Great Lakes Field Trials Conducted aboard the *Federal Yukon*

The following briefly summarizes the field trials conducted aboard the M.V. *Federal Yukon* as the ship transited from Chicago, Illinois (cargo unloading and ballast water loading) through to Milwaukee, Wisconsin (complete cargo unloading, ballasting complete) and finally to Duluth, Minnesota (cargo pick up and ballast water discharge). Relevant dates and events are as follows:

November 25, 2001 – Cargo unloading operations. Preliminary testing. Determined ballast water chlorine demand, and ballast water biological characteristics (bacteria levels and organism density and makeup).

November 26, 2001 – Cargo unloading operations. Test set up. Collected sediment (60L) from #5 P/S. Sediment loaded into test chambers. Filled decant tanks and barrels with ballast water for hypochlorite and controls tests. P/S #2 and #5 tanks filled with 50 tonnes, 200ppb copper ion (theoretical). Biological analyses and sampling.

November 27, 2001 – Depart to Milwaukee. P/S #2 and #5 ballasted fully to maintain ship trim.

November 28, 2001 – Arrive Milwaukee. Unloading operations commence. Chemical/Physical testing and monitoring.

November 29, 2001 – Cargo Unloading operations. Chemical/Physical testing and monitoring. Tour of the *Federal Yukon*.

November 30, 2001 – Cargo unloading operations. Chemical/Physical testing and monitoring.

December 01, 2001 – Depart to Superior, WI. Chemical Physical testing and monitoring.

December 02, 2001 – arrive Superior, WI. Chemical/Physical/Biological monitoring and testing.

December 03, 2001 – Cargo loading operations. Complete biological monitoring. Sampling of ballast water and sediment. Prepare and ship samples to laboratory. Test termination, clean up, and equipment packing and stowage.

December 04, 2001 – Depart Ship.

Table 8.1: Type and Relative Abundance (% of total) of Zooplankton Organisms in Ballast Water at each Trial Location

Organism	Freshwater	Saltwater
<u>Cladocerans</u>		
Chydorus sphaericus	2.8	-
Chydorus ovalis	<1	-
Bosmina spp	13.1	-
Eubosmina spp	<1	-
<u>Cyclopoida</u>		
Diacyclops spp	23.0	-
Acanthocyclops spp	5.2	-
<u>Harpacticoida</u>		-
Calanoida	9.1	-
<u>Copepodites</u>		
Cyclapoid	23.8	8.8
Calanoid	6.3	<1
Nauplii	11.1	90
Bivalve larvae	<1	<1
Nematodes	1.2	-
Polychaete larvae	-	<1
Keratella	1.6	-
Cephalodella	<1	-
Tricocera	<1	-

Table 8.2: Organisms Recovered from Sediments Collected from Test Chambers following Saltwater Shipboard Trials (Presence/Absence)

Test Chamber	Hypochlorite		Copper	
	Decant	Barrel	Test 1	Test 2
<u>Organism</u>				
<u>Diatoms</u>				
<i>Navicula spp.</i>	X	X	-	X
<i>Nitzschia sigmoidea</i>	X	X	-	X
<u>Protozoa</u>				
Ciliates	X	X	X	-
Flagellates	X	X	X	X
Foraminiferans	X	X	X	X
Amoeba	X	X	X	-
<u>Invertebrates</u>				
Copepods	X	-	X	-
Nematodes	X	X	X	X
Ostracods	X	-	X	-
Rotifers	-	-	X	-

Table 8.3: Summary of Analytical Results for Sediments used in Field and Laboratory Studies

Analysis	Units	Ballast Tank 3 Sediment	Ballast Tank 5 Sediment	Lab Sediment	EQL
Total organic carbon	%	2.70	3.20	9.10	0.01
Total inorganic carbon	%	0.80	0.30	3.10	0.01
Total carbon	%	3.50	3.50	12.20	0.01
Total Solids	%	21.2	35.0	23.2	0.1
METALS					
Aluminum	mg/Kg	25600	20300	6940	5
Barium	mg/Kg	54	54	75	4
Beryllium	mg/Kg	1	1	<1	1
Boron	mg/Kg	62	27	9	2
Cadmium	mg/Kg	<0.5	<0.5	<0.5	0.5
Chromium	mg/Kg	59	44	15	2
Cobalt	mg/Kg	14	11	5	2
Copper	mg/Kg	182	366	16	2
Lead	mg/Kg	70	53	14	4
Manganese	mg/Kg	518	467	613	2
Molybdenum	mg/Kg	3	2	<2	2
Nickel	mg/Kg	35	26	12	5
Silver	mg/Kg	<1	<1	<1	1
Strontium	mg/Kg	135	144	163	2
Titanium	mg/Kg	862	957	203	2
Vanadium	mg/Kg	61	52	14	2
Zinc	mg/Kg	1240	903	58	1
EQL = Estimated Quantification Limit					

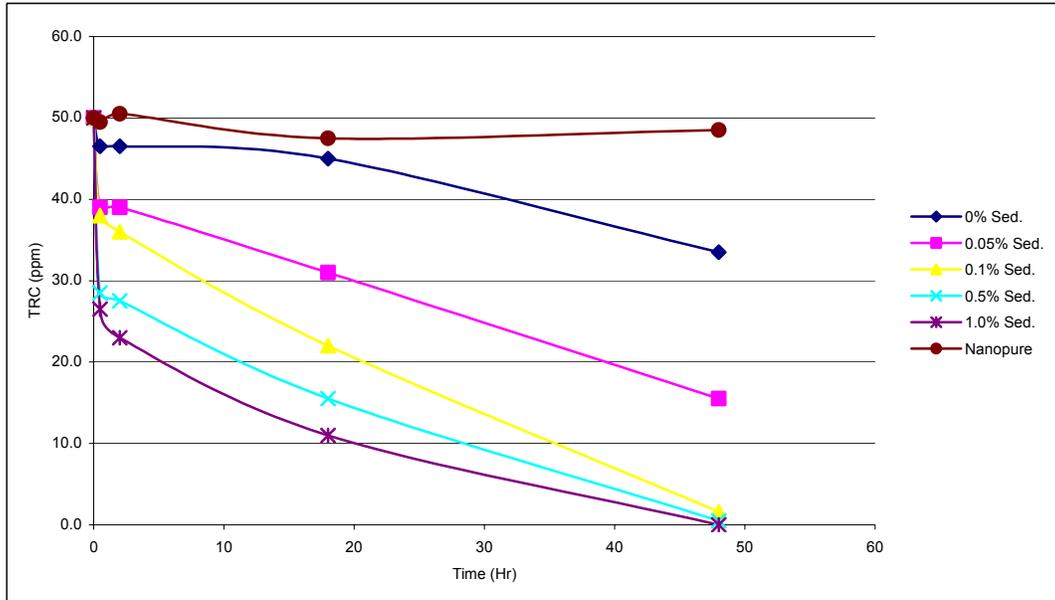


Figure 8.1: Chlorine Decay in Laboratory Saltwater Containing Various Levels of Sediment

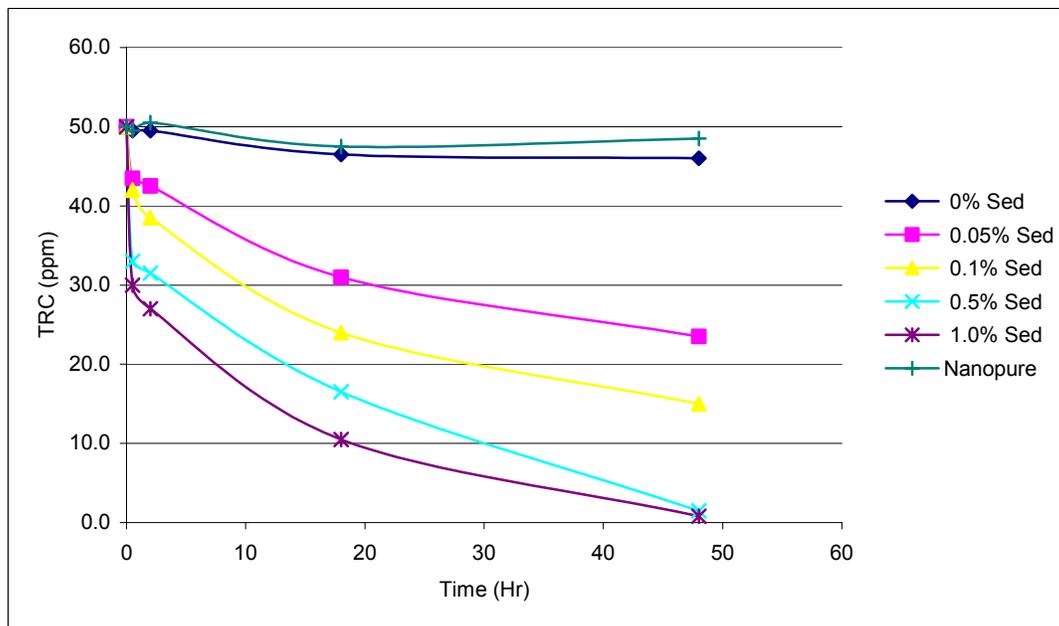


Figure 8.2: Chlorine Decay in Laboratory Freshwater Containing Various Levels of Sediment

NOMENCLATURE

ASTM – The American Society for Testing and Materials.

Barrels – 55 gallon polyethylene barrels with vented lid

Chlorine demand – The amount of chlorine consumed in a known volume of water over a specific time period (i.e., 1/2 hour).

Creepage – is the term used to describe the amount of deterioration of coating experienced at the site of existing damage. It is quantified as the distance the intact coating edge is from the position of original damage.

Decant Tank – A deck mounted metal holding tank which separates solid material from the water used to clean the inside of cargo holds prior to discharge.

Definitive test – A toxicity test set up using a linear dilution series (i.e., 10, 5, 2.5 etc.) used to identify the toxicity of a substance. The highest concentration of the series is determined using the range-finding test.

IC99 – the concentration that results in 99% inhibition (i.e., growth reduction, hatchability) in a population.

ISM – International Management Code for the Safe Operation of Ships and for Pollution Prevention. Adopted by the International Maritime Organization as the standard for management practices in operating ships safely, this code requires ship operator to integrate a safety management system into all its ship and shore based functions.

LC99 – the lethal concentration of a substance that results in 99% mortality in a population.

Range finding test – A toxicity test set up using a logarithmic dilution series (i.e., 100, 10, 1, etc.) used to identify the range of toxicity of a substance.

Sediment – is the general term used to describe the solids found in ballast water. In this study these are differentiated in to 2 types;

- (a) bottom sediment is the solids that have “settled out” of the water and accumulated on surfaces of the tank, often in small piles at or around structural components where the rinsing action of ballast water operations and ship motions is nil and
- (b) suspended sediment are the solids in suspension in the ballast water as it enters the ship.

Test Chamber – A polyethylene 55 gallon barrel or a section of the decant tank used to hold test solutions during the efficacy evaluations.

Total Residual Chlorine (TRC) – the amount of uncombined chlorine (in ppm) available in a sample (primarily as hypochlorous acid and the hypochlorite ion)

Organisms

Artemia salina cyst – the resting egg of brine shrimp

Bacillus subtilis spore – freshwater bacteria (resting stage)

Cyprinodon variegatus – sheepshead minnow

Cyprinus carpio – common carp

Daphnia magna ehippia – the resting egg of the freshwater water flea

Dreissena polymorpha veliger – free swimming larval form of the zebra mussel

Eohaustorius estuaries – saltwater amphipod

Lumbriculus variegates – freshwater oligochaete (worm)

Vibrio fischeri – saltwater bacteria

REFERENCES

A series of references are also included in the Test Protocol document Appendix D Item 1. The following references were used in the preparation of this document.

Geo. Clifford White. Handbook of Chlorination and Alternative Disinfectants. Fourth Ed. John Wiley and Sons. New York.1999.

Guidance Manual for the Disposal of Chlorinated Water. 2001. American Water Works Association Research Foundation. Denver CO.

<http://www.epa.gov/OGWDW/mdbp/dbpfr.html>

http://www.hc-sc.gc.ca/hpb/lcdc/publicat/cdic/cdic193/cd193b_e.html

Welsh, P.G., Lipton J., Chapman G. A., Podrabsky T.L., 2000. Relative importance of calcium and magnesium in hardness based modification of copper toxicity. Env. Toxicol. and Chem. Vol. 19, NO. 6, pp. 1624-1631.

Pollutech Environmental Ltd. (1992), A Review and Evaluation of Ballast Water Management and Treatment Options to Reduce the Potential for the Introduction of Non-native species to the Great Lakes, Appendix A - Ballast Water Characterization, Report to the Canadian Coast Guard, Pollutech Environmental Ltd.

Bolch C. J. and Hallegraeff, G. M. 1993. Chemical and physical treatment options to kill toxic dinoflagellate cysts in ships ballast water. J. Marine Env. Engg., Vol. 1, pp.23-29.

Whitby G.E., Lewis D. P., Schafer M., Wiley C. J. (1999) A Microbiological, Chemical, and Physical Survey of Ballast Water on Ships in the Great Lakes. In: Claudi, R., Leach J.H. (Eds.), Nonindigenous Freshwater Organisms. 2000. Lewis/CRC Press, Boca Raton.

Tanker Structure Cooperative Forum: Condition Evaluation and Maintenance of Tanker Structures, Witherby & Co. 1992

APPENDIX A

**ITEM 1 – DISINFECTION BYPRODUCTS LEVELS IN HYPOCHLORITE
TREATED BALLAST WATER AND SEDIMENT SAMPLES**

Table A.1: Disinfection Byproduct Levels in Control Hypochlorite Treated Ballast Water Samples

Analysis	CAS No.	Control 1	Control 2	Treated 1	Treated 2	RL	Units
1,1,1,2-Tetrachloroethane	630-20-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,1,1-Trichloroethane	71-55-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,1,2,2-Tetrachloroethane	79-34-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,1,2-Trichloroethane	79-00-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,1-Dichloroethane	75-34-3	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,1-Dichloroethylene	75-35-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,2,3-Trichlorobenzene	87-61-6	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
1,2,3-Trichloropropane	96-18-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,2,4-Trichlorobenzene	120-82-1	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
1,2,4-Trimethylbenzene	95-63-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,2-Dibromo-3-chloropropane	96-12-8	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
1,2-Dibromoethane	106-93-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,2-Dichlorobenzene	95-50-1	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,2-Dichloroethane	107-06-2	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,2-Dichloropropane	78-87-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,3,5-Trimethylbenzene	108-67-8	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,3-Dichlorobenzene	541-73-1	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
1,4-Dichlorobenzene	106-46-7	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
2-Butanone (MEK)	78-93-3	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
2-Hexanone	591-78-6	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
2-Methylnaphthalene	91-57-6	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
4-Methyl-2-pentanone (MIBK)	108-10-1	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Acetone	67-64-1	N.D.	25.	31.	23.	20.0	ug/L
Acrylonitrile	107-13-1	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Benzene	71-43-2	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Bromobenzene	108-86-1	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Bromochloromethane	74-97-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Bromodichloromethane	75-27-4	N.D.	N.D.	8.2	10.	1.0	ug/L
Bromoform	75-25-2	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Bromomethane	74-83-9	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Carbon disulfide	75-15-0	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Carbon tetrachloride	56-23-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Chlorobenzene	108-90-7	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Chloroethane	75-00-3	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Chloroform	67-66-3	N.D.	N.D.	110.	160.	1.0	ug/L
Chloromethane	74-87-3	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
cis-1,2-Dichloroethylene	156-59-2	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
cis-1,3-Dichloropropene	10061-01-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Dibromochloromethane	124-48-1	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Dibromomethane	74-95-3	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Dichlorodifluoromethane	75-71-8	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Diethyl ether	60-29-7	N.D.	N.D.	N.D.	N.D.	5.0	ug/L

Analysis	CAS No.	Control 1	Control 2	Treated 1	Treated 2	RL	Units
Ethylbenzene	100-41-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Hexachloroethane	67-72-1	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Isopropylbenzene	98-82-8	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
m & p-Xylene	108383,106423	N.D.	N.D.	N.D.	N.D.	2.0	ug/L
Methyl iodide	74-88-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Methylene chloride	75-09-2	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
Methyltertbutylether (MTBE)	1634-04-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
n-Butylbenzene	104-51-8	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
n-Propylbenzene	103-65-1	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Naphthalene	91-20-3	N.D.	N.D.	N.D.	N.D.	5.0	ug/L
o-Xylene	95-47-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
p-Isopropyl toluene	99-87-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
sec-Butylbenzene	135-98-8	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Styrene	100-42-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
tert-Butylbenzene	98-06-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Tetrachloroethene	127-18-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Tetrahydrofuran	109-99-9	N.D.	N.D.	N.D.	5.0	5.0	ug/L
Toluene	108-88-3	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
trans-1,2-Dichloroethylene	156-60-5	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
trans-1,3-Dichloropropene	10061-02-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
trans-1,4-Dichloro-2-butene	110-57-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Trichloroethylene	79-01-6	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Trichlorofluoromethane	75-69-4	N.D.	N.D.	N.D.	N.D.	1.0	ug/L
Vinyl chloride	75-01-4	N.D.	N.D.	N.D.	N.D.	5.0	ug/L

ND =Not Detected
 RL = Reporting Limit

**ITEM 2 – LETTER TO SHIP OWNER REGARDING DISCHARGE OF BIOCIDES
IN BALLAST WATER TO SUPERIOR BAY**

January 10, 2002

Mr. John T. Stubbs
 FedNav Ltd.
 1000 Rue de la Gauchetiere
 Suite 3500
 Montreal, PQ
 H3B 4W5

Dear Mr. Stubbs:

RE: Discharge of Biocide in Ballast Water to Superior Bay

As requested, below is a summary of analytical results conducted on treated ballast water prior to discharge at the Port of Duluth/Superior. In the Great Lakes shipboard experiments, starboard ballast tanks (Stbd. Tanks 2 and 5) were treated for the copper ion biocide trials, and the deck mounted decant tanks (Decant Tank 1 and 2) were treated for the hypochlorite biocide trials. The total copper results for tank 2 and 5 include two sampling events, one immediately after ballasting the ship completely, and one just prior to discharge. The hardness of the ballast water loaded in Burns Harbor was 215 mg/L (as CaCO₃). Therefore, the Copper Acute Toxicity Criterion (ATC) as calculated from the formula provided in Attachment B of the permit is 65 ppb (Copper ATC = $e^{[(0.8561 \times \ln \text{hardness}) - 1.1199]}$). The ballast water discharge occurred in Superior, Wisconsin during cargo loading operations on December 2, 2001.

Table 1. Summary of Analytical Results from Treated Ballast Water Discharged at the Port of Duluth/Superior.

Sample Location	Total Recoverable Copper (µg/L)		Mean Total Recoverable Copper (µg/L)	Total Residual Chlorine (µg/L)	Flow (Gal/d)
Stbd. Tank 1 (control)	-	5	5	NA	239,947
Stbd. Tank 2	20	5	13	NA	247,424
Stbd. Tank 5	20	11	16	NA	212,100
Decant Tank 1	NA	NA	NA	<10	788
Decant Tank 2	NA	NA	NA	<10	788

NA = not applicable

Should you have any questions regarding these results, or if anything above requires clarification, please feel free to contact me at (519) 836-6050 ext. 310, at your convenience.

Yours sincerely,

ESG INTERNATIONAL INC.

Martin O'Reilly
Project Manager, Microbiology

MO:mo

cc: David Stocks, Fleet Technology Ltd.
Barry Burns, MDEQ.

APPENDIX B

ITEM 1 – FRESH WATER TOXICITY TEST REPORTS

ITEM 2 – SALT WATER TOXICITY TEST REPORTS

ITEM 3 – MARINE AND FRESHWATER ALGAL TOXICITY TEST REPORTS

APPENDIX C

ITEM 1 – CORROSION TESTS DATA

ITEM 2 – PLOTS OF PAINT DETERIORATION DATA (PHOTGRAPHIC RECORD ON CD)

ITEM 3 _ COATING SUPPLIERS SPECIFICATION DATA

ITEM 4 – MSDS SODIUM HYPOCHLORITE

ITEM 5 – GRANUALTED SALT CHEMESTRY

APPENDIX D

ITEM 1 – EXPERIMENTAL PROTOCOL

**ITEM 2 – PROTOCOL AMENDMENTS ARISING
DURING CONDUCT OF EXPERIMENTS**

**ITEM 3 – ASTM STANDARD “TEST METHOD FOR
EVALUATION OF PAINTED OR COATED
SPECIMENS SUBJECTED TO CORROSIVE
ENVIRONMENTS D 1654-92**

ITEM 4 – COMMENTS ON PROTOCOLS