Global **Ballast Water** Management Programme

GLOBALLAST MONOGRAPH SERIES NO.15

2nd International Ballast Water Treatment R&D Symposium

IMO, LONDON, 21-23 JULY 2003

Proceedings

Eds. Jose Matheickal & Steve Raaymakers

A cooperative initiative of the Global Environment Facility,
United Nations Development Programme and International Maritime Organization.

GloBallast Monograph Series No. 15

2nd International Ballast Water Treatment R&D Symposium

IMO London: 21-23 July 2003

Proceedings

Jose Matheickal and Steve Raaymakers (Eds)[1]

[1] Programme Coordination Unit, Global Ballast Water Management Programme, International Maritime Organization, 4 Albert Embankment, London SE1 7SR, UK

ISSN 1680-3078

Published in September 2004 by the
Programme Coordination Unit
Global Ballast Water Management Programme
International Maritime Organization
4 Albert Embankment, London SE1 7SR, UK
Tel +44 (0)20 7587 3251
Fax +44 (0)20 7587 3261
Email sraaymak@imo.org
Web http://globallast.imo.org

The correct citation of this report is:
Matheickal, J.T. and Raaymakers S. (Eds) 2004. *2nd International Ballast Water Treatment R&D Symposium, IMO London, 21-23 July 2003: Proceedings.* GloBallast Monograph Series No. 15. IMO London.

The Global Ballast Water Management Programme (GloBallast) is a cooperative initiative of the Global Environment Facility (GEF), United Nations Development Programme (UNDP) and International Maritime Organization (IMO) to assist developing countries to reduce the transfer of harmful organisms in ships' ballast water.

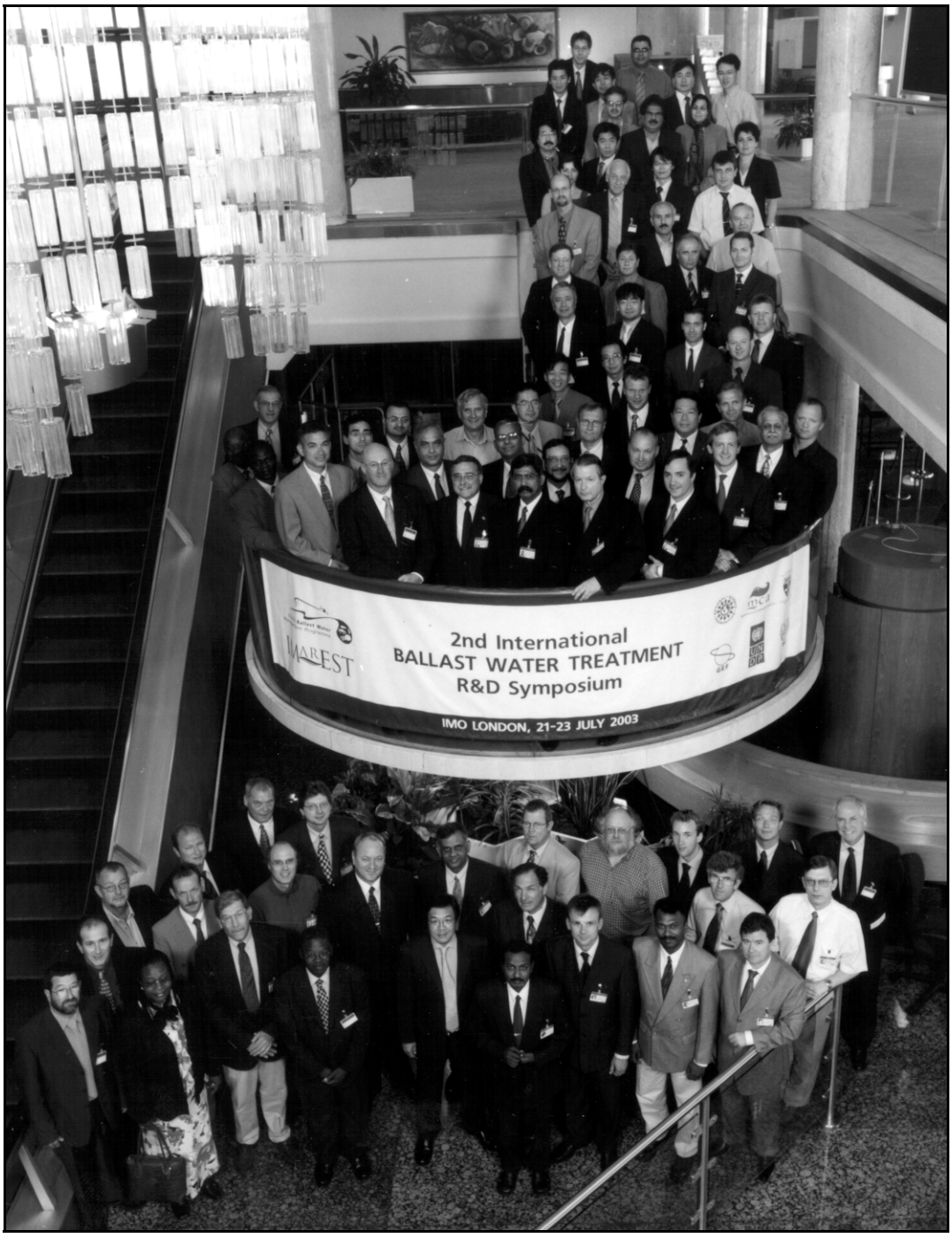
The GloBallast Monograph Series is published to disseminate information about and results from the programme, as part of the programme's global information clearing-house functions.

The opinions expressed in this document are not necessarily those of GEF, UNDP or IMO.

Acknowledgements

The following persons and parties are acknowledged for their contributions to making the Symposium a success:

- The Secretary-General of IMO, Mr William O'Neil for hosting the symposium at IMO Headquarters.
- All session chairpersons for facilitating a smooth running of the technical sessions of the symposium.
- All persons who submitted and presented papers, providing the very substance of the symposium.
- All other symposium participants, without whom the symposium would not be an event.
- The IMO Conference Section for organizational and facilities support.
- The IMO Catering Section for sustaining symposium delegates.
- Mrs Christine Gregory and Mr Leonard Webster for their 'behind the scenes' efforts in supporting the symposium.
- Mrs Sarah Harden and Ms Fiona Morris of IMarEST.
- Prof Thomas Waite (US National Science Foundation), Mr Mike Hunter (UK Maritime and Coast Guard Agency) and Dr Ehsan Mesbahi (University of Newcastle Upon Tyne School of Marine Science and Technology) for organizing sponsorship for the symposium from their respective organizations.
- Mr Leonard Webster of the GloBallast PCU for layout and formatting of this report.



Some of the delegates at the Symposium – nearly 230 attended.

Foreword

Mr. Steve Raaymakers

Chief Technical Adviser, Global Ballast Water Management Programme

The issue of aquatic invasive species, including the transfer of harmful organisms in ships' ballast water and sediments, is considered to be one of the greatest threats to global marine bio-diversity and ecosystems, and also a significant threat to coastal economies and even public health. Global economic impacts from invasive aquatic species, including through disruption of fisheries, fouling of coastal industry and infrastructure and interference with human amenity, are estimated to exceed tens of billions of Euros per year. The US General Accounting Office (2003) has identified biological invasions as one of the greatest environmental threats of the 21st Century. The United Nations Environment Programme (UNEP) and World Conservation Union (IUCN), announced at the World Summit on Sustainable Development (WSSD) in Johannesburg in 2002, that invasive species are the second greatest threat to global bio-diversity after habitat loss. The impacts are set to increase in coming years with a three-fold increase in shipping activity predicted in the next decade.

The main management measure to reduce this risk, as recommended under the existing IMO ballast water guidelines, is ballast exchange at sea. However, it has also been widely recognised that Ballast Water Exchange at Sea has limitations, including:

- serious safety concerns on ballast water exchange operations at sea; and
- the fact that translocation of species can still occur even when a vessel has undertaken the ballast exchange in accordance with the current guidelines.

It is therefore extremely important that alternative, more effective ballast water methods are developed as soon as possible, and the impending Ballast Water Convention provides a powerful, regulatory-driven incentive to support research and development efforts aimed at alternative methods.

Although significant research and development (R&D) efforts are underway by a number of establishments around the world there are no formal mechanisms in place to ensure effective lines of communication between IMO, the R&D community, governments and ship designers, builders and owners on this issue. These are vital if the R&D effort is to succeed.

To help address this situation, the GloBallast Programme initiated an International Ballast Water Treatment R&D Symposium series and the first symposium was held in March 2001 in London. The Symposium was hailed as a major success and participants requested that it become a regular event held every one or two years. In response, the GloBallast has organised this Second Symposium in conjunction with the Institute of Marine Engineering, Science and Technology (IMarEST), and with support from the United Kingdom Maritime and Coast Guard Agency; the University of Newcastle upon Tyne School of Marine Science and Technology; and the National Science Foundation in the United States.

The second symposium which had a truly global scope and highly focused objectives, brought together world's leading experts in the specialised field of ballast water treatment. Over the three days, thirty-six papers were presented, covering all of the main technologies currently being researched and updating the latest results from the major R&D projects, thus catalyzing a more co-ordinated and co-operative global R&D efforts. The symposium attracted nearly 230 participants.

The papers contained in this Symposium Proceedings provide a very useful information resource for all parties interested in the topic of ballast water treatment, management and control.

Ballast water transfers and invasive marine species are one of the most serious environmental challenges facing the global shipping industry. I am pleased that the outcomes of the symposium are

providing important catalysts for progressing the new international ballast water convention and for moving us closer to a practical solution to the 'ballast water problem.'

Symposium Objectives

The objectives of the symposium were to:

- Update the current status of ballast water treatment R&D around the world.
- Enhance communication links between IMO, member countries, the R&D community and ship designers, builders and owners on ballast water treatment issues.

Major Outcomes

Some of the conference highlights and general conclusions from the conference are given below:

In opening the Symposium, the Director of the IMO Marine Environment Division, Mr Koji Sekimizu, speaking on behalf of the Secretary-General, Mr William O'Neil, stated that during the development of the ballast water Convention, it has been widely recognized that the practice of ballast exchange at sea has many limitations, including serious safety concerns and highly variable biological effectiveness. As an example, approximately 15 new species have invaded the North American Great Lakes since 1993, despite mid-ocean exchange becoming mandatory that year for ships entering the Lakes region. This is the same number of invasions that occurred during the 1970s and 80s, indicating that current management efforts are not completely effective. Overall, the current rate of invasions in the Great Lakes is 66% higher than 100 years ago, and similar trends are recorded in other parts of the world where surveys and monitoring are conducted. Mr Sekimizu stated that it is therefore extremely important that alternative, more effective ballast water treatment methods are developed as soon as possible.

In delivering the keynote address at the Symposium, Dr Thomas Waite, Programme Director of Environmental Engineering at the US National Science Foundation stated, *inter alia*, that the search for solutions requires far more input from naval architects and marine engineers, that the initial focus should be on adapting existing water treatment techniques, that the R&D effort should look for synergies between treatment processes, and that non-chemical, reversible treatments such as heat, de-oxygenation and pH extremes should be seriously pursued, along with new techniques such as light-sensitive biocides.

A total of 36 technical papers were presented over the three days covering mechanical and gas-based treatment systems, heat and electro-based systems, chemical-based approaches, multiple technologies and combined systems, with a special session on test protocols and verification procedures.

A general picture that emerged from the technical presentations is summarised as follows:

- Overall, there has been a significant increase in R&D and good progress has been made by several groups in moving closer to viable, practical, effective solutions, although most of the groups still remain at the basic research stage. The lack of finalised treatment standards in the IMO Convention (at the time) was identified as still being the major obstacle to the R&D community.

- It is unlikely that a single treatment technology will suit all vessel types and voyage characteristics. The R&D community should seek to develop different treatment options for

different scenarios, as long as they meet the international performance standard. For example, heat appears to hold significant promise for cruise ships and some tankers that generate significant waste heat, but is unlikely to be an option for bulk carriers with large volumes of ballast but little waste heat.

- It appears that treatment systems will need to involve combined technologies, and that primary filtration or physical separation will almost certainly be necessary, followed by secondary biocidal treatment(s). If primary filtration alone was implemented now, a significant reduction in bio-invasions would be achieved.

- The development of internationally standardised test protocols and verification procedures was identified as the most urgent remaining priority that must be addressed by IMO.

Symposium Programme

Sunday 20 July 2003

1400 – 1800: Registration

Monday 21 July 2003: Day 1

0730 – 0900: Registration

Opening & Keynote Speakers

0900 – 0915: Opening statement: *Mr William O'Neil,* Secretary-General, IMO

0915 – 0935: Keynote address: *Dr T Waite,* National Science Foundation, USA

0935 – 0950: Introduction, background and objectives of the symposium: *Mr S Raaymakers,* GloBallast PCU

0950 – 1010: Official group photograph

1010 – 1040: Tea/coffee

Session One: Mechanical and Gas-Based Treatment Systems

1040 – 1105: The Ternary Effect for ballast water treatment
I Kreisel, N Shimron, Y Kolodny, D Sorek, Arkal Filtration Systems, Israel
Y Sasson, The Hebrew University of Jerusalem, Israel
A Cangelosi, Northeast Midwest Institute
C Blatchley, Purdue University, *M Blacer,* University of Wisconsin,
P Brodie, Balaena Dynamics Ltd,
B Cairns, R Braun, Trojan Technologies Inc

1105 – 1130: Progress report on the 'Special Pipe System' as a potential mechanical treatment for ballast water
T Kikuchi, K Yoshida, S Kino, The Japan Association of Marine Safety, Japan
*Y Fukuyo,*University of Tokyo, Japan

1130 – 1155: Progress report on the AquaHabiStat Deoxygenation system
W J Browning, J Parker Davis, W J Browning III, AquaHabiStat, USA
Capt C Thompson, USCG Retired, USA
Dr R Mann, Virginia Institute of Marine Science, USA

1155 – 1220: Evaluations of Venturi Oxygen Stripping as a ballast water treatment to prevent aquatic invasions and ship corrosions
Dr M N Tamburri, University of Maryland Center for Environmental Science, USA
B J Little, Stennis Space Center, USA
G M Ruiz, Smithsonian Environmental Research Center, USA
P D McNulty, NEI Treatment Systems Inc, USA

1220 – 1245: Ballast water treatment by De-oxygenation with elevated CO2 for a shipboard installation – a potentially affordable solution
M Husain, R Apple, D Altshuller, C Quirmbach, MH Systems Inc, USA
H Felbeck, Scripps Institution of Oceanography, USA

1245 – 1315: Session one panel discussion

1315 – 1430: Lunch

Session Two: Heat and Electro-Based Treatment Systems

(each presentation 20 min + 5 min questions)

1430 – 1455: Does heat offer a superior ballast water treatment option?
G Rigby, Reninna Pty Limited, Australia
G Hallegraeff, University of Tasmania, Australia
A Taylor, Alan H Taylor & Associates, Australia

1455 – 1520: Treatment of residual ballast water in the NOBOB ship using heat
D T Stocks, BMT Fleet Technology Ltd, Canada
M O'Reilly, ESG International Inc, Canada

1520 – 1550: Tea/coffee

1550 – 1615: The use of heat for ballast water disinfection – the AquaTherm method
G A Thornton, Hi Tech Marine Pty Ltd, Australia

1615 – 1640: Application study of ballast water treatment by electrolyzing seawater
K Dang, P Yin, P Sun, Y Song, Dalian Maritime University, P R China

1640 – 1705: Electro-sanitization of ballast water
C E Leffler, B Paul, P Trupiano, A Salamone, Marine Environmental Partners Inc, USA
A Rogerson, S Grubbs, C Cox, Nova South Eastern University, USA

1705 – 1730: Superconducting magnetic separator for ballast water treatment
Dr N Saho, H Isogami, T Mizumori, N Nishijima, HITACHI Ltd, Japan

1730 – 1800: Session two panel discussion

1800 – 2030: Reception – IMO delegates' lounge
Sponsored by IMarEST, the University of Newcastle upon Tyne and GloBallast

Tuesday 22 July 2003: Day 2

0800 – 0900: Registration (at registration desk, ground floor, IMO)

Session Three: Chemical-Based Treatment Systems

(each presentation 20 min + 5 min questions)

0900 – 0925: Sodium Hypochlorite as a ballast water biocide
D T Stocks, BMT Fleet Technology Ltd, Canada
M O'Reilly, ESG International Inc, Canada
W E McCracken, Consultant, USA

0925 – 0950: Effects of chlorination treatment for ballast water
S Zhang, J Xiao, D Yang, W Gong, Q Wang, Dalian Maritime University, P R China

0950 – 1015: Use of chlorine for ballast water treatment
J da Silva, F da Costa Fernandes, Instituto de Estudos do Mar
Almirante Paulo Moreira – IEAPM, Brazil

1015 – 1045: Tea/coffee

1045 – 1110: SeaKleen®: a potential product for controlling aquatic pests in ships' ballast water
J Cutler, H G Cutler, Garnett Inc, USA
Glinski, Planta Analytica, USA
D Wright, R Dawson, University of Maryland Center for Environmental Science, USA
D Lauren, HortResearch Ruakura, New Zealand

1110 – 1135: Peraclean® Ocean – a potential treatment option for ballast water
Dr R Fuchs, Degussa AG, Germany

1135 – 1200: Acrolein as a potential treatment alternative for control of micro-organisms in ballast tanks: five day sea trial
Dr J E Penkala, M D Law, J K Cowan, Baker Petrolite, USA

1200 – 1230: Session three panel discussion

1230 – 1345: Lunch

Session Four: Multiple Technologies and Combined Systems

(each presentation 20 min + 5 min questions)

1345 – 1410: Solution to ballast water pollution: ship shape and ports escape?
E. Donkers, Port of Rotterdam, The Netherlands

1410 – 1435: Latest results from testing seven different technologies under the EU MARTOB project – where do we stand now?
Dr E Mesbahi, University of Newcastle upon Tyne, UK

1435 – 1500: The TREBAWA ballast water treatment project
Capt K Hesse, Reederei Hesse GmbH and Co, Germany

1500 – 1530: Tea/coffee

1530 – 1555: Shipboard trials of ballast water treatment systems in the United States
D A Wright, R Dawson, University of Maryland Center for Environmental Science, USA
P Mackey, Hyde Marine Inc, USA
H G Cutler, S J Cutler, Mercer University, USA

1555 – 1620: Development and design of process modules for ballast water treatment onboard
Dr Ing A Kornmueller, Berkefeld Water Technology/RWO Marine Water Technology, Germany

1620 – 1645: Hydrodynamic cavitation and filtration treatment of ballast water
A Andryushchenko, Engineering Center TRANSZVUK, Ukraine

1645 – 1715: Session four panel discussion

1715: Close day two

Wednesday 23 July 2003: Day 3

0800 – 0900: Registration (at registration desk, ground floor, IMO)

Session Four contd: Multiple Technologies and Combined Systems

(each presentation 20 min + 5 min questions)

0900 – 0925: A new modular concept for the treatment of ships' ballast water - the Hamann project
Dipl Ing H Röpell, Dipl Ing T Mann, Hamann Wassertechnik GmbH, Germany

0925 – 0950: A portable pilot plant to test the treatment of ships' ballast water
S Hillman, Dr P Schneider, Dr F Hoedt, James Cook University, Australia

0950 – 1015: Ballast water treatments R&D in The Netherlands
J L Brouwer, Royal Haskoning, The Netherlands
Dr C C ten Hallers-Tjabbes, Netherlands Institute for Sea Research (NIOZ), The Netherlands

1015 – 1045: Tea/coffee

1045 – 1110: Ballast water treatment research and interim approval in Washington State
S S Smith, Washington Department of Fish and Wildlife, USA

1110 – 1135: Corrosion effects of ballast water treatment methods
E Dragsund, A B Andersen, B O Johannessen, J O Nøkleby, Det Norske Veritas, Norway

1135 – 1205: Session four (contd) panel discussion

1205 – 1310: Lunch

Session Five: Test Protocols and Verification Procedures

(each presentation 20 min + 5 min questions)

1310 – 1335: A proposed frame-work for approving ballast water treatment technologies
Dr D O Mountfort, M D Taylor, T J Dodgshun, Cawthron Institute, New Zealand

1335 – 1400: Ballast water treatment verification protocol – DNV proposal
E Dragsund, A B Andersen, B O Johannessen,
Det Norske Veritas, Norway
K Tangen, Oceanor, Norway

1400 – 1425: The Artemia Testing System for ballast water treatment options
Dr M Voigt, dr. voigt-consulting, Germany

1425 – 1450: Development of dinoflagellate "cyst-on-demand" protocol and comparison of particle monitoring techniques for ballast water treatment evaluation
Dr J T Matheickal, Prof T J Hwa, S Mylvaganam, L Loke, Institute of Environmental Science and Engineering, Singapore
Dr M Holmes, Tropical Marine Science Institute, Singapore

1450 – 1520: Tea/coffee

1520 – 1545: Test procedure for evaluation of ballast water treatment systems using copepods as zooplankton and dinoflagellates as phytoplankton
T Kikuchi, K Yoshida, S Kino, The Japan Association of Marine Safety, Japan
Y Fukuyo, University of Tokyo, Japan

1545 – 1610: Testing ballast water treatment equipment
Prof A E Holdø, University of Hertfordshire, UK

1610 – 1635: Performance verification testing of ship ballast water treatment technologies by USEPA/NSF Environmental Technology Verification programme
T G Stevens, NSF International, USA
R M Frederick, US Environmental Protection Agency, USA
R A Everett, J T Hurley, US Coast Guard, USA
C D Hunt, D Tanis, Battelle, USA

1635 – 1705: Session five panel discussion

1705 – 1730: Conclusions and recommendations
Close Symposium

Contents

Papers presented

Session 1: Mechanical and Gas Based Systems

Session 2: Heat and Electro-based Treatment Systems

Session 3: Chemical-based Treatment Systems

Session 4: Multiple Technologies and Combined Systems

Session 5: Test Protocols and Verification Procedures

Papers submitted (not presented at the Symposium)

Appendix 1: List of Participants

Papers presented

Disclaimer

Papers have been included in these Proceedings largely as submitted, with basic editing and formatting only, and without scientific or technical peer review.

Neither the GloBallast Programme, the International Maritime Organization (IMO), the Institute of Marine Engineering, Science and Technology (IMarEST) nor the symposium sponsors take any responsibility whatsoever for any statements and claims made in these papers, for the quality, accuracy and validity of data presented, or for any other contents of these papers.

Individuals and organisations that make use of any data or other information contained in these papers do so entirely at their own risk.

Inclusion of papers in these proceedings in no way constitutes any form of endorsement whatsoever by IMO, GloBallast, IMarEST or the symposium sponsors.

Session 1:
Mechanical and
Gas Based Systems

The ternary effect for ballast water treatment

I. Kriesel[1], Y.Kolodny[1], W.L. Cairns[2], B.S. Galil[3], Y. Sasson[4], A.V. Joshi[4], A. Cangelosi[5], E.R. Blatchley III[6], M.C. TenEyck[7], M.D. Blacer[7] & P. Brodie[8]

[1] *Arkal Filtration Systems, Israel.*
itayk@arkal.com

[2] *Trojan Technologies Inc.,*
London, Ontario, Canada

[3] *Israel Oceanographic and Limnological Research,*
Israel

[4] *The Hebrew University of Jerusalem, Israel*

[5] *Northeast Midwest Institute, USA*

[6] *Purdue University, USA*

[7] *University of Wisconsin-Superior, USA*

[8] *Balaena Dynamics Ltd., Canada*

Abstract

We have designed assembled and preliminarily tested a hybrid ballast water treatment prototype that is potentially environmentally safe and compatible.

The concept is based upon an advanced filtration stage combined with controlled generation of oxygenated free radicals in the water. The technology is designed to cope with the following challenges:

- *Inactivation of substantially more than 95% of aquatic organisms in a wide range of taxa.*
- *Targeting the resistant organisms, particularly those smaller than the exclusion limit of the filter.*
- *Variable water quality (composition and turbidity).*
- *Avoidance of residual toxic chemicals in discharged water.*
- *Forestalling corrosion in the ballast tanks.*
- *Applicability to a range of ship classes.*

The technology consists of the following phases:

A. An ex-situ phase (outside the ballast tanks) with the following stages:

1. *Catalytic formation of oxygenated free radicals from precursors that include hydrogen peroxide at minimal dose and dissolved oxygen. The reaction is enhanced by a metal oxide-based catalyst that is suspended in the water medium.*
2. *Disc filtration using Arkal Spin Klin® patented technology. The channels within the discs efficiently capture aggregated particles that are created at the first step, and therefore filtration efficacy is enhanced.*
3. *UV irradiation. Direct UV disinfection is enhanced by the higher inlet UV transmittance induced by the second stage. Disinfection efficacy is enhanced by further photocatalytic formation of free radicals within the UV reactor in the presence of hydrogen peroxide, a high oxygen level and the metal oxide catalyst.*

The three steps described above are synergistic. The whole process is entitled the ***Ternary Effect****.*

B. An in situ phase (within the ballast tanks):

In this phase, disinfection continues via peroxide /radical mechanisms. Generally, an increased holding time within the ballast tank improves (to a limit) the organism inactivation.

Phases A & B, integrated together constitute a flexible multiple barrier approach to invasive species control.

The technology is protected by two pending patents: (IL/US/PCT).

Members of the Consortium

Arkal Filtration Systems: providers of water separation solutions for the agricultural and industrial sectors. Manufacturers of the unique disc filter system (Spin-Klin®). Typical performance of the latter is displayed in Figure 1.

Trojan Technologies: providers of systems for UV disinfection and chemical contaminant treatment of wastewaters, potable waters and industrial waters using UV and advanced oxidation approaches.

NEMW Institute: expertise in the problems and applications of different ballast water treatment technologies, and closely interfaced with the shipping industry, academic community and regulatory community that will be making decisions on invasive species control and the selection criteria that must be met by acceptable technologies.

Bella Galil is a marine biologist with the National Institute of Oceanography, Israel Oceanographic and Limnological Research. Galil participated in the pioneering studies testing the bioefficacy of ballast water exchange. She serves as a consultant to MOT.

Yoel Sasson is a Professor of applied chemistry at the Hebrew University of Jerusalem and consultant to several chemical process industries, and specializes in homogeneous and heterogeneous catalytic processes R&D.

E.R. Blatchley III is a Professor of Environmental Engineering in the School of Civil Engineering at Purdue University. He conducts research in the area of physico/chemical processes of environmental engineering, with particular emphasis on the dynamic behavior of disinfection systems used in the treatment of water.

Lake Superior Research Institute (Mary Balcer and Matthew TenEyck) are scientists at the University of Wisconsin-Superior with expertise in aquatic ecology, zooplankton taxonomy and ecology, and environmental toxicology. They are involved in dose response and residual toxicity tests.

Balaena Dynamics (Paul Brodie): marine biology expertise and originator of closed loop concepts for ballast water treatment.

Research on process optimization (Ternary Effect) is being conducted by Arkal Filtration System on a pilot in Israel with consultancy in physics and chemistry from Professor Yoel Sasson and consultancy in marine biology from Dr. Bella Galil. Research on process optimization (oxidation-disinfection) is being conducted in parallel with the NEMW Institute and Professor Blatchley using equipment and guidance from Trojan, Arkal and Yoel Sasson. Balaena Dynamics is assessing optimization of the closed-loop option both for use with the new integrated oxidation-filtration-disinfection process and as a means to minimize sedimentation buildup in the ballast tanks.

Introduction

The transport of potentially invasive species in ballast water is considered a major threat to the environment, the economy and human health (Ruiz, 2000; Anil, 2002; Elliot, 2003; Topfer, 2002). Given the safety and efficacy concerns expressed about Ballast Water Exchange (BWE) on the high seas, there is a strong incentive to explore various methodologies of Ballast Water Treatment (BWT). A self-contained BWT process allows independence of seas state/ice pack, etc; independence of ship delays and independence of onshore work disruption. Given a probable 20-25 year phase-out of existing vessels, retrofitting of validated BWT systems becomes an essential consideration in addition to designing BWT systems for new ship outfitting (Champ, 2002).

The above described consortium of collaborators has been formed to configure, design, optimize and validate a new Ballast Water Treatment (BWT) process that is compatible with a set of selection criteria, design options and strategic considerations that are defined in this article. The novel process integrates various technologies (enhanced particle aggregation and filtration, UV disinfection/advanced oxidation and catalytic oxidation). The new platform implements a patent-pending ex situ (outside the ballast tank) process to promote particle aggregation and improve filtration, and provides both an ex situ and an in situ (within the ballast tank) disinfection components. The process has the flexibility of being used in single pass, dual pass (ballasting and deballasting) and optionally, during the ship voyage. The process is compatible with Ballast Water Exchange (BWE) where it is deemed practicable and safe, but otherwise is totally self-contained.

The plankton (organisms in the water column that are unable to maintain their position independent of the movement of water masses) is divided according to their size: microplankton (20-200 μm), nanoplankton (2-20 μm) and picoplankton (0.2-2.0 μm) including bacterioplankton. It is conceivable that one disinfection technology will not impact effectively all taxa and that a hybrid solution incorporating several methodologies is essential. In the course of this study we have demonstrated that the larger microplankton can be removed by a disc filter of a size between 50μ−100μ, the microorganisms are eradicated with UV irradiation and the smaller plaktonic organism can be treated and eliminated using advanced photochemical and catalytic oxidation processes based on hydrogen peroxide.

The new process is built around two commercially available platforms:

1. the depth filtering capability of the Arkal disk filters and
2. the UV disinfection and advanced oxidation technologies of Trojan Technologies.

The process builds on Trojan's experience in UV photolysis of hydrogen peroxide to produce hydroxyl radicals within the reactor to disinfect organisms that are resistant to disinfection by UV alone. The process also incorporates additional proprietary oxidation processes of Arkal to enhance the filtration efficacy and to continue disinfection within the ballast tank

Primary treatment of ballast water by filtration

Filtration is one of the separation technologies of choice for BWT by virtue of the need to separate according to particle size and not just particle density as the density of the organisms in many cases is close to the density of water.

The Spin-Klin® disc filtration system manufactured by Arkal Filtration Systems has several unique features that are advantageous for ballast water treatment (see Figure 1). It has an efficient and precise particle separation (down to size of 10 μm), there is no "break through" of the retained material, easy and effective backwash – very low energy and water consumption, very low maintenance and corrosion free construction materials. The filtration system can be configured to provide a small foot print suitable for ship installation.

In a recent study (Parsons, 2002) Spin Klin® system was critically tested and assessed along side other separation technologies for ballast water filtration in a full scale experiment (340 m^3/hr) in the Great Lakes area (August-September 2001). It was concluded that the 100 µm disc filter performs better in particle removal as compared to other filters and hydrocyclones. Typically all particles above 200 µm were removed along with 91.4% of all the particles above 100 µm.

Agglomeration and flocculation induced by hydrogen peroxide

Initial experiments aimed at assessing the potential of hydrogen peroxide (HP) for the sterilization of ballast water resulted in a surprising discovery. It was established that HP, at concentrations of 10-50 mg/liter performs as a flocculant, inducing the agglomeration of nanoplankton (mainly diatoms, dinoflagellates and blue-green algae) into filterable flocs. Thus treatment of Mediterranean sea water with HP with 10-50 seconds of retention time resulted in coagulation of an oxidized biomass which functions as the basis for further aggregation, since the oxidized organics possess high adhesion power. When these aggregates were examined under magnification it was observed that they contain not only oxidized and inert biomass but also occluded inorganic particles as well as live microorganisms. This oxidation-sorption interaction improves the efficiency of the filtration. Consequently, the filtration is successful in removing large quantities of particles where the original size of which, before aggregation, was small enough to escape removal. Using a 50 µm disc filter, 96% of the microplankton (size > 80 µm) was removed. Comparison of the post filtration sample with the control showed reduction in nanoplankton population (size > 3 µm) in correlation with the concentration of HP. Application of 30, 40 and 50 mg/liter HP resulted in 53, 56 and 76% reduction respectively.

Model I BWT Pilot Unit: Combined activity of disc filtration, uv irradiation and hydrogen peroxide

With the objective of testing whether organisms that escape disc filtration (mainly nano- and picoplankton) may be eradicated by exposure to UV irradiation in the presence of hydrogen peroxide, we designed and built a 10 m^3/hr demonstration unit. The pilot unit was placed and tested on a towing dock at the port of Hadera on the Mediterranean coast of Israel (Figure 2). The pilot was operated from April to June 2001 and processed more than 3000 tons of sea water. The apparatus contained two alternating serpentine pipe reactors (2.2 and 20 meter long, residence time 5 and 48 sec. respectively). HP (30%) was continuously injected into the flowing sea water to generate a 20-50 mg/liter concentration. The treated water was transferred to a disc filter (single or dual) with filtration degrees ranging between 20-100 micron, followed by a UV irradiation unit (several types of UV technologies using medium or low pressure lamps were tested) at UV doses ranging between 33-200 mJ/cm2.

The planktonic organisms in the treated and untreated samples were studied. In the untreated samples eleven microplankton taxa (at different taxonomic levels) were identified. The most common taxa were the foraminiferans and crustaceans. Comparing the post HP/filtration/UV sample with the control, a 93% reduction in abundance of the microplankton (size > 80 µm) was observed. Six nanoplankton taxa (at different taxonomic levels) were identified. The most numerous taxa were diatoms and Ebriida. Of the nanoplankton specimens (size > 3 µm) 35-42% were removed utilizing a single disc filter unit, and 61-62% were removed with the dual filter system in the HP/filtration/UV treatment.

The microbial diversity in the treated and untreated sea water samples was studied by Professor Norbert Hulsmann of the Free University of Berlin. He concluded that the treated samples still contained particles of organismic origin (diatom frustules, dinoflagellate cell walls, loricae of phytoflagellates up to about 50 µm) with putative plasmatic remnants as well as particles of unknown origin (mainly fibers with a length of 100 µm and more). However, no living cells could be detected in the samples, neither after addition of yeast cells as food organisms to sub-samples, nor after a

period of more than three weeks of inspection. In all the treated samples, the development of biofilm was inhibited or strongly suppressed, indicating quasi-sterile conditions. Addition of living cells from an untreated control sample to dishes with treated seawater led to moderate biocidal effects mainly for flagellates and heliozoans, but not for naked amoebae. The controls (untreated and sieved crude material) showed the normal picture of a moderate microbial diversity typical for marine water of oligotrophic origin.

We concluded that Model I system was quite efficient in removing the larger microplankton (size > 80 μm), but only moderately effective in removing the nanoplankton (size > 3 μm). Conclusions of this phase prompted us to explore the potential of catalytic activation of hydrogen peroxide in seeking higher disinfection activity for the eradication of the smaller nanoplankton and picoplankton.

Advanced Oxidation Processes (AOP) for ballast water treatment

Reactive oxygen species (ROS) such as superoxide radical anion, hydroxyl radical, perhydroxyl radical, singlet oxygen or ozone are potentially highly appealing disinfection agents for various water treatment applications. The most potent oxidant in the above list is the hydroxyl radical with oxidation potential of 2.8V that is second only to elemental fluorine (3.0V). Hydroxyl radical and other ROS are devastating to various constituents of the living cell, mainly to membrane lipids, proteins and DNA. Remarkable recent ROS life science applications are in photodynamic therapy (Lane, 2003) and in crop protection (Heitz, 1995).

An area where hydroxyl radical intermediate is the ordinary mode of action is in industrial effluent management, particularly of toxic streams that are impervious to standard aerobic or anaerobic biological treatment. The widespread methodology for generation of hydroxyl radicals is via the Fenton chemistry which is based on diluted hydrogen peroxide and ferrous ion (Neyens, 2003):

Basic Fenton chemistry cannot be considered for BWT as it requires acidic conditions (pH < 4). Improved technologies which have emerged in the last decade under the general term AOP (Advanced Oxidation Processes) integrate and facilitate Fenton reaction with UV-VIS irradiation, special catalysts, ozone or oxygen. Another novel approach is photocatalysis based on semiconductors such as titanium dioxide which generates ROS from water and oxygen. The main advantage of ROS as chemical reagents is their inherent ability to induce a destructive chain process, in the presence of an organic material, which utilize dissolved oxygen in the propagation step and hence is essentially self sustained.

In an early paper Waites et al. have demonstrated the synergistic effect of UV and hydrogen peroxide in destruction of bacterial spores (Waites, 1988). However, no report on disinfection of drinking or recycled water using catalytic AOP has been published hitherto.

In a series of experiments aimed at assessment of AOP as a core technology for ballast water treatment (May-October 2002) we have utilized salicylic acid (SA) as a chemical scavenger to monitor the rate of formation of hydroxyl radicals. In the presence of the latter, salicylic acid is swiftly oxidized to a mixture of 2,3- and 2,5-dihydroxybenzoic acid which can be assayed by high pressure liquid chromatography (HPLC) using a UV detector. The degree of conversion of SA is proportional to the number of hydroxyl radical generated in a given system.

We examined several AOPs for the oxidation of salicylic acid in Mediterranean Sea water under irradiation using a 150W medium pressure UV lamp, equipped with a quartz sleeve (TQ-150, Heraeus Nobel Light Ltd.) with calculated UVC average intensities of 50-180 mW/cm^2 in the 1-4 litre reaction vessels used.

Our results clearly show that medium-pressure UV irradiation of sea water results in generation of hydroxyl radicals. This amount was strongly affected by the presence of oxygen and/or hydrogen peroxide (HP). Thus, irradiation of sea water containing 250 mg/liter of SA (neutralized by NaOH to

pH=7.9) and saturated with argon gas resulted in 6.3% conversion of SA after 90 minutes. The same experiment done under air gave 8.4% conversion. Addition of 10 mg/liter of HP, with otherwise identical conditions, raised the conversion to 11.6% and saturation with oxygen increased it to 15.1%. Combined addition of 10 ppm HP and saturation with oxygen boosted the conversion to 20.3%.

We were quite astonished to realize that none of the previously proven metal or metal oxide catalysts as well as other metal salts or oxides that we have tested generated any detectable superfluous activity under irradiation. Thus salts and oxides of Fe, Ni, Co. Ag, Ru, Pt, Cu, W and V all failed to show any synergic catalytic effect with the UV irradiation. TiO_2 demonstrated some activity when irradiated with wavelength above 300 nm but was practically ineffective when exposed to the complete spectrum of the medium pressure lamp.

The molar extinction coefficient of hydrogen peroxide is relatively low (18.6 dm^3. $mol^{-1}.cm^{-1}$ at 254nm). Consequently, only a small fraction of incident light is actually exploited. The rate of photolysis of aqueous hydrogen peroxide has been found to be pH dependent and to increase with higher alkalinity. This may be primarily due to the higher molar absorption coefficient of the peroxide anion, which at 254nm is 240 $dm^3.mol^{-1}.cm^{-1}$ (Legrini, 1993) These essentials prompt us to examine the potential role of basic catalysts on the behavior of the system. Indeed, at pH=9.5 and particularly at pH=10.0 the measured rate of SA oxidation using the $UV/H_2O_2/O_2$ system was 100 and 140% respectively, faster than the rate at pH=8.0 (note however that HP is intrinsically unstable at basic conditions)

Altering the pH of the ballast water in the course of the treatment is not viable, so we have envisaged the application of a non-soluble solid base catalyst which would display a surface basicity without affecting the overall pH of the processed sea water. The obvious material that drew our attention was magnesium oxide. The latter is a natural refractory mineral (periclase) and an industrial product (magnesia) with numerous commercial (including pharmaceutical) applications. MgO is a strong solid base with remarkable surface base strength of $+26.5 > H_- > +22.3$ (Higuchi et al. 1993) and is only very slightly soluble in water (0.6 mg/100 ml).

We used a magnesium oxide sample supplied by Aldrich with surface area (BET) of 11.4 m^2/gr, bulk density of 3.58 gr/cm^3 and micropore volume of 0.000973 cm^3/g.

When a slurry of 20 mg/liter of MgO in sea water (0.8 liter) containing 250 mg/liter of SA was irradiated with a medium pressure UV lamp (intensity of 180 mW/cm^2) conversion of 10.5% was obtained after 90 minutes (compared with 8.4% in the absence of MgO). The conversion increased to 15.4% when 10 mg/liter of HP was added to the above slurry and to 27.3% when a continuous stream of oxygen (50 ml/min) was introduced together with MgO and HP in the above capacity. These experiments are presented in Figure 3.

Although the major rationale to apply MgO stems from its basic properties we attribute part of the synergic effect observed in the above experiments to the unique characteristic of magnesium oxide to stabilize ROS on its surface. This attribute was established by Giamello (1993) who showed that hydroxyl radical and other ROS formed on the surface of the MgO upon contact with HP are stable up to a temperature of 200°C.

Application of MgO as a component in a hybrid ballast water treatment is particularly appealing due to several other beneficial attributes of this material which are described below:

- Recent studies disclose the unique bactericidal characteristic of MgO particularly when fabricated as nano-particles (Sawai, 2000, Stoimenov, 2002). This trait probably stems from surface ROS (Sawai, 1996).
- MgO was advocated as a scavenger of hydrogen sulfide in wastewater systems. (Higgins, 2003). This is advantageous for ballast water tanks where anaerobic sulfate reducing bacteria (SRB) are abundant (Parker, 1996).

- Corrosion inhibitor: Due to its neutralizing properties magnesia is used to neutralize acidity in various boilers and water treatment facilities.
- Coagulant and flocculant: magnesium ions and oxide are used for coagulation-flocculation of biological material in industrial and municipal waste water treatment (Semerjian 2003, Hughes 2002).

Effects of HP, MgO and UV radiation on rotifers

Background

Ultraviolet (UV) radiation is known to be effective for inactivation of waterborne microorganisms that are of concern in conventional (potable) water and municipal wastewater treatment operations, including many bacteria, viruses, and protozoa. However, among higher life forms, the effects of UV irradiation on waterborne organisms are not as well defined. For ballast water treatment operations, available evidence suggests that these higher life forms, which are generally larger than the microorganisms listed above, may be resistant to UV-based treatment technologies.

To address this issue, experiments were conducted to characterize the responses of relevant waterborne organisms (February 2003 to date). The focus of experiments described herein is on freshwater rotifers. Organisms were subjected to UV irradiation in the presence of hydrogen peroxide (H_2O_2) and magnesium oxide (MgO). H_2O_2 and MgO were added to the solution because they have the potential to generate oxygenated radical species; both compounds have been shown to have antimicrobial characteristics as well. It was hypothesized that these compounds (and radicals formed in their presence) would augment the UV-based inactivation of rotifers in that they provided a different mechanism of stress on the organisms. Furthermore, there is evidence to suggest that these compounds and UV radiation may act in a synergistic manner, such that the antimicrobial responses of the combined treatment would be greater than the responses attributable to either UV radiation or the chemicals alone.

Materials and methods

Two freshwater rotifers (*Philodinia sp.* and *Brachionus calyciflorus*) were selected for study. These organisms are representative of the two major classes of rotifers found in freshwater communities and the Great Lakes. *Brachionus calyciflorus* is a loricate member (containing a stiffened cuticular body wall composed of scleroprotein and glycoprotein) member of the class Monogonota while *Philodina sp.* is an illoricate member of the class Bdelloida. A hypothesis of these experiments was that the presence/absence of a lorica would affect the sensitivity of the organism relative to UV irradiation and chemical treatments. *Brachionus calyciflorus* are commonly used as a test specimen in toxicological studies and has been cited in many studies.

Rotifer cultures were maintained in 2.0 L glass- flasks containing Lake Superior water that had been passed through a 20 µm nylon mesh screen and allowed to rest for one week prior to use in the rotifer cultures. Approximately 3.0 mL of *Selenastrum capricornutum* algae (10^8 cells/mL) was added three times per week along with 0.5 mL of Roti-rich©, a yeast based food. Densities were checked weekly and maintained at approximately 90-100 rotifers per mL of water. Gentle aeration (1-3 bubbles/sec) was used to facilitate gas exchange and maintain adequate dissolved oxygen concentration.

Test organisms were subjected to UV irradiation in aqueous solutions containing H_2O_2 and MgO at concentrations of 20 and 10 mg/L respectively. UV irradiation was accomplished using a large-diameter collimated-beam. The source of radiation is two low-pressure, high-output mercury amalgam lamps, which provide essentially monochromatic output at a characteristic wavelength of 254 nm. The device produced a 15.5-cm diameter beam of radiation at an incident intensity of approximately 1.0 mW/cm^2. The beam produced by this device was collimated and spatially uniform.

The background matrix for all rotifer exposures was a laboratory water supply taken from the municipal drinking water supply for the city of Superior, WI. The municipal drinking water supply in Superior, WI is chlorinated prior to distribution. The water used in these experiments was further treated prior to use. First, the water was passed through an activated carbon column to remove residual chlorine and some residual organics. This was followed by passage though a weak acid cation exchange column (Amberlite® DP-1) for removal of iron and other soluble metals. In-house treatment concluded with the addition of sodium sulfite to ensure complete removal of residual chlorine.

Stock solutions H_2O_2 and MgO were prepared at concentrations of 20 mg/L and 10 mg/L respectively. This solution was then transferred to a 15-cm diameter Petri dish for UV exposure under the collimated beam. Approximately 150 rotifers were added per dish. Suspensions were subjected to a UV dose of 200 mJ/cm^2; delivered dose was defined as the product of the depth-averaged radiation intensity and the period of exposure. All exposures were replicated (n=5) to allow statistical evaluation of the resulting data.

Following UV irradiation, test solutions were transferred to an Erlenmeyer flask for incubation. Petri dishes were rinsed several times with appropriate exposed test solutions to promote transfer of rotifers. Flasks were incubated at a 16:8 hour light:dark cycle at a temperature of approximately 23±2°C. During incubation, organisms were fed 250 µL of algae (*Selenastrum*, 10^8 cells/mL) and 250 µL yeast-trout chow-cereal (YTC, total suspended solids = 1720 mg/L). Dissolved oxygen was maintained at near saturation conditions by continuous, gentle bubbling of air into the suspensions.

Subsamples (25 mL) were collected from each flask for microscopic examination of the condition of the rotifers after 24, 96, and 168 hours of incubation. Organisms in each sample were classified as alive or dead based on observed responses of swimming and internal movement of body parts.

Results and discussion

The survival of *Philodina* following UV irradiation in the aqueous mixtures described above is illustrated in Figure 4. The number of live organisms may have been slightly underestimated at time 24 and 96 hours due to the tendency of *Philodinia sp.* to adhere to the sides of the culture flask. At the end of the recovery period (168 hours), the flask was rinsed to ensure removal of all organisms.

During the period of incubation, the control (unexposed) rotifers reproduced, causing an increase in the population size. In contrast, the treated samples showed a continuous decline in live numbers over the period of incubation. While it is possible that reproduction could have taken place, any reproductive activity in the treated samples was substantially suppressed relative to the controls. Live numbers of *Philodina* decreased by more than one order of magnitude over the period of incubation, as compared with initial numbers. When compared with the number of live organisms in the control, treatment accomplished roughly 2 $\log_{10}$ units decrease in the concentration of live *Philodina* from roughly 10/mL to 0.1/mL.

The survival of *Brachionus calyciflorus* following UV irradiation in the aqueous mixtures described above is illustrated in Figure 5. As a loricate rotifer, it was anticipated that *Brachionus* would be somewhat more resistant to UV irradiation and the mixed oxidants provided by hydrogen peroxide and magnesium oxide than the illoricate rotifer *Philodinia*. The data presented in Figure 5 do not support this hypothesis. In particular, these data indicate roughly 2 $\log_{10}$ units of inactivation among the *Brachionus* in samples that had incubated for 24 hours. Continued incubation of the control revealed evidence of *Brachionus* reproduction.

At 96 hours, the average density in the controls peaked at roughly 20 rotifers/mL. Due to overcrowding, the population then declined to roughly 0.3 rotifers/mL at 68 hours. In the treated samples, rotifer density remained low through out the recovery period, averaging less than 0.1 rotifers/mL.

BWT Model II prototype device integrating the ternary effect

The three components (filtration, irradiation and catalysis) were incorporated into an integrated Model II continuous pipe-reactor pilot unit ($10m^3$/hr., Figure 6). The unit was erected on a dock at Hadera port on the Mediterranean Eastern coast (May 2003 to date).

Sea water is pumped, at a programmed rate, into a first stage reactor into which a measured amount of hydrogen peroxide and slurry of magnesium oxide (both at a rate resulting in final concentration of 5-30 ppm) are continuously injected. Air is pumped into the system via an injector at a predetermined rate to keep the sea water at saturation with oxygen. The mixture is then transferred into a battery of disc filters followed by a photoreactor (with optional additional injectors of HP at this stage). The treated water is discharged into the sea. The system is equipped with controllers and monitors of flow rate for the sea water feed, the hydrogen peroxide concentrated solution (30%), the MgO slurry in water (30-40%) and air. The system also continuously monitors and records the inlet and outlet pH, oxygen concentration, redox potential, water turbidity, temperature and irradiation intensity. There is also a continuous monitoring of the filtration unit delta pressure and backflush regime. Samples of intake and outflow are withdrawn at regular intervals and analyzed for hydrogen peroxide concentration and the quality of water (total suspended solids, volatile suspended solids, particle size distribution and total organic carbon) the material accumulating at the filter is also sampled and scrutinized chemically and biologically at given intervals.

The diversity of the taxa will also be closely examined.

The issue of corrosion will be closely followed in cooperation with a classification company at different retention times from hours to several months.

While this manuscript was being written (June 2003) the depicted pilot plant unit was in operation.

References

Anil, A.C., Venkat, K., Sawant, S.S., Dileepkumar, M., Dhargalkar, V.K., Ramaiah, N., Harkantra, S.N. & Ansari, Z.A., 2002. Marine bioinvasion: Concern for ecology and shipping. *Current Science*, 83, pp. 214-218.

Champ, M.A. 2002. Marine testing board for certification of ballast water treating technologies. *Marine Poll. Bull.* 44, pp. 1327-1335.

Eliot, M. 2003. Biological pollutants and biological pollution - an increasing cause for concern. *Marine Poll. Bull.* 46, pp. 275-280.

Giamello, E., Calosso, l., Fubini, B. & Geobaldo,F. 1993. Evidence for stable hydroxyl radicals and other oxygen radical species generated by interaction of hydrogen peroxide and magnesium oxide. *J. Phys. Chem. 97*, pp. 5735-5740.

Heitz, J.R. & Downum, K.R. (Eds.) 1995. *Light activated pest control* ACS Symposium Series 616. American Chemical Society, Washington DC.

Higuchi, K., Onaka, N. & Izumi, Y. 1993. Solid acid and base catalyzed cyanosilylation of carbonyl compounds with cyanotrimethylsilane. *Bull. Chem. Soc. Jpn*., 66, pp. 2016-2032.

Hughes, K. 2002. *Composition of insoluble magnesium containing minerals for use in fluid filtration*. WO 02/076577.

Lane, N. 2003. New light on medicine, *Scientific American*, January 26-33.

Legrini, O., Oliveros, E. & Braun, A.M. 1993. Photochemical processes for water treatment. *Chem. Rev.*,*93*, pp. 671-698.

Neyens, E. & Baeyens, J. 2003. A review of Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater.*, 98, pp. 33-50.

Parker, S. 1996. Is there an SRB in your tank? *Motor Ship*, March, 75, 57.

Parsons, M.G. & Harkins R.W. 2002. Full scale particle removal performance of three types of mechanical separation devices for the primary treatment of ballast water. *Marine Technology*, 39, pp. 211-222.

Ruiz G.M., Rawlings T.K., Dobbs F.C., Drake L.A., Mullady T., Huq A. & Colwell R.R. 2000. Global spread of microorganisms by ships - Ballast water discharged from vessels harbours a cocktail of potential pathogens. *Nature* 408, pp. 49-50.

Sawai, J., Kawada, E., Kanou, F., Igarashi, H., Hashimoto, A., Kokugan, T. & Shimizu, M. 1996. Detection of active oxygen generated from ceramic powders having antibacterial activity. *J. Chem. Eng. Jpn.* 29, pp. 627-633.

Sawai, J., Kojima, H., Igarashi, H., Hashimoto, A., Shoji, S., Sawaki, T., Hakoda, A., Kawada, E., Kokugan, T. & Shimizu, M. 2000. Antibacterial characteristics of magnesium oxide powder, *World J. Microbiol. & Biotech.* 16, pp. 187-194.

Semerjian, L. & Ayoub, G.M. 2003. High pH coagulation-flocculation in wastewater treatment. *Adv. Environ. Res.*, 7, 389-403.

Stoimenov, P.K., Klinger, R.L., Marchin, G.L. & Klabunde, K.J. 2002. Metal oxide nanoparticles as bactericidal agents. *Langmuir*, 18, pp. 6679-6686.

Topfer, K. UNEP, *Globallast* 8, p.2.

Waites, W.M. Harding, S.E., Fowler, D.R., Jones, S.H., Shaw, D. & Martin, M. 1988. The destruction of spores of Bacillus subtilis by the combined effects of hydrogen peroxide and ultraviolet light. *Lett. Appl. Microbiol.* 7, pp. 139-140.

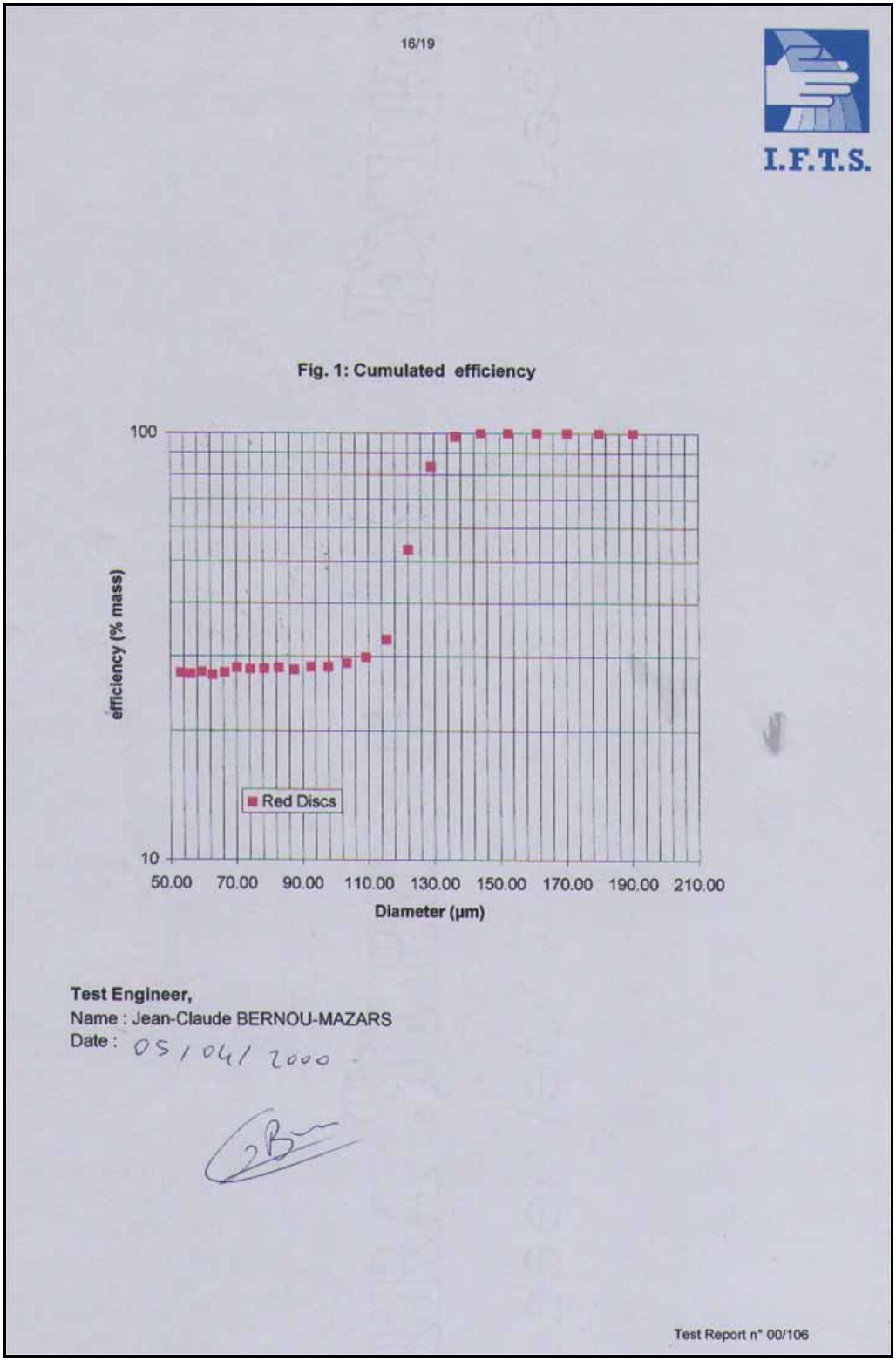


Figure 1. *Performance of Arkal Spin-Klin® 130µm Disc Filter.*

Figure 2. *Model I BWT Pilot Unit-General view.*

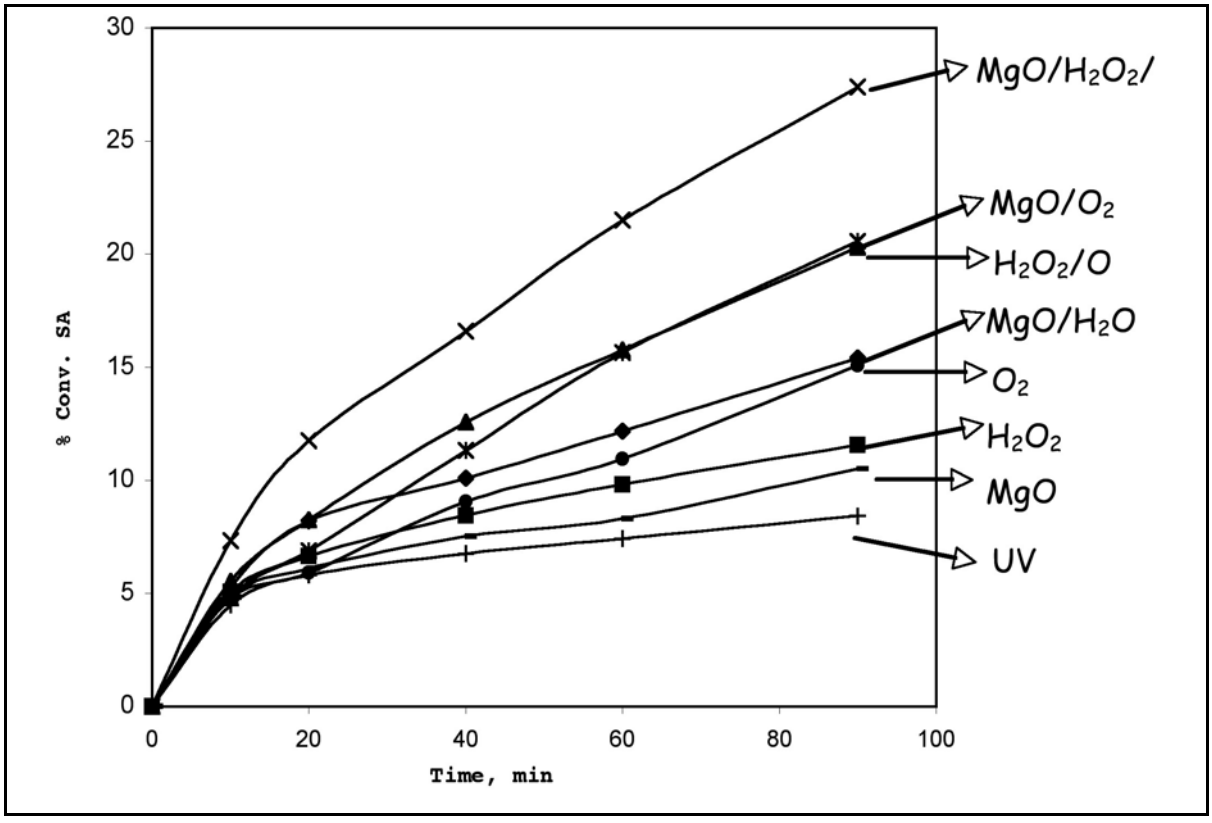


Figure 3. *Synergistic Effect of $MgO/H_2O_2/O_2$ System in Sea Water- Conversion of salicylic acid as function of time. Reaction Conditions: salicylic acid 250 ppm, H_2O_2 10 ppm, MgO 20 ppm, O_2 50 cm^3/min, UV medium pressure, quartz sleeve, Volume = 800 ml, irradiation intensity = 180 mW/cm^2.*

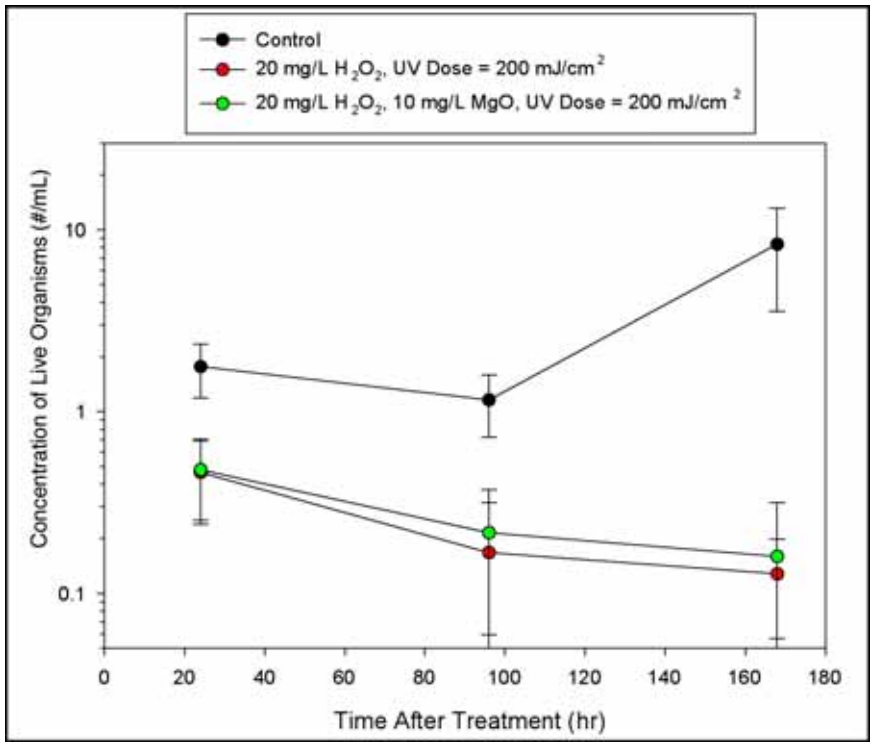


Figure 4. *Measured responses of* Philodina *to UV irradiation (dose = 200 mJ/cm^2), hydrogen peroxide (20 mg/L) and magnesium oxide (10 mg/L). Error bars represent the standard deviation among 5 replicate measurements.*

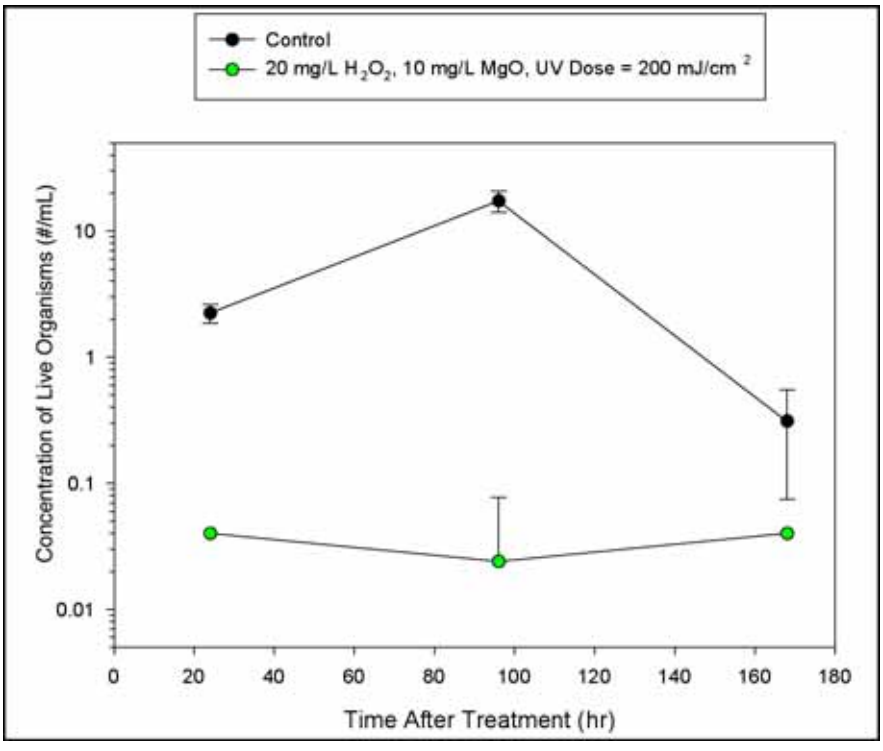


Figure 5. *Measured responses of* Brachionus calyciflorus *to UV irradiation (dose = 200 mJ/cm^2), hydrogen peroxide (20 mg/L) and magnesium oxide (10 mg/L). Error bars represent the standard deviation among 5 replicate measurements. Note that at t=24 and 168 hours no error bars are indicated for the treatment because no live organisms were found in any of the samples; the values indicated on the graph for these conditions represent the limit of detection for this method (< 1 organism per 25 mL).*

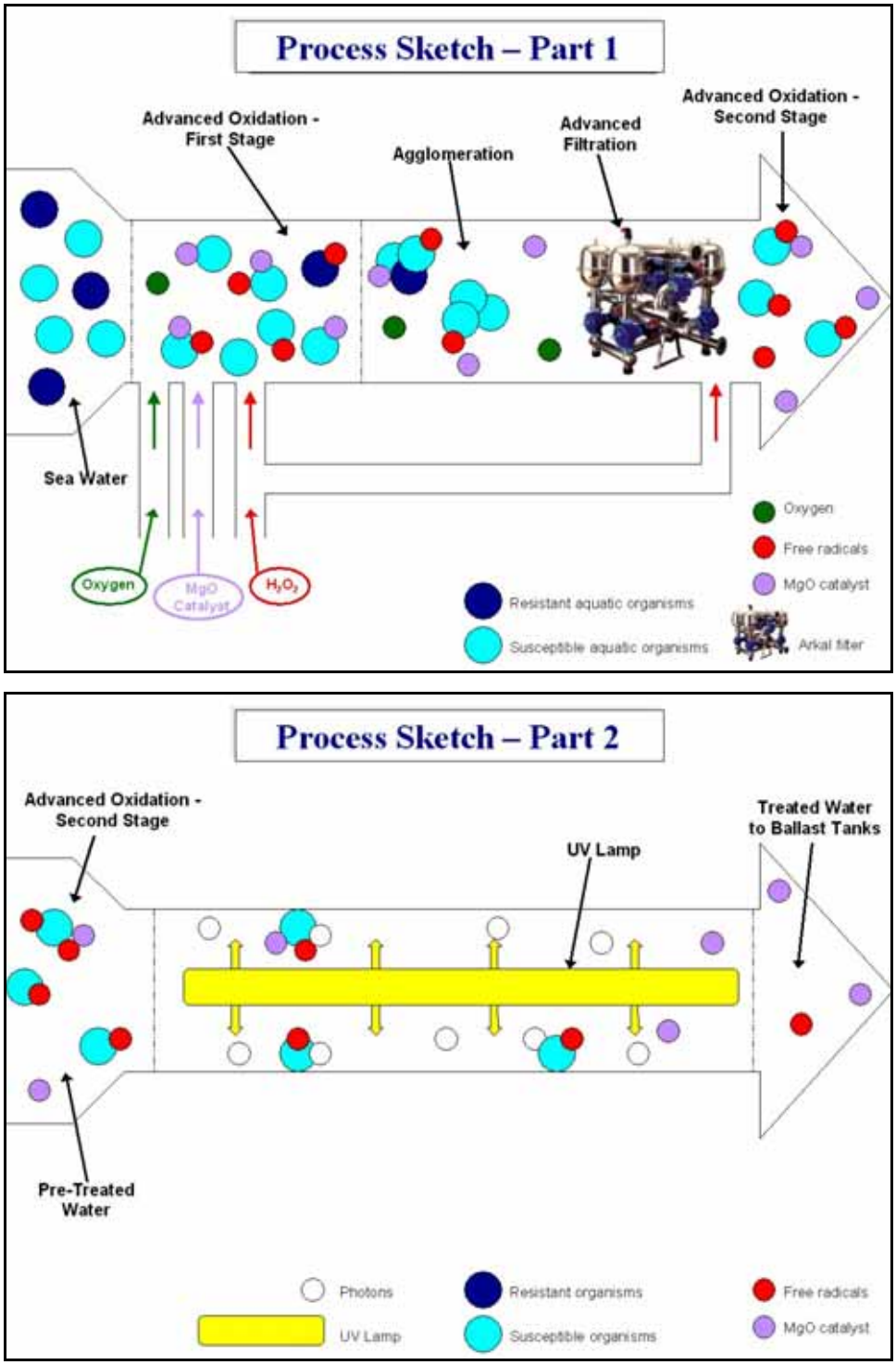


Figure 6. *Layout of Model II BWT Pilot Plant prototype-general sketch.*

Progress report on the 'Special Pipe System' as a potential mechanical treatment for ballast water

T. Kikuchi[1], K. Yoshida[1], S. Kino[1] & Y. Fukuyo[2]

[1]*The Japan Association of Marine Safety,*
kikuti@oak.ocn.ne.jp, yoshida@lasc.co.jp,
mti@felco.ne.jp

[2]*Asian Natural Environmental Science Center,*
University of Tokyo
ufukuyo@mail.ecc.u-tokyo.ac.jp

Name of project

The project "Research and Development of the Special Pipe System for Ballast Water Treatment" conducted by the Japan Association of Marine Safety under the sponsorship by the Nippon Foundation has two components: 1) improvement of the special pipe system to achieve better effectiveness in the termination of zooplankton and phytoplankton, and 2) development of the procedure and standard for evaluation of the effectiveness. This paper describes the first component, and the second one is also explained in another article recorded in the same proceedings.

Treatment options being researched

The instrument designed in the special pipe system uses the options that can be categorized in a mechanical treatment, because it applies shear stress and cavitations generated in the instrument for termination of organisms in ballast water. During the development stage of the prototype pipe system, which was reported verbally at the 1st GloBallast Symposium held more than two years before, injection of ozone into ballast water before a passage of the pipe was tried to increase termination efficacy. But mixture of such chemicals has not been applied to the new system, mostly because of the difficulty in the installation of an instrument for provision of chemicals to the system.

Timeframe of the project

The project has three phases, commencing from April 1999.

Phase 1: 1999-2000
Basic research of the special pipe system with and without addition of ozone to the system

Phase 2: 2001-2002
On harbor testing of the improved special pipe systems

Phase 3: 2003 (in planning and to be carried out before March, 2004)
On board testing of the improved special pipe systems

Aims and objectives of the project

The objective of this study is to develop a ballast water treatment system to terminate and eliminate harmful aquatic organisms contaminated in ballast water with special attention to criteria related to safety of ship and crew, practicability in terms of operational complexity and installation on board ships, cost effectiveness, and consequential environment impacts in addition to the effectiveness of treatment.

Research methods test protocols and experimental design

The prototype special pipe system was designed to use shear stress to terminate planktonic organisms. The potential was high, as reported at MEPC 44 in 2000, and verbally at the 1st International Ballast Water Treatment Symposium (2001, London) and at the First International Conference on Ballast Water Management (2001, Singapore). This structure was, however, not suitable for practical use, because its pressure loss in passing water was high and needed higher pressure in a pipe with a larger diameter. The higher pressure could not cause higher damage to organisms in the pipe.

Then the special pipe was re-designed with a unit generating shear stress and cavitations. Comparison of effectiveness between the former and the developed special pipe systems was made to ascertain the higher level of effect on marine organisms and the smaller pressure loss in the case of developed one.

Evaluation of effectiveness of the prototype special pipe

The analysis of the effectiveness of the prototype special pipe system was conducted in laboratory with and without adding ozone produced by an ozonizer using natural seawater collected in a harbor area at Imari Bay in Kyushu Island, western Japan.

The inner diameter of the special pipe used for the experiments was 40 mm. The seawater flow rate was 20 m^3/hr. The concentration of ozone as oxidant in sea water was 1mg/L, when injected.

Evaluation of effectiveness of the improved special pipe

Termination efficacy of the improved special pipe system was analyzed by using the system installed in the harbor with natural seawater taken in at the harbor area at Imari Bay in Kyushu Island, western Japan. The experiment flow is shown in the figure 1. Figure 2 shows the appearance of the main part of the improved special pipe. The inner diameter of the pipe used for the experiments is 100 mm. Two different flow rates of seawater, 115 m^3/hr and 150 m^3/hr were applied at the experiments.

In case of 115 m^3/hr flow rate, the quantification of live phytoplankton and zooplankton was carried out 5 times using method described below, and an average individual number of live organisms was calculated by subdividing all organisms into 4 different size range groups; smaller than 20 um, between 20 and 50 um, between 50 and 100 um, and larger than 100 um. Total individual number of phytoplankton and zooplankton was also calculated from the data of these four subgroups.

In case of 150 m^3/hr flow rate, only one data set has been available for the moment, as more experiments are now in planning. Numbers of live organisms were counted separately for those smaller and larger than 20 um by the method described below.

Measurement of the termination rate by quantification of live organisms

The effectiveness of the special pipes was measured by the termination rate of phytoplankton and zooplankton, comparing the number of live organisms in initial seawater and treated seawater after passage of the pipes. Dead or live of the organisms in the water samples was judged based on the change of appearance, i.e. shape and color, of individual phytoplankton and zooplankton. Examples of the normal and terminated phytoplankton and zooplankton are shown in Figure 3. Quantification was made by counting live organisms in one ml portion of water samples taken onto a Sedgewick-Rafter chamber under a regular compound microscope.

Preparation of seawaters samples for microscopic observation was different between organisms larger than 20 um and the rest (smaller than that). The former was observed after concentrating the seawater samples 1,000 times using 20 um plankton net cloth, because individual number larger than 20 um was not high. On the other hand, the latter was observed without concentration.

Relationship between flow rate and termination rate of zooplankton

Termination efficacy of the improved special pipe system in relation to flow rate was analyzed by using the system installed at Imari Bay in Kyushu Island, western Japan. The inner diameter of the pipe used for the experiments is 50 mm. Termination rate was calculated using zooplankton larger than 20 um as test organisms, and quantification of individual zooplankton was made three times at three flow rate, 10.5, 16 and 21 m^3/hr.

Results

Effectiveness of the prototype special pipe

Termination rates of phytoplankton and zooplankton with and without injection of ozone are shown in Table 1. One-passage treatment gave an effectiveness of about 55% of phytoplankton and about 65% of zooplankton and they increased to about 99 and 89%, respectively, by injecting ozone.

Effectiveness of the improved special pipe

The improved special pipe system can terminate about 70 and 95% of all phytoplankton and zooplankton, respectively, in natural seawater in the case of one-passage treatment at the seawater flow rates 115 m^3/hr (Table 1). This effectiveness was obtained using 60% of the energy of the prototype pipe. This effectiveness increased about 80 and 100%, respectively, by two-times passage treatment, and furthermore, they reached 85 and 100%, respectively, at flow rates 150 m^3/hr. (Table 1).

Table 1. *Termination rate by the prototype and improved special pipe systems*

	The prototype special pipe system		**The improved special pipe system**		
	Flow rate: 20m^3/hr	Flow rate: 20m^3/hr Oxidant concentration: 1mg/L	Flow rate: 115m^3/hr One-passage treatment	Flow rate: 115m^3/hr Two-passage treatment	Flow rate: 150m^3/hr One-passage treatment
Termination rate (%) of all phytoplankton	54.8	99.3	69.6	81.1	84.1
Termination rate (%) of all zooplankton	65.1	88.9	94.3	99.3	99.9

Table 2 and 3 show the details of the result with size fractions obtained at 115 and 150 m^3/hr, respectively. These results indicates that larger phytoplankton and smaller zooplankton are more effectively terminated than the others.

Table 2. *Termination rate by one and two-times passage treatments using the improved special pipe at flow rate 115 m^3/hr*

Phytoplankton

Size range	Cells number/ml			Termination rate (%)	
	Initial	After one-passage	After two-passage	One-passage	Two-passage
100μm≤	0.6	0.1	0.0	87.4	95.1
<100μm~≥50μm	14.5	1.3	0.2	91.1	98.6
<50μm~≥20μm	965.9	387.4	206.6	59.9	78.6
<20μm	1781.2	450.0	315.6	74.7	82.3
Total	2762.2	838.8	522.5	69.6	81.1

Note: The values in the table are the average of 5 times of experiments

Table 2 cont. *Termination rate by one and two-times passage treatments using the improved special pipe at flow rate 115 m^3/hr*

Zooplankton

Size range	Individuals number/L			Termination rate (%)	
	Initial	After one-passage	After two-passage	One-passage	Two-passage
100μm≤	24.2	5.6	2.2	76.7	90.7
<100μm~≥50μm	45.7	10.2	3.2	77.8	93.1
<50μm~≥20μm	210.0	19.0	3.2	90.9	98.5
<20μm	954.8	35.0	0.0	96.3	100.00
Total	1234.7	69.8	8.6	94.3	99.3

Note: The values in the table are the average of 5 times of experiments

Table 3. *Termination rate by one time passage treatments using the improved special pipe at flow rate 150 m^3/hr*

Phytoplankton

Size range	Cells number/ml		Termination rate (%)
	Initial	After one-passage	One-passage
≥20μm	3.2	0.3	91.3
<20μm	688.9	110.0	84.0
Total	692.1	110.3	84.1

Note: The values in the table are the data of one time experiment

Zooplankton

Size range	Individuals number/L		Termination rate (%)
	Initial	After one-passage	One-passage
≥20μm	351.6	4.8	98.6
<20μm	4312.0	0.0	100.0
Total	4663.6	4.8	99.9

Note: The values in the table are the data of one time experiment

Relationship between flow rate and termination rate of zooplankton

Figure 4 shows the termination rate of zooplankton in response to flow rates in the pipe. It is obvious that the higher flow rate produced higher treatment effectiveness.

Size of system and installation cost

The main part of the system can be installed as a part of ballast water intake line or discharge line. The size is 1m long and 0.5m height in case of pipe having the inner diameter 100 mm. Figure 5 shows the model prepared for on board ship test which will be practiced in the latter half of this year 2003. The installation cost of the system could be estimated as 100,000 US$ per a unit, and the running cost could be 0.01 US$/ton.

Conclusion

Termination efficacy of the improved special pipe system is very high. Only one time passage through the pipe kills more than 84% of phytoplankton and almost 100% of zooplankton (Table 1 and 3). As expected from the data using a pipe of inner diameter 50 mm shown in the Figure 4, it is not difficult to have higher termination rate in the pipe of 100 mm inner diameter, if faster flow speed can be applied. Multiple passage through the pipe, or application of the pipe system for both intake and discharging waters can produce higher termination rate.

The mechanical treatment by using the improved special pipe system may be one of the treatment options by its practicability in terms of easiness in installation on board a ship, safe in operation and maintenance and cost performance, in addition to effectiveness in termination of organisms

contaminated in ballast water. The authors have a plan of on board test in this year, and expect that the system become available and practical in quite near future.

References

Japan (1999): Mixer pipe method as an alternative ballast water management technique, MEPC 44/INF.9, 7pp.

Japan (2002): Outcome of a study on Mechanical Treatment System, MEPC 47/INF.18, 2pp.

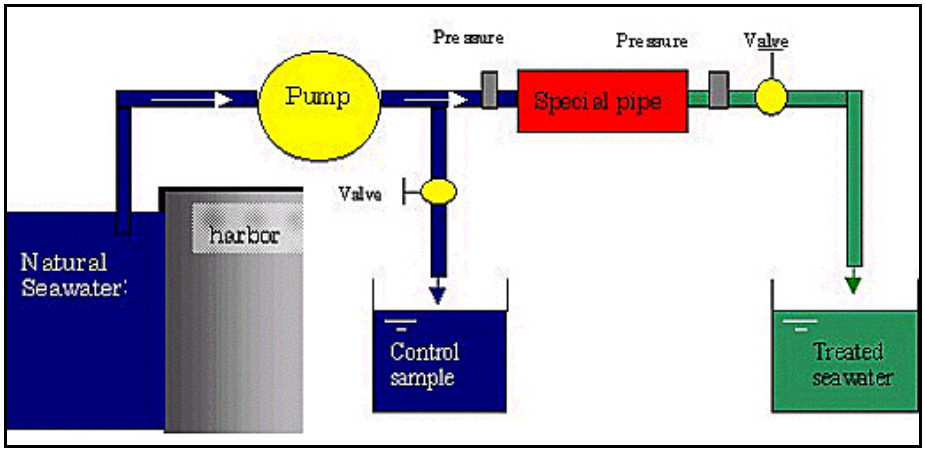


Figure 1. *The experiment flow.*

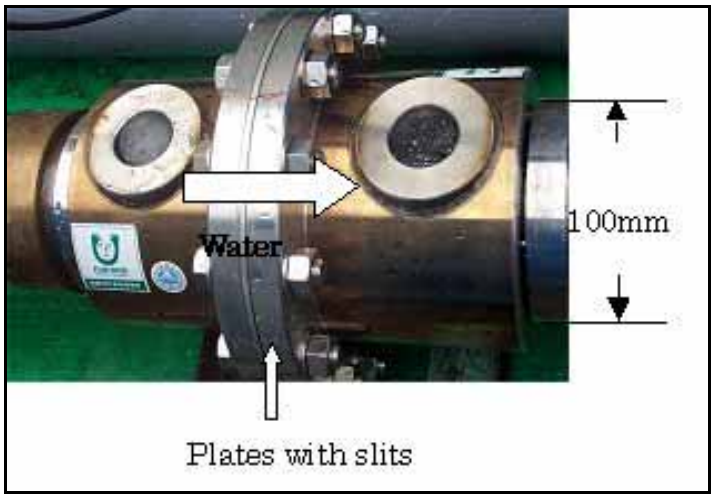


Figure 2. *The improved special pipe.*

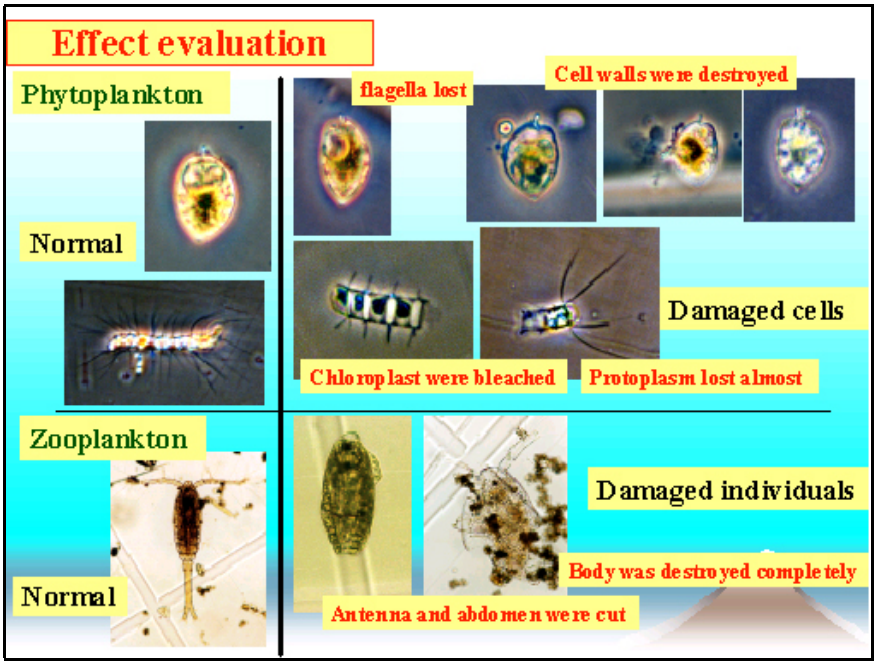


Figure 3. *Examples of the normal and terminated phytoplankton and zooplankton.*

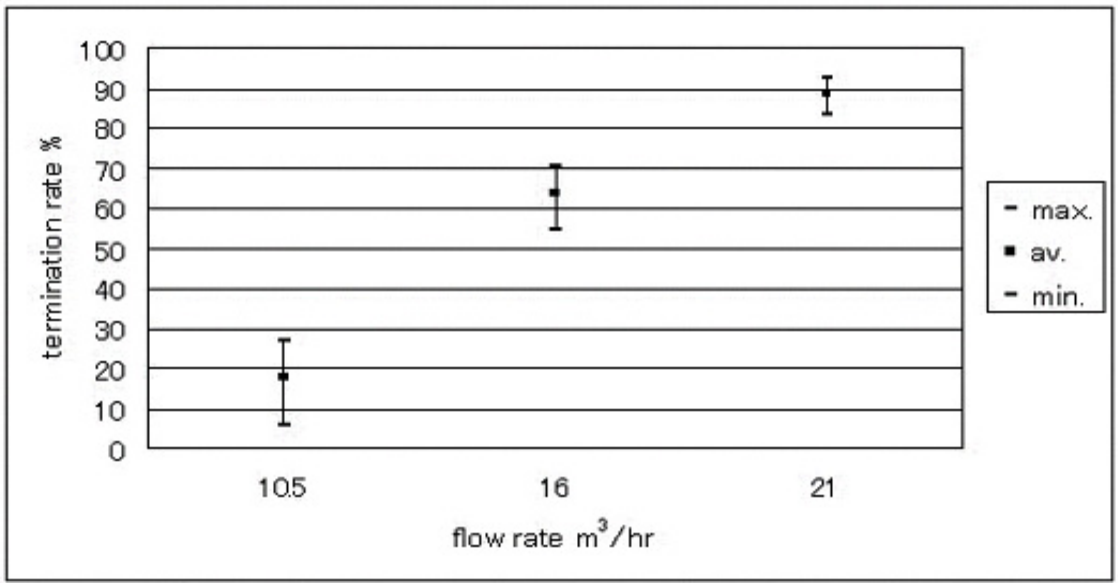


Figure 4. *The termination rate of zooplankton in response to flow rates in the pipe.*

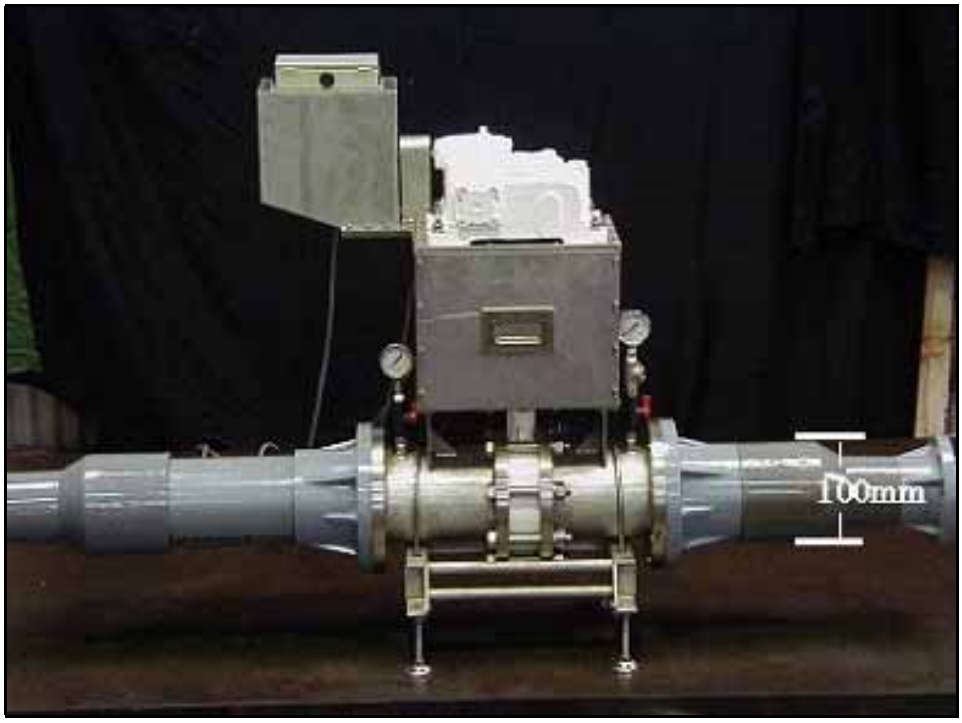


Figure 5. *The special pipe system prepared for onboard ship.*

Progress report on the AquaHabiStat deoxygenation system

W. J. Browning Jr., J. P. Davis & W. J. Browning III

AquaHabiStat
USA
Email@aquahabistat.com

Treatment options being researched

Current

The AquaHabiStat, or AHS, system is a patented purely mechanical ballast water treatment system and removes dissolved oxygen (DO) from the ballast water as it is taken on board. The system utilizes inbound ballast pumps to transfer water into a specially-constructed steel tank. In the tank, a vacuum is drawn on the water by a vacuum pump. A centrifugal pump then removes the water from the tank and moves it to the ships ballast hold. The marine life in the water suffocates in the ballast hold during the voyage. After two to three days, the marine life is eradicated and the vessel may discharge the water, which regains the oxygen on discharge and therefore leaves no ancillary environmental side effects. The entire system of the pumps and tank connects with a controller unit that the operator may run with a laptop PC. From the computer, the operator can turn the unit on and adjust the rate of flow, the water level inside the tank and the vacuum force. A shipboard model may also have the capabilities of satellite monitoring by compliance organizations who would have the ability to remotely query the system and monitor the vacuum levels, flow rates and the time the system has run.

Future

AHS is investigating the benefits of an additional mechanical hyper-pressurization zone prior to the above mentioned vacuum process and/or the addition of combustion inert gasses to further lower the oxygen content and/or to lower the pH of the ballast water being treated. AHS further wishes to expand the number of samples subjected to phytoplankton and biomass testing, given the encouraging results from limited ATP testing.

Time frame of the project

The full-scale prototype research in a dockside setting was completed in three 10-day time series tests in May and June of 2000 and two 10-day time series tests in December of 2000. The results of these tests were presented at the first IMO GloBallast conference in 2001. The prototype was able to show an efficacy of 100% reductions of zooplankton over a two day period at an initial 72 ton per hour flow rate. AHS is in the planning stages of "optimizing" the prototype for full scale onboard testing at higher flow rates in the summer and fall of 2003. Additional testing will likely include the determination of the appropriate mix of certain variables such as cost, biological efficacy, corrosion reduction via deoxygenation and/or pH changes, the introduction of inert gasses into the ballast water treatment process, and the safety issues or other side effects associated with these variables.

Aims and objectives of the project

The main objective of the original testing of AHS and the current plan for testing is to show that the AHS system is both effective at reducing nearly all larval aquatic invaders in the ballast water of ships and capable of doing so at high flow rates. While the AHS prototype has demonstrated functionality suitable for many commercial vessels, it would like to broaden the spectrum of flow rate capabilities

to coordinate with the cargo discharge rates of the normal operational procedures of larger vessels such as tankers.

The tests performed in 2000 demonstrated this effectiveness at a 72 ton per hour flow rate, using water piped from the Chesapeake Bay into the prototype through the system and then immediately into multiple swimming pools, which simulated ballast tanks. Biological testing was performed over a ten day time period, to simulate a typical transatlantic voyage between Europe and the US East Coast.

Current planning and funding is in process to show that the same prototype system will maintain this high reduction rate at an anticipated flow rate of about 300 tons per hour, onboard a vessel or barge. AHS anticipates executing comparison tests that will allow it to gather direct data of the effects of vacuum deoxygenation as compared directly to ballast exchange procedures. Such a direct comparison is necessary due to the fact that the tests performed in 2000 showed that the probable effect of biological oxygen demand rendered the control samples nearly as effective but not as reliable as the deoxygenated "treated" samples at controlling both zooplankton and total biomass. Therefore, it may be assumed that over a 10 day voyage, leaving ballast water alone, to become naturally hypoxic, may be preferable to ballast exchange that actually re-aerates the ballast water.

Research methods, test protocols, experimental designs

Upcoming

Roger Mann, of the Virginia Institute of Marine Science (VIMS), is expected to be the Principle Biological Investigator in our upcoming demonstration event, and his biological test plan will be available in the near future.

Completed experiments

The following is a summary of the research methods under our original testing in 2000 under DRs. Andrew Gordon and Anna Rule. A complete description is in the previous AHS report to IMO in 2001.

Microorganisms including zooplankton (>75 and 80 μm) as well as biomass were monitored in treated and untreated water samples using 18 foot diameter 20,000 liter pools loosely covered with black plastic for better simulation of a dark ballast tank. The water in the pools was monitored for water quality (dissolved oxygen, temperature, salinity, conductivity, and pH). Biological samples were analyzed by two independent laboratories: the Old Dominion University Department of Biological Sciences (ODU) (at 80 μm), and the Hampton Roads Sanitation District (HRSD) (at 75 μm).

Pool sampling

ODU monitored zooplankton populations from the pool ballast tank simulation using standard 80 μm plankton net pulls through the swimming pools. This produced samples within the 10 day time series test that could be compared with prior work done on actual ballast water utilizing similar nets. ATP levels were monitored, in the > 20 μm fraction and >10 μm fraction. Microscopic evaluation conducted at ODU utilized one sample collected at the surface and one sample collected at the bottom for each pool and each day sampled. In addition, a one-liter surface sample was collected from each pool during every sample date and brought back to ODU for ATP extraction and analysis to determine biomass. Samples were provided to the Hampton Roads Sanitation Department (HRSD) for comparative work.

Flow samples were collected for HRSD, which took its samples in 20 liter carboys, all at the time that the treated water was first put into the swimming pools. They collected 40 carboys in total, 20 treated and 20 of control untreated water. They were stored in a dark space in ambient air temperature, and sacrificed 4 per day; 2 treated and 2 of control. Thus no statistical corrections were necessary due to prior sampling.

Microscopic evaluation (ODU)

All microscopic enumeration focused on the largest zooplankton found in each sample. These are termed meso-zooplankton and are generally greater than 200 μm in length. The most abundant zooplankton are the adult stages of cyclopoid, calanoid, and harpactacoid copepods. Equally abundant are the larval or nauplii stages of these copepods. Copepods are categorized and tallied according to these two stages. All other zooplankton identified were placed into the following general categories: Barnacle nauplii, which encompass the early stage of a barnacle, polychaete larvae, ascidian, cladoceras, crab zoea, which encompass the early stages of a crab, shrimp larvae, and unknown.

All "dead" zooplankton were first enumerated. Zooplankton not moving or slightly twitching were considered dead or non-viable. The sample was then preserved with Lugol's iodine and all zooplankton enumerated again. The difference in counts between the initial "dead" counts and the total preserved counts were the numbers of zooplankton alive and moving within the sample. When a sub-sample was used, it was preserved immediately after enumeration of dead zooplankton so that the same water was analyzed.

ATP extraction and analysis (ODU)

Water samples from the surface of each pool were collected in a 1-liter media bottle. The samples were taken to ODU for analysis. Each one-liter sample was divided for filtration purposes and ATP extraction. Extracted ATP was stored in the freezer until the last day of sampling. All samples were then analyzed as a group. Each one-liter surface water sample was divided and 500 ml filtered through a Whatman #1 filter paper, which retained organisms >20 μm.

HRSD used similar manual microscope counts as a counting technique and the results of both labs were similar.

Results

Please note graphs of results following the References section. The AHS system has shown the following:

- The AHS system removed dissolved oxygen (DO) from ballast water to levels below 1 ppm with a vacuum equivalent of negative 14.2 psi
- The AHS system has shown that in limited ATP testing that it eliminates approximately 80% of all biomass above 20 microns less than three days, while certain data points (which are averaged in the attached graph) indicated 100% reduction.
- After three days in the treated water, all larval stages that could become "nuisance species" and other organisms 75 microns and above were eliminated.
- The system can be "ship friendly" with pumps, tanks and control devices of types normally found aboard ships. (It can be designed to fit within existing engine room spaces.)
- The AHS system is automated and is run from a laptop computer, which is applicable to any size of vessel and, for regulatory needs, can be monitored through electronic records that can be read remotely.
- The system is easily adaptable to match any ship size. (The prototype was built as a one tenth scale model of a 130,000 dwt bulk carrier with a 72 ton per hour capacity.)

Conclusions

Based upon our findings to date, this technology shows the potential to be one of the lowest cost and most effective forms of ballast water treatment available within the burgeoning market for such treatment alternatives. Being entirely mechanical, the AHS system is simple in concept and design

and has many benefits to the ship owner. It has been engineered and tested to comply with regulatory standards as drafted. It is comprised of pumps, tanks, piping, valves and instruments that are suitable for installation aboard ship and can be installed in the vessel's normal ballast intake piping system. The system is easy to manage, so that any typical vessel crew can operate the system's controls and the control device can be easily installed into the typical control board of the vessels cargo and ballast plan. The AHS system is effective with one pass of the ballast water on intake through the vacuum tank, therefore eliminating costly and confusing procedures and the need to exchange ballast water at sea. Most importantly, the system has no harsh environmental side effects because it is not adding harmful substances during its process.

The system uses an automatic control unit to keep the vacuum tank from overflowing or running empty. This is run by a simple laptop computer and an off-the-shelf software program that contains a feature of recording periodic readings of all settings to be stored for later access. If various concerned authorities accessed these readings, they might know exactly when and where the vessel took on ballast and to which tank. The readings of any instrumentation could be known at any given time, such as the oxygen meter valve readings to each tank, for example. Thus, remote query may enable appropriate authorities to know the vessel's ballast history long before the vessel reached its port of discharge.

The system is also flexible. It has the potential to be effective in all types of water, regardless of turbidity. Other technologies, such as UV, ozone, or biocides, could be added to the process if desired. Perhaps more important, because it is mechanical, the system can be scaled to broad ballasting flow rate needs. The current AHS prototype has proven to be effective on land at a flow rate of 72 tons per hour. The system can support lower or less demanding flow rates such as those for cruise vessels. AHS is confident in its ability to achieve significantly higher flow rates to meet the needs of larger vessels such as tankers, given the mechanical nature of the system and the theoretical ability to scale the design to a larger size without altering the test results. The tanks of the system can be multiplied to address high flow rates as well.

It is important to note that, under its current configuration, AHS aims to achieve environmental soundness because absolutely nothing is added to the ballast water. AHS only removes most of the oxygen, allows natural respiration to remove the rest, and leaves natural suffocation as the actual control method. Any negative effects of the hypoxic ballast water on discharge areas can be corrected either by utilizing a simple compressor to re-aerate the ballast water or pumping the ballast out above the waterline so that it may re-aerate in the open air.

The system is of low cost up front and over the life cycle, with no expensive or hazardous chemical agents to buy and manage. Relative to the operational cost of the ballast exchange procedure in particular, the cost of the AHS system reduces overall ballast costs for the ship owner by cutting total time spent ballasting in half, reducing fuel expenses, and extending the life of the ballast pumps and the vessel itself. The broader deoxygenation process has demonstrated a reduction in the corrosion of the ballast tanks and therefore a strong probability of a reduction of inner tank coating costs (Tamburri, 2001).

Investigators

Wilson J. Browning, Jr.
Inventor, Coordinating Investigator

Dr. Robert Ash
Eminent Scholar and Professor of Engineering, ODU: Consultant to AHS

Captain Claude Thompson
US Coast Guard (Ret.), Former Chief of the Engineering Faculty of the USCG Academy: Consultant to AHS, Expected Principle Engineering Investigator for planned AHS experiment

Dr. Andrew Gordon
Professor and Former Chairman of the Department of Biology, ODU: Principle Biological Investigator of the 2000 testing procedures

Dr. Anna Rule
Chief of Laboratories, HRSD: Principle Biological Investigator of the 2000 testing procedures

Dr. Roger Mann
Professor of Marine Biology and Deputy Director of the Virginia Institute of Marine Science: Expected Principle Biological Investigator for planned AHS Experiment

References

Gordon, Andrew, Old Dominion University and Rule, Anna, Hampton Roads Sanitation District (HRSD): *Biological Evaluation of the AquaHabiStat (AHS) System for Treatment of Ballast Water*, September 2000.

Gordon, Andrew, Old Dominion University: *AHS Supplemental Report*, January 16, 2001.

Tamburri, et al: *Ballast Water Deoxygenation Can Prevent Aquatic Introductions While Reducing Ship Corrosion*, Elsevier Science Ltd, 2001.

Clesceri, et al. (eds): *Standard Methods for the Examination of Water and Wastewater.* 17th edn. pp. 10-40 - 10-42. APHA-AWWA-WPCF 1989.

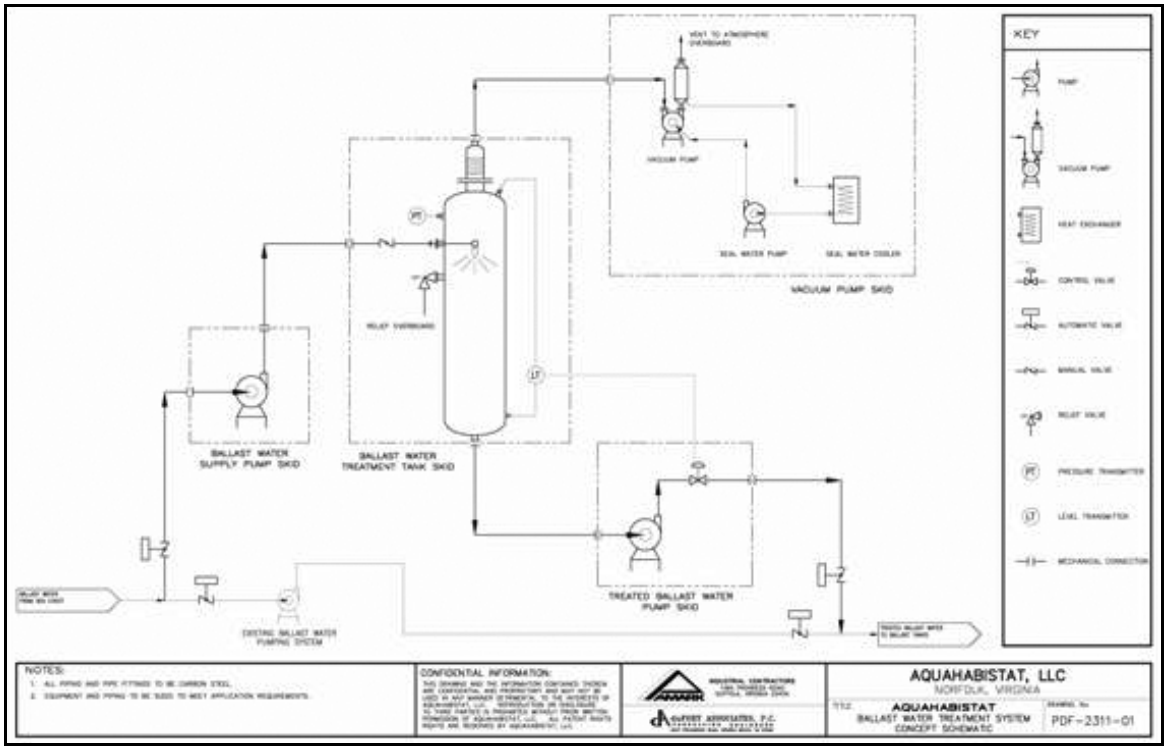


Figure 1. *AHS System Design.*

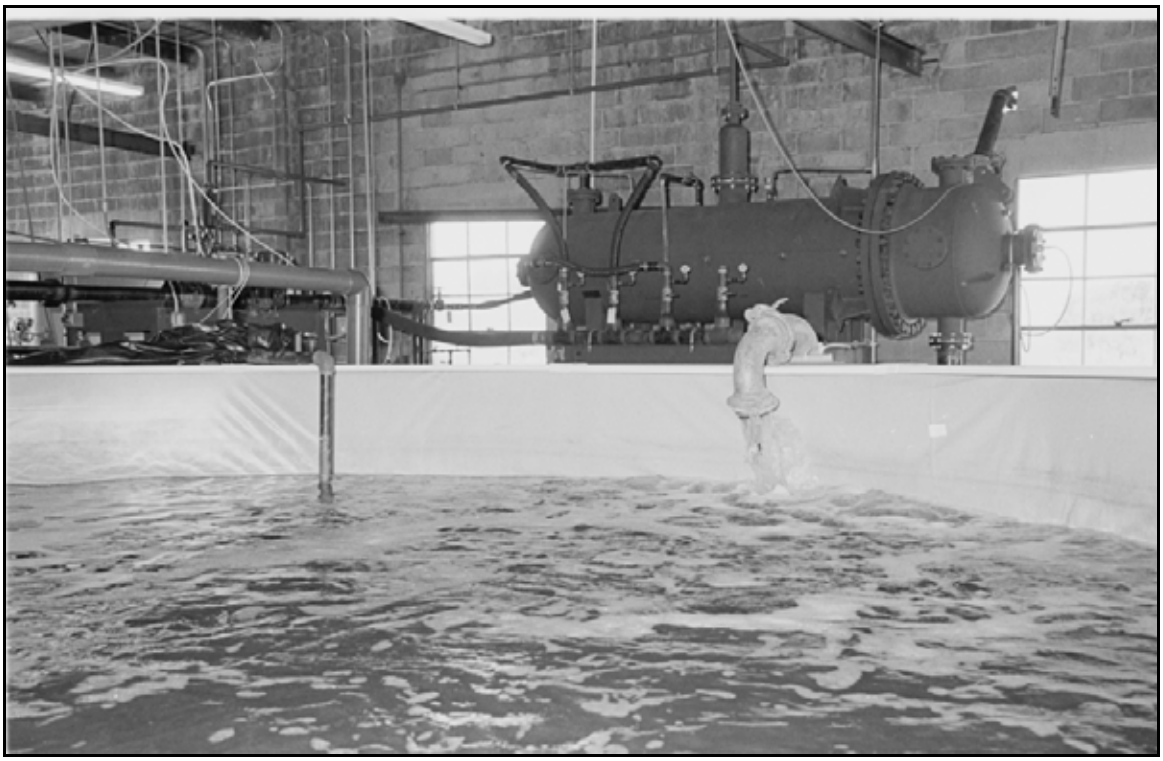


Figure 2. *AHS Prototype.*

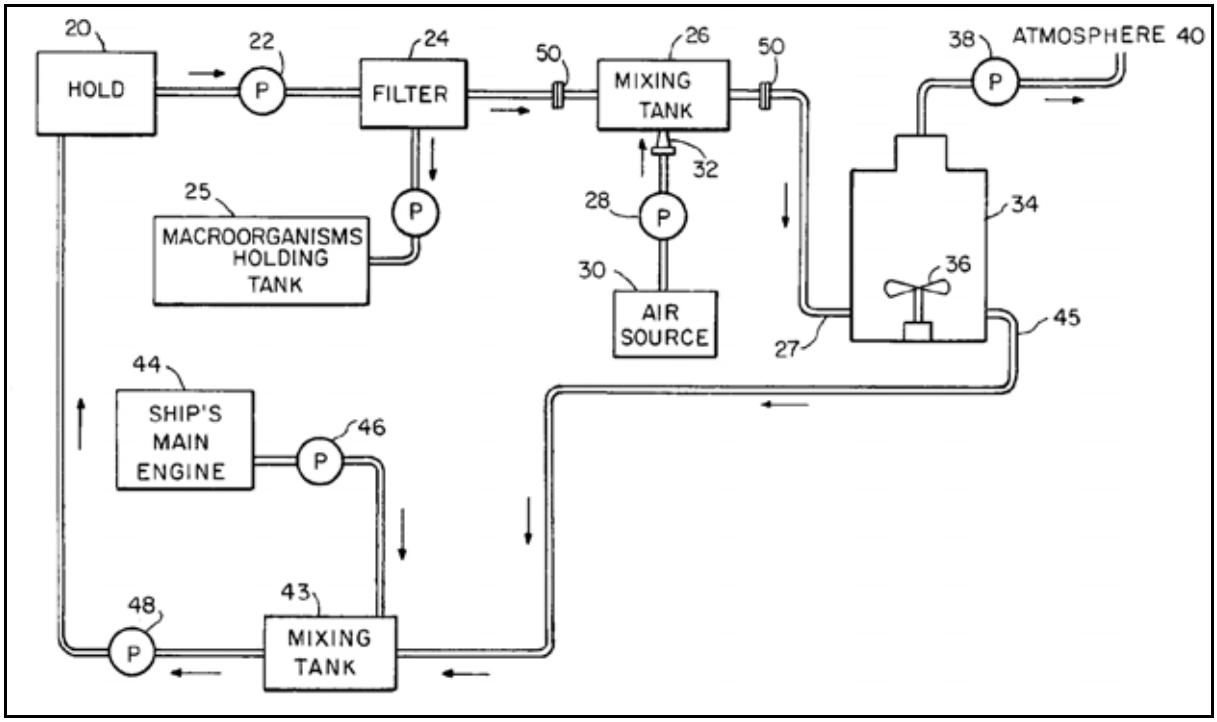


Figure 3. *AHS System Process Diagram.*

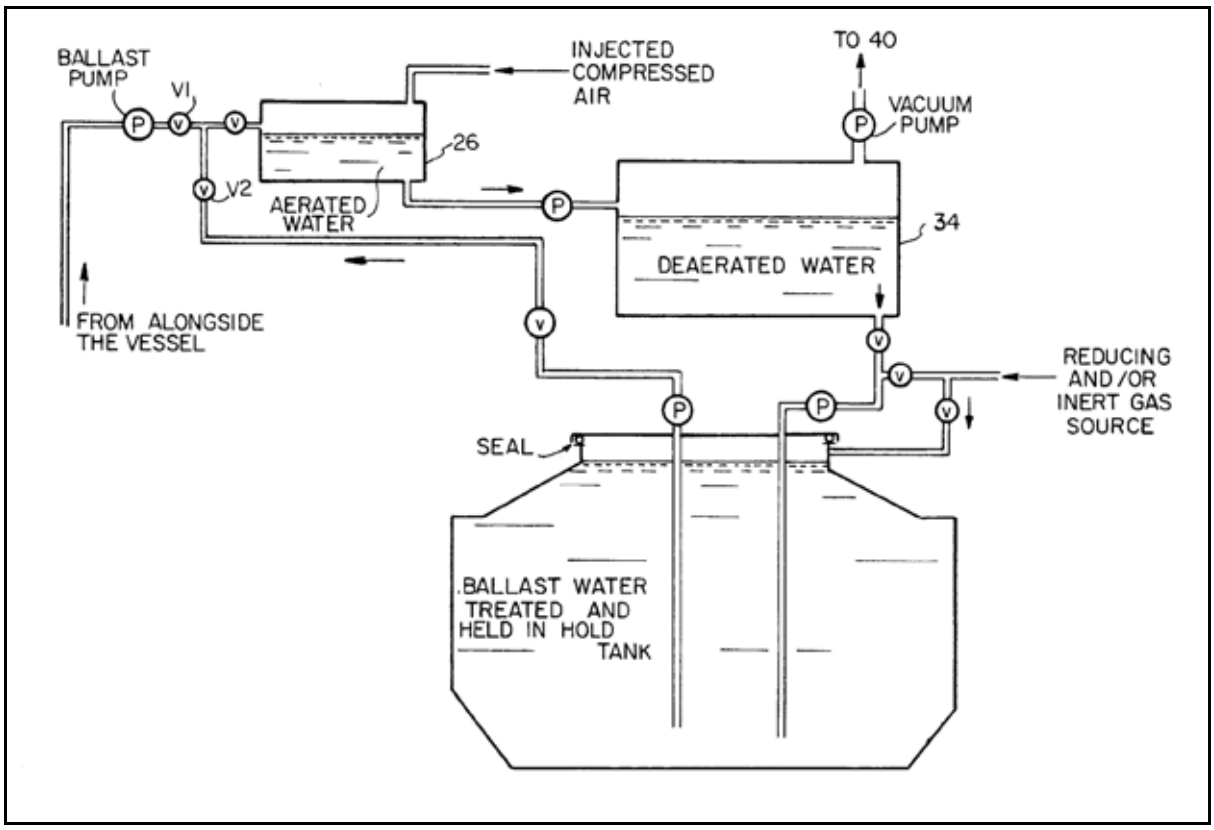


Figure 4. *AHS Vessel Configuration.*

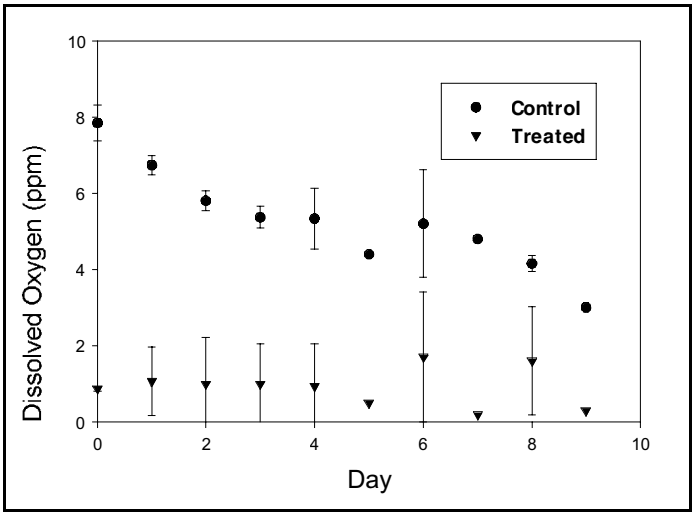


Figure 5. *Dissolved oxygen levels in treated and untreated water.*

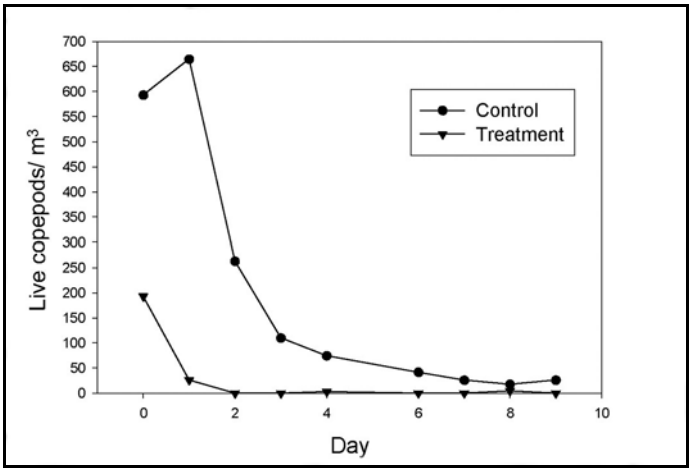


Figure 6. *Test Results, Copepods.*

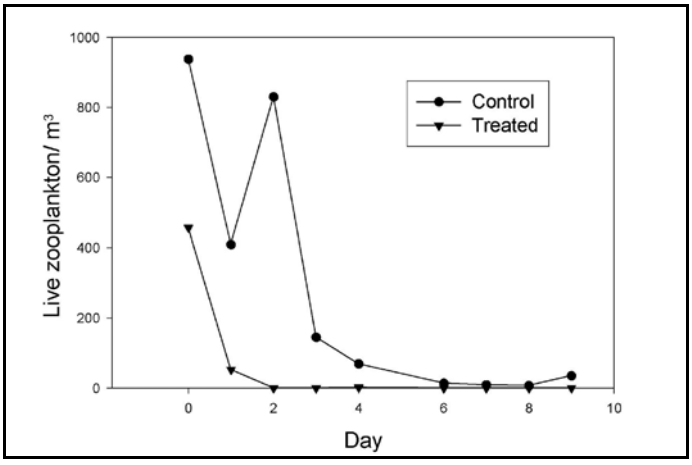


Figure 7. *Test Results, Zooplankton.*

Evaluations of Venturi Oxygen Stripping™ as a ballast water treatment to prevent aquatic invasions and ship corrosion

M. N. Tamburri, B. J. Little, G. M. Ruiz, J. S. Lee, & P. D. McNulty

Chesapeake Biological Laboratory
University of Maryland Center for Environmental Science
USA
tamburri@cbl.umces.edu

Treatment option

Gas-Based Deoxygenation

Time frame of current project

January 1, 2003 through June 30, 2004

Aims and objectives of project

Statement of Problem

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

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

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

Corrosion of ballast tanks from exposure to seawater is typically destructive and costly for individual vessels and the shipping industry as a whole. Currently painting and sacrificial anodes are used almost exclusively as the means to prevent ballast tank corrosion, but they are expensive and time-consuming. Investigators from Sumitomo Heavy Industries, Ltd. of Japan have therefore proposed an

alternative corrosion prevention technique that purges oxygen from ballast tanks with nitrogen gas (Matsuda et al. 1999). This new anticorrosion technology was derived from the basic concept that removing oxygen from the ballast tanks will limit the oxidation of metallic structures and thus greatly reduce the problems associated with corrosion. Our initial proof-of-principle and laboratory studies on the effectiveness of deoxygenation to prevent the transport on non-native species and the full-scale, field study on ballast tank corrosion demonstrated that this approach may both save the shipping industry money on corrosion prevention while removing a large proportion of the organisms typically found in ballast waters (Tamburri et al., 2002).

Current objectives

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

Background and previous work on ballast water invasions

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

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

Small plant and algal parts (fragments, spores, and seeds) as well as single-celled phytoplankton, protoctists, fungi, and bacteria are also often transported in ballast water. These microscopic components of ballast water have not been thoroughly characterized. However, it appears from our reviews that their tolerances for low oxygen environments will vary greatly. There are examples of species that are very sensitive to hypoxic conditions (e.g., filamentous fungi, Padgett et al., 1989; zoospores of the seaweed *Undaria pinnatifida*, Mountfort et al., 1999), as well as counter-examples of

species that can withstand low oxygen levels (e.g., resistant cysts of dinoflagellates, Hallegraeff, 1998). Marine bacteria, in particular, will have dramatically different responses to the conditions created in nitrogen treated ballast tanks. While most obligate aerobic strains will be unable to grow over extended periods of hypoxia, some facultative and obligate anaerobic bacteria may actually thrive under the conditions found in treated ballast. We therefore conclude that ballast water deoxygenation (maintaining hypoxia) would likely be highly effective at reducing introductions of aquatic animals (larvae, juveniles, and adults stages) but may have mixed success at eliminating introductions by members of other taxa.

Table 1. *A representative sample of time until significant mortality (LD_{50}, LT_{50}, or survivorship in treatment significantly less than control) was found for aquatic organisms held under various low oxygen concentrations. Adapted from Tamburri et al., 2002.*

Species	O_2 level (mg/l)	Time to significant mortality	Source
Astronotus ocellatus fish - adults	0.4	24 hours	Muusze et al. 1998
Ophiura albida brittle star - adults	0.1	60 hours	Vistisen and Vismann, 1997
Gammarus pseudolimnaeus amphiod - adults	1.5	24 hours	Hoback and Barnhart, 1996
Platichthys flesus fish - juveniles	1.0	2 hours	Tallqvist et al. 1999
Loimia medusa polychaete - adults	0.5	72 hours	Llanso and Diaz, 1994
Meganyctiphanes norvegica krill - adults	1.8	2 hours	van den Thillart et al. 1999
Cancer irroratus crab - larvae	1.7	4 hours	Vargo and Sastry, 1977
Crassostrea virginica oyster - larvae	0.02	18 hours	Widdows et al. 1989

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

Background and previous work on ballast tank corrosion

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

One area in a ship where corrosion is of particular concern is in the ballast tanks. Prolonged exposure of the ballast tank structure to water (often salt water) creates a condition conducive to rapid corrosion. The cost to paint ballast tanks is typically at least $5.00 to $10.00 per square meter with the

cost to repair corroded areas at approximately $500 per square meter (Fairplay, 1993). With large cargo vessels and oil tankers having hundreds of thousands of square feet of ballast tank surface area, preventing and treating corrosion is extremely costly.

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

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

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

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

Research Methods

Optimizing Deoxygenation

A key to the success of deoxygenation as a ballast water treatment is to design and develop the most efficient method for maintaining levels of oxygen in tanks that both kills the majority of aquatic organisms while also reducing corrosion rates – below 1.0 mg/l. The deoxygenation method proposed by Sumitomo Heavy Industries for ballast water treatment entails bubbling an inert gas into the ballast tanks after they have been filled. The shipboard trial by Matsuda and colleagues (1999) included

vertical pipes installed into a ballast tank from which pure nitrogen gas was pumped into the water for the "sparging" of oxygen. The tank was also sealed at the deck to permit nitrogen purging of the headspace. This method may achieve some deoxygenation through the contact of the nitrogen bubbles with the water, but primarily relies on diffusion of oxygen through the water surface in the tanks. Although hypoxic conditions were achieved, the sparging and purging of oxygen took days and relied on both the presence of a large headspace in the ballast tank filled with nitrogen gas (a free surface condition that is typically avoided since it can destabilize the vessel as water moves within tanks) and on large volumes of expensive inert gas. Although the basic principles are sound and experimental results on corrosion significant, the method used by Sumitomo Heavy Industries for deoxygenation appears to be inefficient and relatively costly to employ (approximately $3.5 million for installation on a vessel).

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

Survivorship of natural planktonic organisms subjected to deoxygenated water

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

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

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

Rates and mechanism of corrosion under deoxygenated conditions

Laboratory experiments are underway to examine: A) how deoxygenation influences bulk water chemistry, biofilm formation and biofilm/metal interfacial chemistry, B) if microbiologically influenced corrosion occurs under deoxygenated conditions and if so by what mechanism, and C) the

impact of O_2 on corrosion mechanisms and rates under deoxygenated conditions. The corrosion experiments are being conducted at the Naval Research Laboratory (NRL), Corrosion Facility, in Key West, FL and at the NRL, Stennis Space Center, MS.

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

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

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

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

The carbon steel coupons have been oriented in rows both horizontally and vertically in each chamber to simulate tank bottoms and sidewalls, respectively. Triplicate samples from both containers are removed every two months, fixed in glutaraldehyde and examined to assess the extent of biofilm formation and corrosion morphology. Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) are being used to characterize the corrosion morphology, biofilm structure and corrosion product composition on the metal surface. Swabs made of the coupon surface and serial dilutions are used to determine the microbial composition of the biofilm and microelectrodes are used to make O_2 profiles through the biofilms. Finally, polarization resistance and open-circuit potential is being used to monitor electrochemistry and corrosion of the carbon steel continuously over the one year experiment.

Results

Optimizing deoxygenation

Evaluations of several approaches and a series of pilot studies have led to the conclusion that Venturi Oxygen Stripping™ represents the most effective and economical method of deoxygenation for use aboard vessels. Venturi Oxygen Stripping™ is a patent-pending rapid, in-line deoxygenation system that mixes inert gas directly into ballast water as it is drawn into the vessel. The inert gas is produced

by combusting low-sulfur marine diesel (generating mostly nitrogen with small amounts of carbon dioxide and only trace levels of oxygen) in a device similar to the inert gas generators commonly used on tankers. The gas is mixed with the ballast water using a venturi injector that is installed in-line, just down-stream of the ballast pump. The venturi injector creates a micro-fine bubble emulsion where dissolved oxygen quickly diffuses out of the water into the gas. Because adding carbon dioxide in solution forms both carbonic and carboxylic acid, the pH of treated water is also reduced. This system is designed so that the same inert gas is also used to blanket all headspaces and the entire ballast tank when empty to maintain permanent hypoxia. Continuously maintaining a deoxygenated environment in ballast tanks appears to be a critical factor for corrosion prevention (see below).

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

Survivorship of natural planktonic organisms subjected to deoxygenated water

Although the experiments on the ability of Venturi Oxygen Stripping™ to kill planktonic organisms are still ongoing, initial results are striking. The dissolved oxygen levels and pH in the control cylinders were between 8.18 – 11.01 mg/l and 7.61 – 8.20 respectively, whereas the dissolved oxygen levels and pH in the treated cylinders dropped to 0.26 – 0.87 mg/l and 5.46 – 5.62 respectively. In treated tanks, these changes to the physical environment lead to a greater than 99% mortality of Chesapeake Bay zooplankton (copepods, barnacle larvae, polychaete larvae, cladocerans, crustacean nauplii, bivalve larvae, and nematodes) in less than 48 hours while the majority of zooplankton survived in the control cylinders (Figure 3). In addition to hypoxia and lowered pH, many of the larger zooplankton (mostly copepods) also appeared to be killed instantaneously by being damaged as they passed through the venturi injector which created large amounts of cavitation and turbulence (Figure 4). Furthermore, no intact individuals scored as dead after 48 hours recovered after being placed back in aerated water for 24 hours. Therefore zooplankton are not simply narcotized but are being effectively killed.

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

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

Rates and mechanism of corrosion under deoxygenated conditions

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

hypoxic environment. In fact, alternating back and forth from water that is deoxygenated to air may enhance corrosion rates.

Conclusion

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

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

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

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

References

Alanis, I., Berardo, L., De Cristofaro, N, Moina, C., and Valentini, C. 1986. In *Biologically Induced Corrosion*, 102, Houston, National Association Of Corrosion Engineers.

Andersen, A.B., 2001. Ballast Water Treatment by Ozonation. *1st International Ballast Water Treatment R&D Symposium. International Maritime Organization, London 26-27 March 2001: Proceedings*. GloBallast Monograph Series No. 5, IMO London.

Bailey, S.A., Duggan, I.C., van Overdijk, C.D.A., Jenkins P.T., & MacIsaac. H.J. 2003. Viability of invertebrate diapausing eggs collected from residual ballast sediment. *Limnology and Oceanography.* 48: pp. 1701-1710.

Bibb, M. 1986 In *Biologically Induced Corrosion*, 96, Houston, National Association Of Corrosion Engineers.

Boyer, H.E. & Gall, T.L., 1985. *Metals Handbook*, American Society for Metals: Metals Park, OH.

Carlton, J. T. & Geller, J. B. 1993. Ecological roulette: The global transport of nonindigenous marine organisms. *Science*, 261, pp. 78-82.

Cohen, A.N., and Carlton, J.T. 1998. Accelerating invasion rate in a highly invaded estuary. *Science*, 279, pp. 555-558.

Cooper, W.J., Dinnel, P. A., Gensemer, R. W., Herwig, R. P., Kopp, J. A., Ruiz, G. M., Sonnevil, G., Stubblefield, W. A., & VanderWende, E. 2002. Ozone, Seawater and Aquatic Nonindigenous Species: testing a full-scale ozone ballast water treatment system on an American Oil Tanker. *11th International Conference on Aquatic Invasive Species, Alexandria, VA*.

Dias, O.C., and Bromel, M.C., 1990. *Material Performance*, 29**:** 53.

Diaz, R. J. & Rosenberg, R. 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioral responses of benthic macrofauna. *Oceanography and Marine Biology Annual Review*, 33, pp. 245-303.

Drake, J.M., Lodge, D.M. & Lewis, M. 2003. Combining allometric parameters of biological processes with recent progress in invasion theory: Implications for ballast water standards. *12th International Conference on Aquatic Invasive Species, Windson, Ontario, Canada.*

Eashwar, M., Subramanian, G., Chandrasekaran, P. & Balakrishnan, K. 1990. *Proc. Corrosion '9*0, No. 120; Las Vegas, National Association Of Corrosion Engineers.

Eidsa G. & Risberg, E. 1986. *Biologically Induced Corrosion*, 109, Houston, National Association Of Corrosion Engineers.

Fairplay, April 1993. *Special Report: Paints and Coatings - Covering the Costs*.

Grieshaber, M.K., Hardewig, I., Kreutzer, U. & Poertner, H. O. 1994. Physiological and metabolic responses to hypoxia in invertebrates. In: Blaustein, M.P. (Ed.), *Reviews of Physiology Biochemistry and Pharmacology 125*. Springer-Verlag, New York, pp. 43-147.

Hallegraeff, G.M., 1998. Transport of toxic dinoflagellates via ships' ballast water: Bioeconomic risk assessment and efficacy of possible ballast water management strategies. *Marine Ecology Progress Series, 168*, 297-309.

Hamilton, W.A. & Maxwell, S. 1986. Biological and Corrosion Activities of Sulphate-Reducing Bacteria within Natural Biofilms. In *Biologically Induced Corrosion*, Dexter, S. C. ed., National Association of Corrosion Engineers: Houston, TX, pp. 131- 136.

Honneysett, D.G., Van Den Bergh, W.D. and O'brien, P.F., 1985. *Material Performance*, 24: 34.

Hardy, J.A. & Bown, J.L., 1984. The Corrosion of Mild Steel by Biogenic Sulfide Films Exposed to Air. *Corrosion*, 40, pp. 650-654.

Hoback, W.W., and Barnhart, M.C. 1996. Lethal limits and sublethal effects of hypoxia on the amphipod *Gammarus pseudolimnaeus*. *Journal of the North American Benthological Society*, 15, pp. 117-126.

Iverson, W.P. 1974. *Microbial Iron Metabolism*, New York, Academic Press.

Kasahara, K. & Kajiyama, F. 1986. In *Biologically Induced Corrosion*, 171, Houston, National Association Of Corrosion Engineers.

King, R.A., Skerry, B.S., Moore, D.C.A., Stott, J.F.D. & Dawson, J. L. 1986. In *Biologically Induced Corrosion*, 83, Houston, National Association Of Corrosion Engineers.

Lee, W.C., Lewandowski, Z., Okabe, S., Characklis, W.G., and Avci, R. 1993. Corrosion of Mild Steel Underneath Aerobic Biofilms containing Sulfate-Reducing Bacteria Part I: At Low Dissolved Oxygen Concentration. *Biofouling* 7, pp. 197-216.

Lee, W.C., Lewandowski, Z., Morrison, M., Characklis, W.G., Avci, R. & Nielsen, P. H. 1993. Corrosion of Mild Steel Underneath Aerobic Biofilms containing Sulfate-Reducing Bacteria Part I: At High Dissolved Oxygen Concentration, *Biofouling* 7, pp. 217-239.

Licina, G.C. 1988. *Sourcebook For Microbiologically Influenced Corrosion In Nuclear Power Plants*, Palo Alto, Electric Power Research Institute.

Llanso, R.J., and Diaz, R.J. 1994. Tolerance to low dissolved oxygen by the tubicolous polychaete *Loimia medusa*. *Journal of the Marine Biological Association of the United Kingdom*, 74, pp. 143-148.

Lutz, R.V., Marcus, N.H. & Chanton, J.P. 1994. Hatching and viability of copepod eggs at two stages of embryological development: anoxic/hypoxic effect. *Marine Biology*, 119, pp. 199-204.

Marine Engineering Review, January 1991. Life Corrodes Away.

Matsuda, M., Kobayashi, S., Miyuki, H. & Yoshida, S. 1999. *An anticorrosion method for ballast tanks using nitrogen gas*. Ship and Ocean Foundation Technical Report.

McCracken, W. 2001. Ballast Water Treatment with Available Biocides, *1st International Ballast Water Treatment R&D Symposium. International Maritime Organization, London 26-27 March 2001: Proceedings*. GloBallast Monograph Series No. 5, IMO London.

Miller, J.D.A. & Tiller, A.K. 1970. In *Microbial Aspects Of Metallurgy*, 61, New York, Elsevier.

Mountfort, D.O., Hay, C., Dodgshun, T., Buchanan, S. & Gibbs, W. 1999. Oxygen deprivation as a treatment for ships' ballast water: laboratory studies and evaluation. *Journal of Marine Environmental Engineering*, 5 (3).

Muusze, B., Marcon, J., Van Den Thillart, G. & Almeida-Val, V. 1998. Hypoxia tolerance of Amazon fish: respirometry and energy metabolism of the cichlid *Astronotus ocellatus*. *Comparative Biochemistry and Physiology* A, 120, pp. 151-156.

National Research Council, 1996. *Stemming the tide: controlling introductions of nonindigenous species by ship's ballast water*. National Academy Press, Washington, D.C.

Pacheco, A., Dishinger, T.D. & Tomlin, J. L. 1987. In *Proc. Corrosion '87*, No. 376, San Francisco, National Association Of Corrosion Engineers.

Padgett, D.E., Celio, D.A., Hearth, J.H. & Hackney, C. T. 1989. Growth of filamentous fungi in a surface-sealed woody substratum buried in salt-marsh sediments. *Estuaries*, 12, pp. 142-144.

Pope, D.H. 1986. *A Study Of MIC In Nuclear Power Plants And A Practical Guide For Countermeasures*, Final Report Np-4582, Palo Alto, Ca, Electric Power Research Institute.

Pope, D.H. 1987. *Microbial Corrosion In Fossil-Fired Power Plants - A Study Of Microbiologically Influenced Corrosion And A Practical Guide For Its Treatment And Prevention*, Palo Alto, Electric Power Research Institute.

Pope, D.H. & Morris, E.A. 1995. Some Experiences with Microbiologically Influences Corrosion of Pipelines. *Materials Performance*, 34, pp. 23-28.

Pope, D.H., Zintel, T.P., Kuruvilla, A.K. & Siebert, O. W. 1988. In *Proc. Corrosion 88*, No. 79, St. Louis, Mo, National Association Of Corrosion Engineers.

Postgate, J.R. 1979. *The Sulphate Reducing Bacteria*, Cambridge, England, Cambridge University Press.

Roman, M.R., Gauzens, A.L., Rhinehart, W.K. & White, J.R., 1993. Effects of low oxygen waters on Chesapeake Bay zooplankton. *Limnology and Oceanography*, 38, pp. 1603-1614.

Sanders, P.F. & Hamilton, W.A. 1986. In *Biologically Induced Corrosion*, 47, Houston, National Association Of Corrosion Engineers.

Smith, L.D., Wonham, M.J., McCann, L.D., Ruiz, G.M., Hines, A.H. & Carlton, J. T. 1999. Invasion pressure to a ballast-flooded estuary and an assessment of inoculant survival. *Biological Invasions*, 1, pp. 67-87.

Stalder, L.C. & Marcus, N. H. 1997. Zooplankton responses to hypoxia: behavioral patterns and survival of three species of calanoid copepods. *Marine Biology*, 127, pp. 599-607.

Tallqvist, M., Sandberg-Kilpi, E. & Bonsdorff, E. 1999. Juvenile flounder, *Platichthys flesus* (L.), under hypoxia: effects on tolerance, ventilation rate and predation efficiency. *Journal of Experimental Marine Biology and Ecology*, 242, pp. 75-93.

Tamburri, M.N., Wasson, K. & Matsuda, M. 2002. Ballast water deoxygenation can prevent aquatic introductions while reducing ship corrosion. *Biological Conservation*, 103, pp. 331-341.

Tatnall, R., Piluso, A., Stoecker, J., Schultz, R. & Kobrin, G. 1981. *Material Performance*, 19: p. 41.

van den Thillart, G., George, R.Y. & Stromberg, J. O. 1999. Hypoxia sensitivity and respiration of the euphausiid crustacean *Meganyctiphanes norvegica* from Gullmarn Fjord, Sweden. *Sarsia*, 84, pp. 105-109.

Vargo, S.L. & Sastry, A. N. 1977. Acute temperature and low dissolved oxygen tolerances of brachyuran crab (*Cancer irroratus*) larvae. *Marine Biology*, 40, pp. 165-171.

Vistisen, B. & Vismann, B. 1997. Tolerance to low oxygen and sulfide in *Amphiura filiformis* and *Ophiura albida* (Echinodermata: Ophiuroidea). *Marine Biology*, 128, pp. 241-246.

Widdows, J., Newell, R.I.E. & Mann, R. 1989. Effects of hypoxia and anoxia on survival, energy metabolism, and feeding of oyster larvae (*Crassostrea virginica*, Gmelin). *Biological Bulletin*, 177, pp. 154-166.

Williamson, M. 1996. *Biological Invasions*. Chapman and Hall, London.

Winters, M.A. & Badelek, P.S.C. 1987. In *Proc. Corrosion 87*, No. 156, San Francisco, National Association Of Corrosion Engineers.

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

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

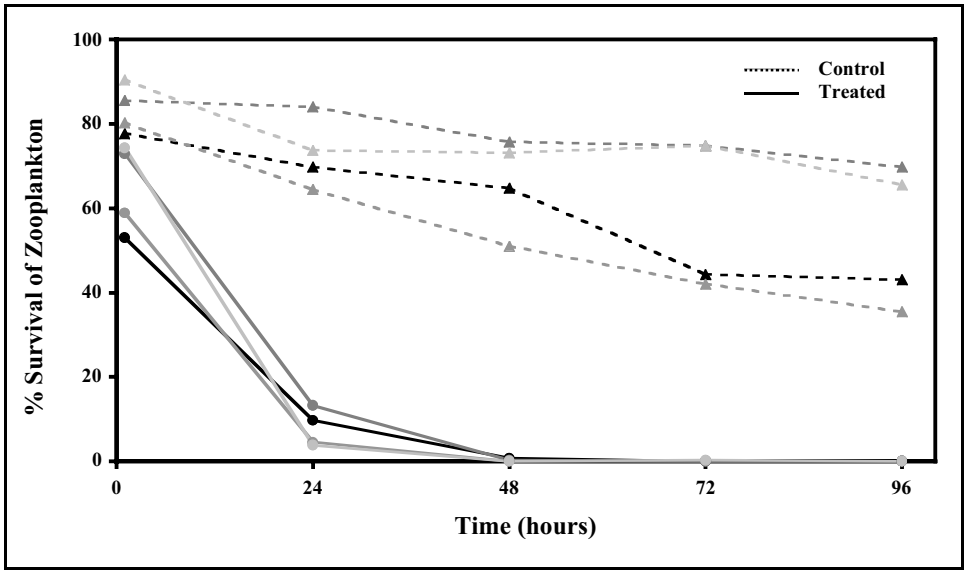


Figure 3. *Percent survival of natural Chesapeake Bay zooplankton (copepods, barnacle larvae, polychaete larvae, cladocerans, crustacean nauplii, bivalve larvae, and nematodes) in control and treated (deoxygenated) chambers after 1, 24, 48, 72, and 96 hours for the first four replicate trials of an ongoing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

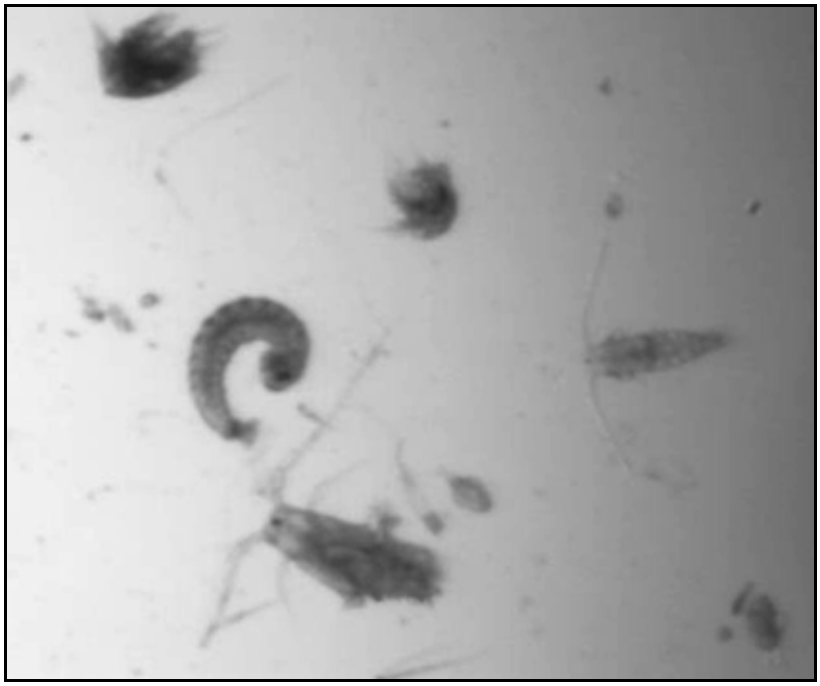


Figure 4. *A damaged copepod (lower middle) after passing through the Venturi Oxygen Stripping™ system. In all current trials examining the impacts of this treatment on zooplankton, the initial (after 1 hour) percent survival is 5 to 20 percent lower in treated versus control (see Figure 3) because of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

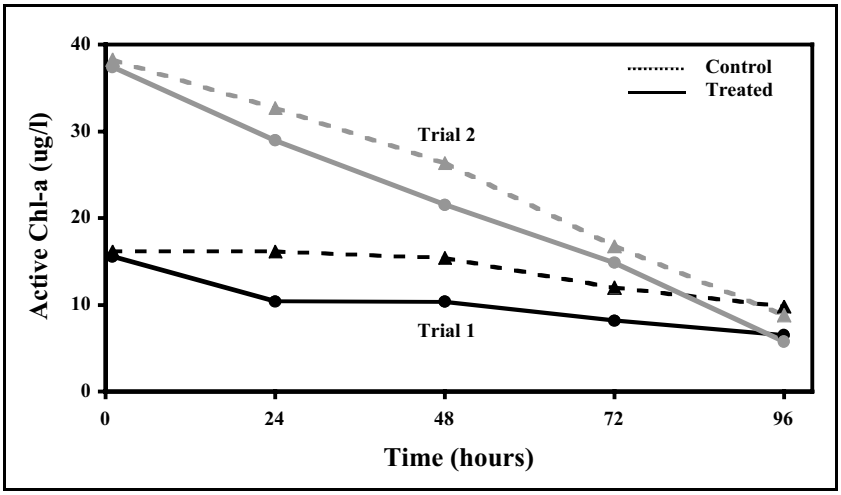


Figure 5. *Active chlorophyll-a concentrations in control and treated (deoxygenated) chambers after 1, 24, 48, 72, and 96 hours for the first two trials of an ongoing experiment.*

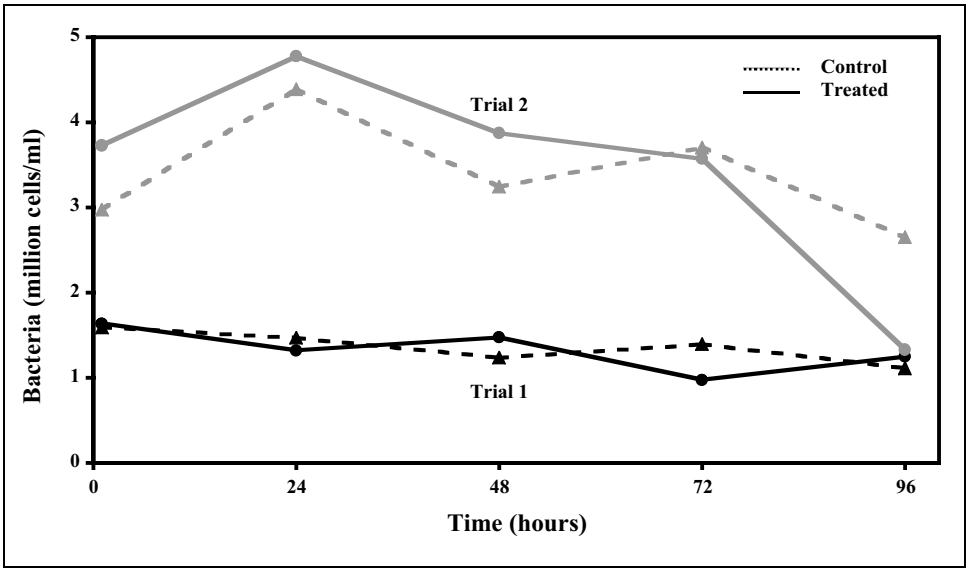


Figure 6. *Abundance of bacterial cells in control and treated (deoxygenated) chambers after 1, 24, 48, 72, and 96 hours for the first two trials of an ongoing experiment.*

Ballast water treatment by de-oxygenation with elevated CO_2 for a shipboard installation – a potentially affordable solution

M. Husain[1], H. Felbeck[2], R. Apple[1], D. Altshuller[1] & C. Quirmbach[1]

[1]*MH Systems, Inc., USA*
husainm@mhsystemscorp.com

[2]*Scripps Institution of Oceanography, University of California USA*

Treatment options being researched

It is estimated that 21 billion gallons of ballast taken on in foreign ports are discharged by commercial vessels annually in the waters of the United States (Carlton et al. 1993). Specifically, ballast water transport is a major vector for the introduction of potentially invasive aquatic species.

The concept to combat Aquatic Nuisance Species (ANS) invasion resulting from ballast water discharge, described in this paper, is a technical extension of MH Systems' American Underpressure System (AUPS). The AUPS utilises a slight negative pressure in the tank's ullage space, in an inert environment, to prevent or minimize oil spillage from tankers (Husain et al. 2001).

The ballast water treatment method consists of bubbling the inert gas via a row of pipes (orifices at the bottom of the pipes) located at the bottom of the tank, while maintaining a negative pressures of –2 psi at the ullage space. The inert gas from a standard shipboard inert gas generator is composed of 84% Nitrogen, 12-14% CO_2 and 2% Oxygen. The ballast water will be equilibrated with gas from an inert gas generator. As a result, the water will become hypoxic, will contain CO_2 levels much higher than normal, and the pH will drop from the normal pH of seawater (pH 8) to approximately pH 6.

Ballast water treatment standards

Standards for treatment of ballast water are still in a state of flux. Efforts to define standards are ongoing in the US Congress, International Maritime Organisation (IMO), and other individual maritime nations. The US Congress (NAISA 2002) proposes an Act that will, among other considerations, set the interim standards for ballast water treatment (BWT). It states, "The interim standard for BWT shall be a biological effectiveness of 95% reduction in aquatic vertebrates, invertebrates, phytoplankton and macroalgae." There are discussions about setting micron standards, i.e., x microns cut-off for living organisms.

Currently, a fifty (50) micron standard is being discussed in various circles, including IMO and US Coast Guard. The default standard appears to be the Ballast Water Exchange (BWE), or something close to it. Cangelosi (2002) states "… the Coast Guard has set forth a "do-it-yourself" approach, directing interested ship owners to conduct complex shipboard experiments (post-installation) to undertake direct and real-time comparisons between BWE and treatment. If the comparison is favourable and defensible, the Coast Guard will approve the treatment. ….."

Current investigative efforts of alternative technologies

Glosten (2002) provides a review of the numerous treatment systems options being investigated. These include heat, cyclonic separation, filtration, chemical biocides, ultraviolet light radiation, ultrasound, and magnetic/electric field. The methods not mentioned in this reference are hypoxia, carbonation, and their combination. In studies of 18 months duration on a coal/ore vessel (Tamburri et

al. 2002), the ballast water dissolved O_2 level was reduced and held to concentrations at or below 0.8 mg/l by bubbling essentially pure nitrogen. The experiments resulted in a treatment "that can dramatically reduce the survivorship of most organisms found in the ballast water…"

In extensive experiments with gas of varying percent CO_2, N_2 and O_2 (McMahon 1995), the "…results indicate that CO_2 injection may be an easily applied, cost-effective, environmentally acceptable molluscicide for mitigation and control a raw water system macrofouling by Asian clams and zebra mussels".

Corrosion considerations of various treatment systems

Shipboard corrosion mitigation is always a priority consideration. It requires the continual attention of the crew and, if not carefully controlled, can actually compromise the strength of the ship. Any installed ballast water treatment system must not under any circumstances increase the potential for corrosion and, if possible, should decrease the potential. The system discussed in this proposal has considered the corrosion issue. As reported in literature (Tamburri et al., 2002), corrosion might even be mitigated by deoxygenation. Perry et al. (1984) states that unless pH level drops below 4, concerns about corrosion are unfounded.

Timeframe of the project

We present initial proof of concept results, which have been conducted during 2002-2003.

Aims and objectives of the project

Except for ballast water exchange, essentially all treatment concepts involve the chemical change of the water to cause an environment lethal for ANS. The chemical changes described by Tamburri et al. (2002) and McMahon (1995) offer promising results, i.e., reduce the dissolved O_2 in the one case, and carbonate and reduce the pH in the other case. In both cases the process involves the exchange of gases, the extraction of the dissolved O_2 and the introduction of CO_2. Surface contact area and partial pressure differentials permit the gas exchanges to occur. The deoxygenation of the ballast water is based on Henry's Law of gas solubility: The relative proportion of any dissolved gas including oxygen in the ballast water is a function of the concentration, equivalent to partial pressure of the gas (e.g. oxygen), within the mixed gases over the ballast water. The depletion of oxygen in the ballast water is primarily a function of the shared surfaces and concentrations at the interfaces of the inert gases and water.

The pH of the ballast water is lowered by the chemical reaction:

$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

All systems described thus far in the literature, including ballast transfer, has left untreated the sediment buildup in the bottom of the tanks. If the orifices in the lattice work of piping pointed down, then the sediment could be stirred up facilitating the kill of the embedded ANS.

The purpose of the preliminary experiments described here was to obtain initial data on the effects of "inert gas" on marine organisms. "Inert gas", hereinafter called trimix, a commercially available gas mixture of 2% oxygen, 12% CO_2 and 84% nitrogen resembles the gas generated by commercially used marine "inert gas generators". Adult or young adult animals were chosen for two reasons a) to make the size of specimens amenable for the experimental setup and b) to raise the significance of possible effects since adults of a species are typically more tolerant of environmental changes than juveniles or larvae. All animals were collected fresh from the coastal waters off La Jolla, CA and used immediately. The plankton sample was collected with a plankton net from a small boat.

Research methods, test protocols and experimental design

The schematic of the experimental setup is shown in Figure 1. Three parallel incubations were done for each experiment. Several organisms were incubated in 1.5L of seawater at 22°C in large Erlenmeyer flasks. Each incubation was equilibrated with the respective gas using aquarium stones before any organisms were introduced. The aerobic control was bubbled from an aquarium pump for approximately 15 min and left open to the atmosphere after addition of specimens. An anaerobic incubation was bubbled with 99.998% nitrogen for 15 min. After introduction of the organisms, the bubbling was continued for another 10 min and then the container was closed with a rubber stopper or the bubbling was continued. The incubation in trimix was treated similarly except that the gas mix was used instead of nitrogen. The oxygen concentrations were measured after the initial bubbling period using a Strathkelvin oxygen electrode with a Cameron instruments OM-200 oxygen analyser. pH values were determined using a combination electrode and a Radiometer pH meter.

Survival of the specimens was determined visually by checking for motile responses to tactile stimulus (e.g. mussels do not close their shells, barnacles to not withdraw their feet, shrimp do not move their mouthparts, worms appear limp and motionless). After each testing of the animals, the incubation flasks were bubbled for 10 min to reestablish original conditions. To verify survival of the specimens, they were relocated to aerobic conditions and checked again after 30 min. If they still did not respond, they were considered dead. The survival of the bacterium *Vibrio cholerae* strain N16961 was monitored by repeated plating on Luria-Bertani Agar with Rifampicin (100 µg/mL).

This setup allowed us to compare responses to nitrogen and "trimix" while making sure that test specimens were not gravely affected by other experimental parameters. Incubation in pure nitrogen allow for a comparison with published results by others.

Results

Experimental results and discussion.

The oxygen concentrations were measured at "non-detectable" for the nitrogen incubations and 10% air saturation (=16 Torr partial pressure) for the "trimix". The pH value of the water bubbled with trimix reached 5.5 after the initial 10 min of vigorous bubbling. The aerobic and nitrogen bubbled seawater maintained their pH at 8. The incubations showed clearly that "trimix" kills organisms considerably faster than incubations in pure nitrogen Table 1. All organisms except of *Vibrio cholerae* showed no mortality in aerobic conditions. The shrimp and crabs incubated in "trimix" were dead after 15 min and 75 min, respectively. Even a transfer into aerated water did not result in any movement. The brittle stars incubated under nitrogen started to move again after transferred into aerated water. All the mussels incubated in nitrogen and "trimix" were open after 95 min but only the ones in nitrogen still responded to tactile stimuli by closing their shells. The barnacles were judged dead after incubation in "trimix" when they did not withdraw their feet when disturbed, the ones incubated in nitrogen still behaved normally. The plankton sample mainly contained copepods. They stopped moving after 15 min and could not be revived in nitrogen and "trimix" incubations. The results are summarised in Table 1.

Low oxygen concentrations in water are a common natural phenomenon and their effects on live organisms have been widely discussed in the past. Oxygen may not be available to an organism because no water for respiratory purposes is present, e.g., during low tide in the intertidal zone. Oxygen may also be removed in stagnant waters due to bacterial or other "life based" actions, e.g., in ocean basins, fjords, tide pools, or in waters with high organic content and consequently high bacterial counts, e.g., in sewage, mangrove swamps, paper mill effluent. In addition, oxygen can also be removed by chemical reactions, e.g., in hot springs, industrial effluents. The manuscript by Tamburri et al. (2000) summarises survival of a variety of larvae and adults of organisms including some which may be significant as "nuisance species" under hypoxic conditions. The publication supports extensively that most organisms only survive strongly hypoxic conditions for a few hours and only a

few adults for several days. The authors suggest that 72 h of hypoxia will be sufficient to kill most eucaryotic organisms, adults or larvae in ballast water.

Table1. *Effects of Trimix on Marine Species*

Species		Number/ incubation	Nitrogen	Trimix	Comments
Mimulus foliatus	Crab	7/inc	Normal	Dead after 75 min	
Mytilus californianus	Mussel	10/inc	Open but responding	6 dead after 95 min	
Pollicipes polymerus	Barnacle	10/inc	Normal	Dead after 60 min	
Megabalanus californicus	Barnacle	5	Dead after 84 h	Dead after 48 h	
Sebastes diplopora	Rockfish	2	Dead after 19 min	Dead after 7 min	
Ophionereis annulata	Brittle star	5-10	Most survive up to 3 h, most dead after 26 h	Most survive up to 3 h, several dead after 26 h	Mean of 4 experiments
Ophioderma panamanse	Brittle star	8/inc	Not moving but revivable by air	Dead after 50 min	
Unidentified	Caridean shrimp	6	Affected but alive after 30 min	Dead after 25 min	
Unidentified	Caridean shrimp	6	2 dead after 30 min	5 dead after 45 min	
Mysolopsis californica	Mysid shrimp	25	Dead after 15 min	Dead after 15 min	
Lysmata californica	Shrimp	10/inc	Normal	Dead after 20 min	
Plankton mix	Var. copepods	lots	Dead	Dead after 15 min	
Tigriopus californicus	Copepod	8 - 10	Dead after 2 h	Many dead after 2 h	Mean of 3 experiments
Vibrio cholerae	Bacterium	2.5 x106/ml	>>99% dead after 24 h	>>99% dead after 24 h	Aerobic: 30% dead after 24 h

*Trimix (2% oxygen, 12% CO_2 and 86% nitrogen)

The effects of high CO_2 on organisms in natural waters have become a research focus because of proposals to dispose atmospheric CO_2 in the deep ocean (Haugan 1997, Omori et al. 1998, Seibel and Walsh 2001). Two effects have to be distinguished when looking at "trimix" incubations in seawater: a) the lowering of the pH from pH 8 to about 5.5 and b) the raised CO_2 concentrations in the water. While the pH change caused by the incubations in "trimix" are in the range of published experiments, the CO_2 concentration in "trimix" (about 14%) is much higher than those investigated in the published literature (0.1% to 1%). Therefore, the effects of "trimix" incubations should be much stronger than those published previously.

Several publications have shown the detrimental effect of lower pH values and high CO_2 levels on aquatic life. In a recent publication, Yamada and Ikeda (1999) tested ten oceanic zooplankton species for their pH tolerance. They found that the LC_{50} (=pH causing 50% mortality) after incubations of 96 hours was between pH 5.8 and 6.6 and after 48h it was between pH 5.0 and 6.4. Therefore, the pH value caused by incubations with "trimix" is well within the lethal range for this zooplankton. Huesemann et al. (2002) demonstrate that marine nitrification is completely inhibited at a pH of 6. Larger organisms were also investigated, a drop in seawater pH by only 0.5 diminishes the effectiveness of oxygen uptake in the midwater shrimp G*nathophausia ingens* (Mickel and Childress 1978) and Deep sea fish hemoglobin may even be more sensitive to pH changes (Noble et al. 1986). It appears that a common metabolic response to raised CO_2 levels and concomitant lowered pH is a metabolic suppression (Barnhart and McMahon 1988, Rees and Hand 1990). Most recently, first papers were published investigating the effects of environmental hypercapnia in detail (Poertner et al. 1998, Langenbuch and Poertner 2002). The effects of pH changes on phytoplankton growth has been reviewed by Hinga (2002). The review summarises data from 22 studies. Many of the cited studies

use elevated levels of CO_2 to adjust pH. In almost all cases, the growth of unicellular phytoplankton and diatom species was severely affected by low pH below pH 6.5, only the species *Nitzchia closterium* showed significant growth at pH 5.5. Since all of the studies cited were done at high light levels and in aerobic conditions, it can be safely assumed that the conditions in an hypoxic dark environment as is found inside of an inert gas treated ballast tank is even more detrimental to phytoplankton growth.

The trimix combines both of these effects on organisms - hypoxia and hypercapnia. Preliminary results demonstrate the effectiveness of this combination in quickly killing a variety of sample organisms. Contrary to methods using additions of biocides or any chemicals in general, nothing is added to the ballast water and, therefore, nothing will be released into the environment when it is released again. Methods using radiation, heating, or filtering ballast water before or during a ship's trip, can be expensive. The equipment needed to establish a rapid gassing of ballast water is available off the shelf and has been used in the marine environment. The plumbing and gas release equipment has been optimised and has been used in application such as aquaculture, sewage treatment and industrial uses. Extensive supporting literature and research about the design and optimisation of equipment for the aeration of water is available from public resources. Inert gas generators are available for fire prevention purposes on ships and other structures and are already installed on many ships, mainly tankers. They can use a variety of fuels including marine diesel to generate the inert gas.

Several topics have to be further investigated before a conclusive recommendation about the treatment of ballast water with "inert gas" can be made: a) how are larvae, eggs, and plankton effected and b) what is the affect of trimix type inert gas in fresh water? If ballast water is taken up through a screen, larger animals will not be included. The initial tests were made with adults because of easy access to them. However, if adults of a species are effected by "inert gas" it is most likely that their larvae will also be effected probably even more so.

Future tests will be conducted with specimens from plankton and larval cultures and with incubations of mixed plankton collected from the ocean. Determinations of viability will be made by microscopic observations (e.g. movement of mouthparts, swimming behaviour), ATP measurements (the ATP levels rapidly decreases after death of an organism), and the ability to bioluminesce (many planktonic organisms emit light, an ability which ceases after death). Fresh water organisms will be of interest because the pH change is not as much as in seawater. Freshwater in its natural environment can have pH values around 5.5. It has to be proven that raised CO_2 concentrations in combination with hypoxia will also affect these species. Only then can the method be used for both, fresh and salt water ballast.

Analysis and Design Equations

Assumptions

In this section, we present mathematical descriptions of the deoxygenation process and of the transfer of carbon dioxide into the ballast water, which, in turn, leads to lowering of the pH to the levels lethal to most ANS. We obtain closed-form mathematical models, usable in design of a shipboard system from any set of given specifications. The list of symbols used in the equations is given at the end of the paper.

The system being analysed places a mixture of nitrogen and carbon dioxide with a relatively small fraction of oxygen in contact with ballast water. The oxygen level in the ballast water is assumed to have reached equilibrium with air as a result of prolonged contact, and therefore would contain a concentration of oxygen sufficient to support a wide spectrum of life forms. The objective is to reduce the oxygen content to a low level by interchange with the gas mixture. The gas is bubbled through the ballast water, which assures uniform distribution of dissolved gas throughout the ballast tank. Thus, diffusion within the tank can be neglected. Bubbles are assumed to be small and variation of hydrostatic pressure over the vertical dimension of a bubble is neglected.

We do not discuss here the size of bubbles and the frequency of their generation. These two issues are addressed in existing reference literature (see, for example, Perry et al. 1984).

We assume that deoxygenation process follows Henry's Law with equilibrium achieved within the residence time of each bubble. The composition of the mixture in the bubble changes primarily due to transfer of carbon dioxide, a dynamic chemical process assumed to obey the mass action kinetics.

Deoxygenation Process

As trimix gas is flushed through the system, the total weight of oxygen in the ballast water will be reduced. For the purpose of analysing the deoxygenation process we neglect the presence of carbon dioxide in the trimix.

When a small quantity of gas, dQ, is admitted, it contains an oxygen molar fraction y^0. By the time this quantity of gas leaves the system it contains, according to Henry's Law, the molar fraction Y / k_H .

Therefore, we obtain the following differential equation:

$$\frac{dY}{dQ} = y^0 - \frac{1}{k_H} Y$$

Integration of this equation yields: $$Q = k_H \ln \frac{y^0 - Y / k_H}{y^0 - Y_0 / k_H}$$

From this equation it follows that pumping 5,200 m^3 of gas into a 32,200 m^3 tank reduces oxygen concentration to 0.83 ppm. This level of hypoxia is lethal to many ANS. With the flow rate of 38.2 m^3/min this can be achieved in 135 min. The relationship between the size of the tank and the time required to deoxygenate it is linear. Therefore, these results can be scaled to any tank size.

Underpressure in Ullage Space of Ballast Water Tank

Deoxygenation is enhanced by the under-pressure, as can be seen from the following simple argument. Let p be pressure of water at a given depth in the absence of underpressure. Let p_u be the absolute value of the negative pressure at the top. Let Y be the weight fraction of oxygen in the water without underpressure and Y_u – the same weight fraction with underpressure. Then by Henry's Law:

$$\frac{Y - Y_u}{Y} = \frac{k_H yp - k_H y(p - p_u)}{k_H yp} = \frac{p_u}{p}$$

From this equation we conclude that solubility of oxygen is reduced by underpressure. This factor becomes even more significant as a bubble rises to the surface, and the pressure inside decreases.

For example, if p=14.7 psi (the usual value at the surface of the tank) and the absolute value of the underpressure is 2 psi, then the solubility of oxygen is reduced by approximately 14%.

The maintenance of underpressure is not mandatory. The underpressure helps accelerate the de-oxygenation process because, by reducing the oxygen solubility, it also reduces the amount of inert gas needed. For example, 2 psig underpressure will speed up the de-oxygenation by 14%; 0.5 psig underpressure will speed it up by 3.5%. Slight underpressure is also helpful in eliminating the contaminated gas from the ullage space.

Carbon Dioxide Transfer

Since we assumed that the pressure inside the bubble depends only on the pressure of the liquid surrounding it, we can write:

$$\frac{dp}{dt} = -\rho g u\,, \quad p = p^0 - \rho g u t \tag{1}$$

By definition we have $n_{CO2} = xn$. Differentiating this equation we obtain:

$$\frac{dn_{CO2}}{dt} = x\frac{dn}{dt} + n\frac{dx}{dt}\,. \tag{2}$$

However, since the reaction of carbon dioxide with water is the dominant cause of change in the chemical composition, we can write:

$$\frac{dn}{dt} = \frac{dn_{CO2}}{dt}\,.$$

Combining this with the Equation (2) yields the following equation:

$$n\frac{dx}{dt} = (1-x)\frac{dn_{CO2}}{dt}\,. \tag{3}$$

In addition, we can solve $n = xn + n_N$ for n to obtain

$$n = \frac{n_N}{1-x}\,. \tag{4}$$

From the Law of Mass Action kinetics we have:

$$\frac{dn_{CO2}}{dt} = -kp_{CO2} \tag{5}$$

For the partial pressure of carbon dioxide we have, according to Dalton's Law $p_{CO2}=xp$.

Combining the equations (1), (3), (4), and (5) yields:

$$\frac{dx}{dt} = -\frac{k}{n_N}x(1-x)^2(p^0 - \rho g u t)\,.$$

This equation can be integrated to obtain:

$$I(x) - I(x^0) = -\frac{kt}{2n_N}(2p^0 - \rho g u t)\,, \tag{6}$$

where

$$I(x) = \frac{1}{1-x} + \ln\frac{x}{1-x}\,.$$

This equation can be used to calculate parameters of the systems, including the residence time of a bubble, required to achieve the desired molar fraction of carbon dioxide in the bubble. The latter quantity is related to the *pH* and the concentration of carbon dioxide in the water, as we shall see in the next subsection.

Concentration of Carbon Dioxide in Water and pH Calculation

Concentration of carbon dioxide in water can be determined as the ratio of the number of moles transferred from the bubble to the volume of the tank. The number of moles transferred from each bubble can be determined from the value of *x* as follows. By definition, we have:

$$x = \frac{n_{CO2}}{n_{CO2} + n_N}$$

Solving for n_{CO2} we find:

$$n_{CO2} = \frac{x n_N}{1 - x},$$

which gives the following answer for the concentration of carbon dioxide in water:

$$c = \frac{N}{V_t}\left(n^0_{CO2} - \frac{x n_N}{1 - x} \right). \tag{7}$$

The concentration of the hydrogen ions in the water can be calculated from *c* by solving the following equation for *h*:

$$\frac{h^2}{c - h} = K \tag{8}$$

The pH can be then found by taking the $-\log h$.

We can also solve the Equation (8) for c and substitute the result into the Equation (7). This yields after some tedious, but straightforward algebra the following relationship between the desired molar fraction of carbon dioxide in the bubble and the desired concentration of hydrogen ions in the water:

$$x = 1 - \frac{K N n^0_{CO2}}{K N (n^0_{CO2} + n_N) + (K - h) h V_t}. \tag{9}$$

The equations (6) and (9) constitute a closed-form mathematical model of carbon dioxide transfer usable for design of the treatment system.

The MH Systems' Ballast Water Treatment System Description

(Note: The Authors are cognizant that a large tanker of the size as 300,000 DWT may not be an ideal candidate for ballast water treatment features. However, this hypothetical design study can be easily modified for smaller tankers.)

The MH Systems Ballast Water Treatment System is a combination of two other effective treatment systems, i.e. deoxygenation and carbonation. It also is an extension of the MH Systems American Underpressure System – AUPS (Husain et al. 2001). The inert gas, supplied by the standard marine gas generator, is 84% nitrogen, 12-14% carbon dioxide and about 2% oxygen. This inert gas has all the ingredients necessary to combine the two very effective treatments of hypoxia and carbonation at a very reasonable cost. The laboratory tests at Scripps, described previously, show that this gas needs very little contact time to be effective. The analyses described earlier established the flow rates and control time for hypoxia carbonated conditions.

Each ballast tank has rows of pipe at the tank floor with downward pointing nozzles. The pressurized inert gas is jetted downward out of the piping. The jets stir up the sediment for contact with the inert gas bubbles. The bubbles then rise through the ballast water to the space above the water surface, which has previously been underpressurized to –2 psi. For the purposes of this paper, a 300,000 DWT

single hull tanker was used for design studies of this system to test practicality and affordability. Applicability to a 300,000 DWT double hull tanker was also examined. Figure 2 shows inboard profile, deck plan view, piping layout, nozzle detail and section through ballast tank. Figure 3 shows schematic of the system and Figure 4 shows isometric of one tank. A 300,000 DWT double hull tanker has somewhat less installation costs since the tank bottom is smooth as shown in Figure 4.

For the 300,000 DWT tanker, there are 8 ballast tanks as follows in Table 2:

Table 2. *Ballast Water Tank Capacity*

Location	Size M^3	Ft^3
Fore Peak	8,265	291,875
B3S	32,200	1,137,000
B3P	32,200	1,137,000
B6S	16,048	567,000
B6P	16,048	567,000
B Engine Room S	1,645	58,000
B Engine Room P	1,086	74,000
Aft Peak	2,331	82,300
Totals	**110,823**	**3,914,175**

From analyses and experience (Tamburri et al. 2002), it is estimated the hypoxia and pH conditions can be set in at least 8 hours, even in the largest tanks, B3 Port and Starboard. The flow rate is 1350 cfm for each of these tanks. With one 1500 cfm marine gas generator, and treating each tank sequentially, it is estimated that all 8 tanks can be in a hypoxia, low-pH (5.5 - 6) condition in less than 48 hours. Contact time for essentially total lethality may not require more than another 24 hours although the remainder of the 2 to 3 week voyage is available.

The space above the liquid in each tank is underpressurized to about –2 psi and maintained throughout the voyage. As the gas bubbles rise up to the surface, they are evacuated by a blower to maintain the underpressure of the inert gas blanket at the surface. The underpressure further facilitates the solubility of the oxygen (see analysis) and tends to compensate for the oxygen captured in the bubbles as they rise.

Since the ballast tanks are treated sequentially, only two 700 cfm compressors are required to compress the gas. The gas is compressed enough to offset the hydrostatic head plus an additional 25% psi to provide a jet force for stirring the sediment. Two compressors are provided for redundancy. If there are some concerns with the dumping of hypoxia and carbonated treated water, it is easily countered with the system discussed in this paper. The compressors will shift over from the gas generator to atmospheric and the ballast water will be oxygenated within just a few hours. In this same period of time the CO_2 is readily washed out since the air contains no CO_2 component.

Sensors are needed to monitor the pH to ensure that it never goes below about 5.5. Sensors will measure dissolved oxygen content to ensure that adequate deoxygenation is established. Sensors will also monitor the underpressure. The control system will remotely start and stop the gas generator, the compressor and the blower. The control system also remotely controls the valves off of the inert gas manifold to each ballast tank and the valving for the underpressure manifold.

It is expected that system will be controlled by a suitably designed arrangement of programmable logic controllers (PLCs). These devices are commercially available. They are also easy to program and maintain.

A control console with displays will integrate the functions of the inert gas generator and the AUPS ballast water treatment system as well as provide for monitoring, status displays and manual override, if required.

Tests were conducted with the AUPS System installed on a naval reserve fleet tanker. They verified the structural capability of tanks to withstand the pressure of -3 psi and the controls needed to maintain the required underpressure. These findings are applicable to the equipment and controls that will be used for the ballast water treatment system.

The following are the design features of the shipboard system:

- Dry docking is not required for the installation of the system. The system can be retrofitted at pier side.
- The system includes mainly off-the-shelf components.
- The system is fully automated. Data can be transmitted in real time to a shore-side facility, if desired.
- Sensors are installed at different locations inside the tank to determine pH and oxygen levels.
- The system requires low maintenance.

Economic Evaluation of MH Systems' Ballast Water Treatment System for a 300,000 DWT Tanker

In making an economic evaluation, the analysis methodology described in Mackey et al. (2000) was used. This method states, "a logical basis for economic comparisons would be a change in Required Freight Rate (RFR)." Since there would be no change in cargo capacity, then:

$$\Delta RFR = \frac{\left[CRF(i,n)^* \Delta P + \Delta Y\right]}{C}$$

where

$CRF(i,n)$ is Capital Recovery Factor for an interest rate i and n for economic payback years,

ΔP is change in Capital Cost, and

ΔY is net change in annual operating cost and revenue.

Mackey et al. (2000) stated that the economic payback period for conversions is typically 5 years.

The Authors selected a 300,000 DWT tanker for analysis. As stated earlier, a ballast water treatment system applicable for ships must have the capacity for treating huge quantities of ballast water. If a system is practical and economical for treating a ship with 8 ballast tanks of 110,823 cubic meters, then it is practical for all ship types. The economics would have to be assessed for ships of other, smaller ballast capacity, as the economics might not scale. But obviously, the effectiveness as well as the practicality of the system would be established.

Table 3 (over) lists the principal parts and materials in the ballast water treatment system together with estimated prices and labour costs.

The total cost is approximately $3,057,100. All tankers already have some type of inert gas generating capability. The newer tankers have generators with a gas mixture discharge similar to the mix used in the experiments at Scripps. Nevertheless, for conservatism, the generator has been included in the cost. Similarly tankers probably have sufficient excess electrical capacity to supply the load of this equipment – the compressors and blower. This is especially true since this is on the return trip in ballast and the machinery will only run about 48 hours each trip. Nevertheless, again for extreme conservation, a 300 KW generator has been included.

Table 3. *Preliminary cost estimate for ballast water treatment system.*
Note: labor cost is based on US repair shipyard estimates.

Parts and Materials	Capacities or Type	Quantity /Unit	Price/Unit	Material Cost	Labor Cost	Material & Labor
Blower (Exhaust)	2000 CFM-100HP	1	$ 10,000	$ 10,000	$ 75,000	$ 85,000
Reciprocating Compressor	Electric-700 CFM-100HP	2	$ 40,000	$ 80,000	$ 50,000	$ 130,000
Inert Gas Generator	1500 CFM - 50 HP	1	$175,000	$ 175,000	$ 150,000	$ 325,000
Row of pipes at tank bottom PVC	3" SCH 80; Length in Ft.	15000	$ 2	$ 30,000	$ 52,500	$ 82,500
Header Branch Piping - PVC	8" SCH 80 "	1000	$ 5	$ 5,000	$ 105,000	$ 110,000
Header Piping - PVC	10"SCH 80 "	1800	$ 7	$ 12,600	$ 252,000	$ 264,600
Header Piping - Steel	10" SCH 40 (Steel)	2000	$ 22	$ 44,000	$ 650,000	$ 694,000
Brackets	Steel	2000	$ 30	$ 60,000	$ 35,000	$ 95,000
Valves-Electric (Ballast)	10" Butterfly	16	$ 4,500	$ 72,000	$ 7,000	$ 79,000
Valves-Electric (Inert Gas)	10" Butterfly	2	$ 4,500	$ 9,000	$ 1,000	$ 10,000
Diffusers	Coarse Bubbles	2600	$ 50	$ 130,000	$ 10,000	$ 140,000
Fittiings (Elbows, Tees, Couplings)	PVC	4000	$ 20	$ 80,000	$ 140,000	$ 220,000
Generator	300 KW	1	$ 60,000	$ 60,000	$ 15,000	$ 75,000
Sub-Total Materials				$ 767,600		
Sub-Total Labor					$1,542,500	
Sub-Total Materials & Labor						$ 2,310,100
Sensors, Controllers & Computer						
pH Gauges		16	$ 1,000	$ 16,000		
Pressure Gauges for Ullage space		16	$ 500	$ 8,000		
Pressure Controllers for Ullage		16	$ 1,000	$ 16,000		
Controller for Compressor		2	$ 500	$ 1,000		
Oxygen Sensor		16	$ 500	$ 8,000		
Controller for Valves		16	$ 500	$ 8,000		
Electrical		1	$ 40,000	$ 40,000		
Computer Software & Hardware		1	$ 50,000	$ 50,000		
Sub-Total - Material				$ 147,000		
Labor for Installation					$ 250,000	
Sub-Total - Material & Labor						$ 397,000
Other costs						
Engineering & Maintenance						$ 350,000
TOTAL BW SYSTEM COST						**$ 3,057,100**

To make a usefully indicative estimate of operating costs, the following assumptions were made:

- The tanker will operate to 360 days per year.
- Six (6) voyages per year between Persian Gulf and USA.
- Half of the voyages are return trips in ballast, or 6 trips a year.
- Assume the 2 compressors and blower must operate 48 hours to obtain hypoxia and carbonation in all 8 tanks (note that actually the cfm of both compressors is only required for tanks B3 port and starboard and B6 port and starboard.
- Operating costs are primarily the fuel costs for the inert gas generator and the 300 KW generator.
- n is 5 years (economic payback period) and i (interest rate) is 8%.

If the gas and electric generators operate 48 hours for each of 6 voyages, then the total operating time is 288 hours per year for each generator. About 6,000 gallons of diesel fuel would be consumed by the electric generator and for the gas generator about 16,500 gallons. This is a total of 22,500 gallons. At a cost $1.25 per gallon, the yearly operating cost will be about $28,125. Considering the few hours

per year that the machinery operates and the fact that the ship has no cargo and therefore less requirements of the crew, minimal cost has been allocated for maintenance.

Therefore:

$$
\begin{aligned}
CRF(i,n) &= 0.25 \\
\Delta P &= 3{,}057{,}100\ (dollars) \\
\Delta Y &= 28{,}125\ (dollars) \\
C &= 300{,}000\ Tons
\end{aligned}
$$

$$
\begin{aligned}
RFR &= \frac{0.25 \times 3{,}057{,}100 + 28{,}125}{300{,}000 \times 6} \\
&= \$.44 / ton
\end{aligned}
$$

In estimating the cost of treatment per ton of ballast water, the estimated annual operating costs of $28,125 is used. The approximate 4 million cubic feet of ballast is 128,000 tons. Six trips are made in ballast, which is a total of 768,000 tons treated. Therefore, cost of ballast water treatment is 3.7 cents per ton.

This ballast water treatment system is focused on treating the huge amounts of ballast water discharged into US harbours. It has the capacity to readily treat these huge quantities using standard marine components. For tankers that already have the major components on board, it would be very affordable. And for tankers with the AUPS spill containment, the added cost would be even less expensive.

Also, it appears (although not tested) that this system may be adequately effective in treating sediments. Ballast Water Exchange leaves sediment and other residue untreated. In fact, only the filtration concept treats sediment, by eliminating it.

Conclusions and recommendations

Conclusions

Based on the preliminary study, we conclude that a combination of hypoxia and elevated CO_2 levels are expected to kill in excess of 95% of marine phytoplankton, zooplankton, macroalgae, and invertebrates as required by the interim standard proposed by the US Congress. The treatment system proposed requires only off-the-shelf components which can be installed at pier side, without dry-docking. The system can be fully automated. Installing pH and oxygen sensors at multiple locations inside the tank can assure continuous remote monitoring of the ballast water.

Recommendations

It will be necessary to continue the laboratory tests, especially to include experiments on the effects of the system on phytoplankton, cysts and spores. In addition, the practical application of the system should be verified in a large scale effort using land based tanks or ballast water tanks in ships.

References

Barnhart, M.C. & McMahon, B.R. 1988. Depression of aerobic metabolism and intracellular pH by hypercapnia in land snails, *Otala lactea*. *J. exp. Biol.* 138, pp. 289-299.

Boyd, C.E. 1998. Pond water aeration systems. *Aquacultural Engineering* 18, pp. 9-40.

Bryant, C. 1991. *Metazoan life without oxygen*. London: Chapman and Hall.

Cangelosi, Allegra Nov. 14, 2002. Testimony Before the Joint Committee on Resources and Science of the U.S. House of Representatives.

Fenchel, T. & Finlay, B.J. 1995. *Ecology and evolution in anoxic worlds*. New York: Oxford University Press.

Glosten–Herbert-Hyde Marine April, 2002. *Full-Scale Design Studies of Ballast Water Treatment Systems*, Prepared for Great Lakes Ballast Technology Demonstration Project.

Grieshaber, M.K. 1994. Physiological and metabolic responses to hypoxia in invertebrates. In *Review of Physiology, Biochemistry, and Pharmacology*, vol. 125 (ed. M. P. e. a. Blaustein), pp. 43-147. Berlin, New York: Springer verlag.

Haugan, P.M. 1997. Impacts on the marine environment from direct and indirect ocean storage of CO_2. *Waste Management* 17, pp. 323-327.

Hinga, K. 2002. Effects of pH on coastal marine phytoplankton. *Mar. Ecol. Prog. Ser.* 238: pp. 281-300.

Huesemann, M.H., Skilmann, A.D. & Crecelius, E. A. 2002. The inhibition of marine nitrification by ocean disposal of carbon dioxide. *Mar. Poll. Bull.* 44, pp. 142-148.

Husain, M., Apple, R., Thompson, G. & Sharpe, R. 2001. Full Scale Test, American Underpressure System (AUPS) on *USNS Shoshone*, Presented to Northern California Section, SNAME, September 2001.

Johnson, P.D. & McMahon, R.F. 1998. Effects of temperature and chronic hypoxia on survivorship of the zebra mussel (*Dreissena polymorpha*) and Asian clam (*Corbicula fluminea*). *Can. J. Aquat. Sci.* 55, pp. 1564-1572.

Langenbuch, M. & Poertner, H.O. 2002. Changes in metabolic rate and N excretion in the marine invertebrate *Sipunculus nudus* under conditions of environmental hypercapnia: identifying effective acid-base variables. *J. exp. Biol.* 205, 1153-1160.

Laudien, J., Schiedek, D., Brey, T., Poertner, H.-O. & Arntz, W.E. 2002. Survivorship of juvenile surf clams *Donax serra* (*Bivalvia, Donacidae*) exposed to severe hypoxia and hydrogen sulphide. *J. exp. mar. biol. ecol.* 271, pp. 9-23.

Mackey, T.P., Tagg, R.D., Parsons, M.G., May, 2000. Technologies for Ballast Water Management, *Proc. 8th ICMES/SNAME New York Metropolitan Section Symp*.

Matthews, M.A. & McMahon, R.F. 1999. Effects of temperature and temperature acclimation on survival of Zebra mussels (*Dreissena polymorpha*) and asian clams (*Corbicula fluminea*) under extreme hypoxia. *J. Moll. Stud.* 65, pp. 317-325.

McMahon, R.F. 2002. Evolutionary and physiological adaptations of aquatic invasive animals: selection versus resistance. *Can. J. Fish. Aquat. Sci.* 59.

McMahon, R.F., Matthews, M.A., Shaffer, L.R. & Johnson, P.D. 1995. Effects of elevated carbon dioxide concentrations on survivorship in zebra mussels (*Dreissena polymorpha*) and Asian clams (*Corbicula fluminea*). In *The fifth international zebra mussel and other aquatic nuisance organisms conference*, pp. 319-336. Toronto, Canada.

Mickel, T.J. & Childress, J.J. 1978. The effect of pH on oxygen consumption and activity in the bathypelagic mysid *Gnathophausia ingrens*. *Bio. Bull.* 154, pp. 138-147.

NAISA 2002. *National Aquatic Invasive Species Act of 2002 – Summary*, Current as of September 24, 2002.

Noble, R.W., Kwiatkowski, L.D., De Young, A., Davis, B.J., Haedrich, R.L., Tam, L.T. & Riggs, A.F. 1986. Functional properties of hemoglobins from deep-sea fish correlations with depth distribution and presence of a swim bladder. *Biochem. Biophys. Acta* 870, pp. 552-563.

Omori, M., Norman, C.P. and Ikeda, T. 1998. Oceanic disposal of CO_2: Potential effects on deep-sea plankton and micronekton- a review. *Plankton Biol. Ecol.* 45, 87-99.

Perry, R.H., Green, D.W., Maloney, G.O. *Perry's Chemical Engineer's Handbook*, 5th Ed., McGraw Hill, 1984.

Poertner, H.-O., Bock, C. & Reipschlaeger, A. 2000. Modulation of the cost of pHi regulation during metabolic depression: A $_{31}$P-NMR study in invertebrate (*Sipunculus nudus*) isolated muscle. *J. exp. Biol.* 203, pp. 2417-2428.

Poertner, H.-O., Reipschlaeger, A. & Heisler, N. 1998. Acid-base regulation, metabolism and energetics in *Sipunculus nudus* as a function of ambient carbon dioxide level. *J. exp. Biol.* 201, 43-55.

Rees, B.B. & Hand, S.C. 1990. Heat dissipation, gas exchange and acid-base status in the land snail *Oreohelix* during short-term estivation. *J. exp. Biol.* 152, pp. 77-92.

Reipschlaeger, A. & Poertner, H.-O. 1996. Metabolic depression during environmental stress: The role of extracellular versus intracellular pH in *Sipunculus nudus*. *J. exp. Biol.* 199, pp. 1801-1807.

Seibel, B.A. & Walsh, P.J. 2001. Potential impacts of CO_2 injection on deep-sea biota. *Science* 294, pp. 319-320.

Tamburri, M.N., Peltzer, E.T., Friederich, G.E., Aya, I., Yamane, K. & Brewer, P.G. 2000. A field study of the effects of CO_2 ocean disposal on mobile deep-sea animals. *Mar. Chem.* 72, pp. 95-101.

Tamburri, M.N., Wasson K., & Matsuda, M. 2002. Ballast water deoxygenation can prevent aquatic introductions while reducing ship corrosion. *Biological Conservation.* 103, pp. 331-341.

Watanabe, Y., Ishida, H., Yamaguchi, A. & Ishizaka, J. 2001. III-5. Effects of high concentration of CO2 on deep-sea plankton. *Nippon Suisan Gakkaishi* 67, pp. 764-765.

Yamada, Y. & Ikeda, T. 1999. Acute toxicity of lowered pH to some oceanic zooplankton. *Plankton Biol. Ecol.* 46, pp. 62-67.

Nomenclature

c	concentration of carbon dioxide in the water, including ions produced by electrolytic dissociation.
g	acceleration due to gravity.
h	concentration of hydrogen ions in the water.
K	dissociation constant of carbonic acid ($=4.3\times10^{-7}$ mol/liter).
k	reaction rate constant.
k_H	Henry's Law constant for oxygen ($=39.79\times10^{-6}$).
N	total number of bubbles generated.
n	total number of gas moles in the bubble.
n_{CO2}	number of moles of carbon dioxide in the bubble.
n_N	number of moles of nitrogen in the bubble.
p	total pressure inside the bubble.
p_{CO2}	partial pressure of carbon dioxide in the bubble.
Q	gas weight flow rate.
t	time.
u	bubble speed.
V_t	volume of the tank.
x	molar fraction of carbon dioxide in the bubble.
Y	weight fraction of oxygen in the water.
y	molar fraction of oxygen in the bubble.
ρ	density of the ballast water.

Superscript 0 refers to quantities in the gas bubble when it is first introduced into the tank.
Subscript 0 refers to quantities in the water at the time $t=0$.

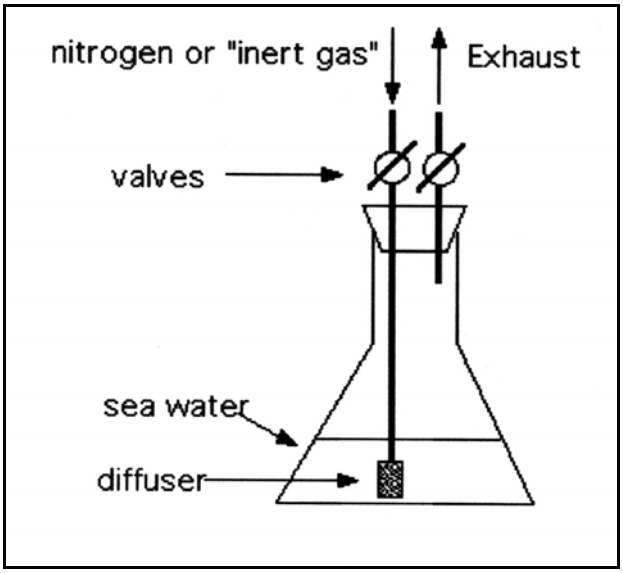


Figure 1. *Schematic of the experimental setup.*

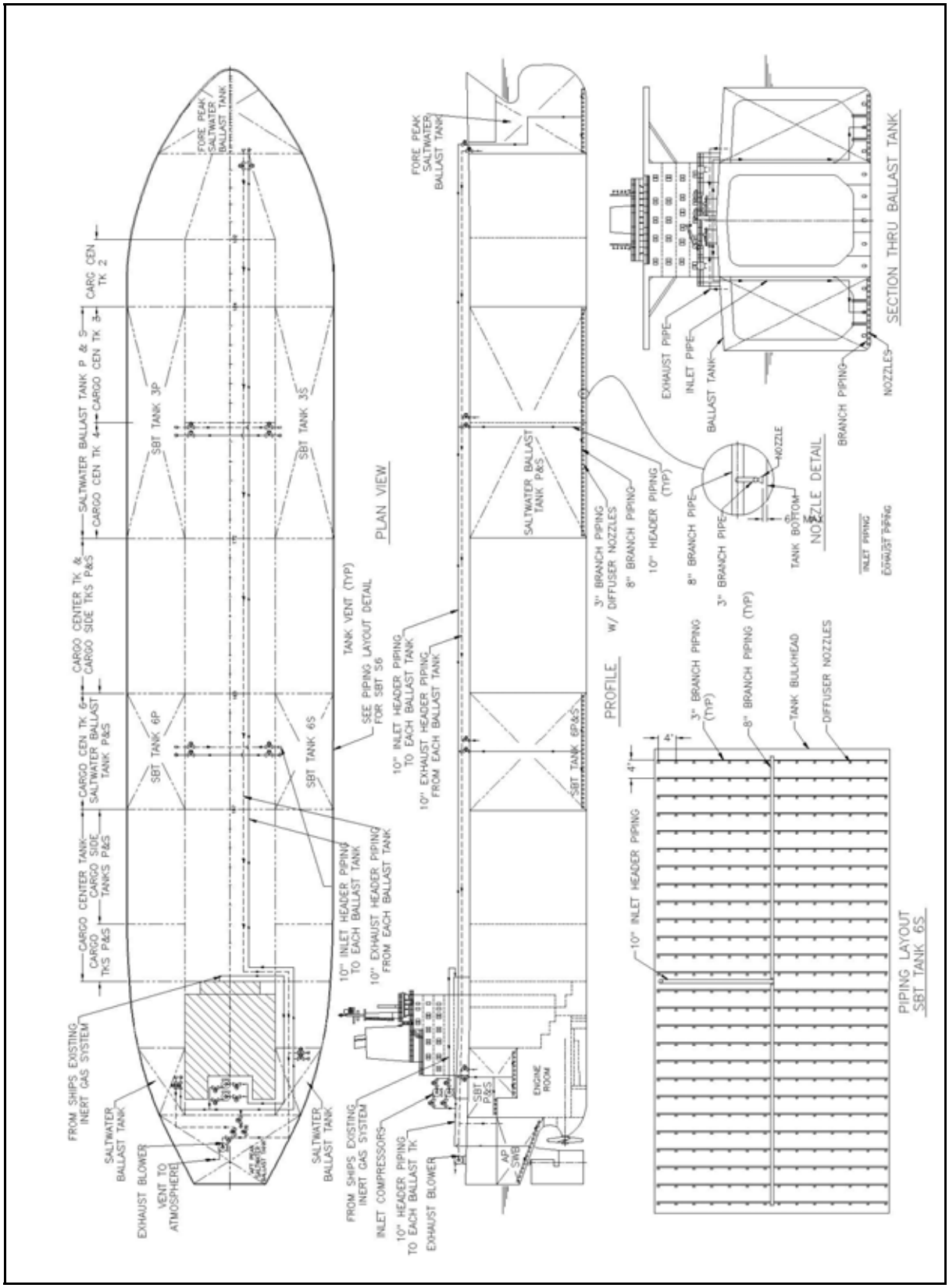


Figure 2. *Inboard profile, deck plan view, piping layout, nozzle details and ballast tank section view.*

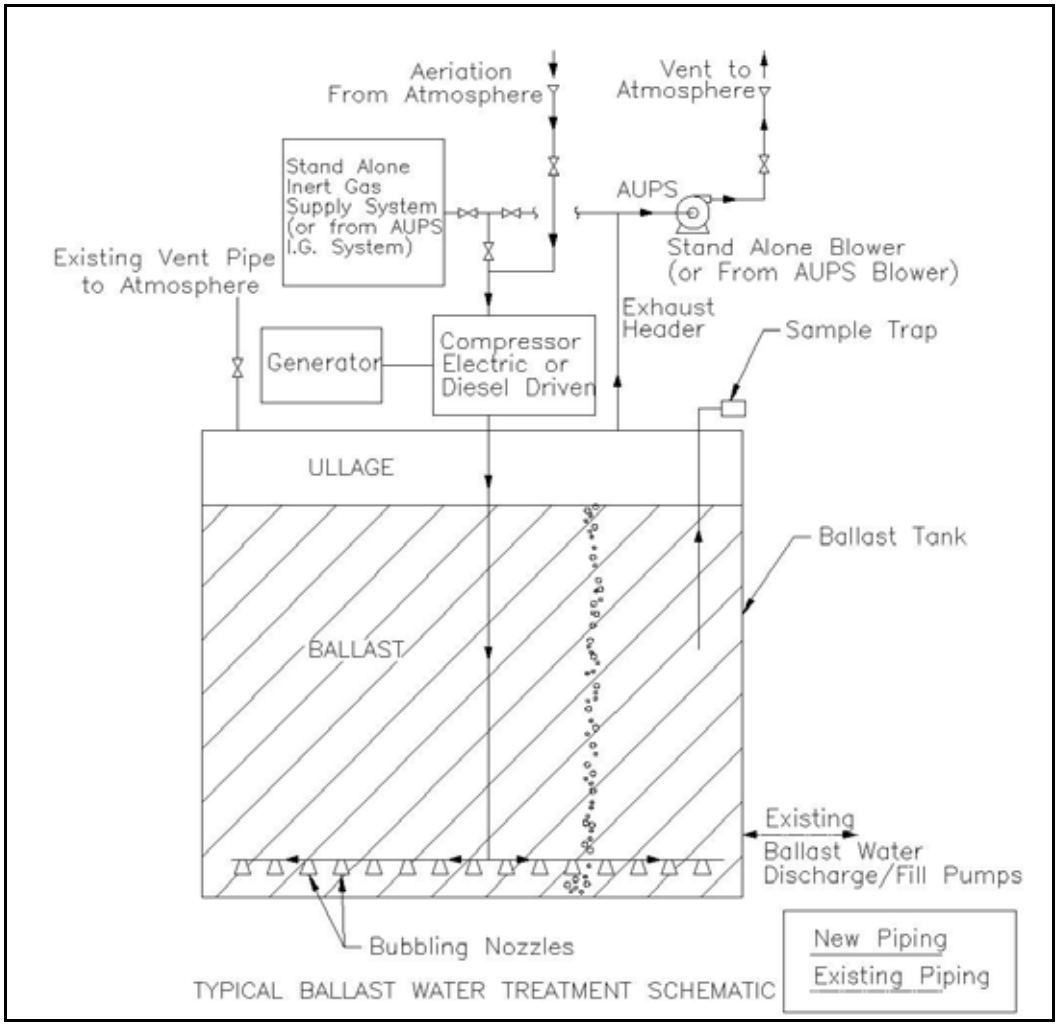


Figure 3. *Typical ballast water treatment schematic.*

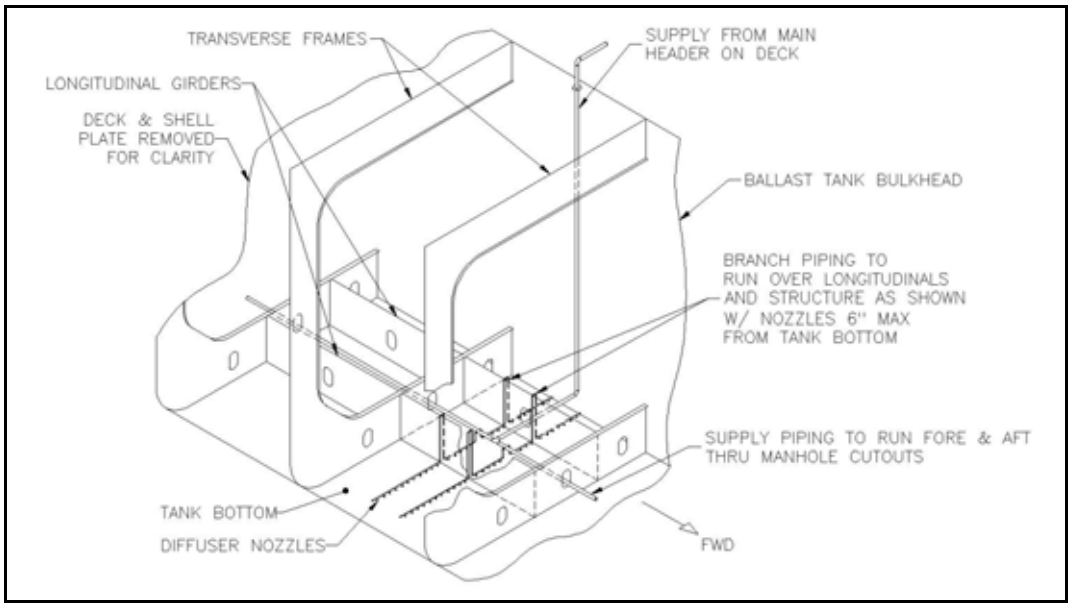


Figure 4. *Typical ballast treatment piping in a single hull tanker segregated ballast tank. In a double hull vessel, the piping system is simplified by installing the nozzle grid on the tank bottom without any structural interference.*

Session 2:
Heat and Electro-based Treatment Systems

Does heat offer a superior ballast water treatment option?

G. Rigby[1], G. Hallegraeff[2] & A. Taylor[3]

[1]*Reninna Pty Limited, Australia.*
rigby@mail.com

[2]*University of Tasmania*
hallegraeff@plant.utas.edu.au

[3]*Alan H Taylor & Associates, Australia*
aht@ahtaylor.com

Treatment options being researched

This work involves the use of heat treatment using various engineering designs to kill or inactivate harmful organisms present in ballast water

Timeframe of the project

The authors' interest in the effect of heat on ballast water organisms and the translation of laboratory results to practical designs for onboard implementation commenced in 1993. The first full scale shipboard trials were undertaken on the bulk carrier, *Iron Whyalla*, in 1998. Further ongoing work has continued to refine biological temperature thresholds and alternative designs as a means of extending this technique to a wider range of vessels and voyages.

Aims and objectives of the project

The primary objective of the recent work has been to gain a better understanding of the biological effects of heat for the range of organisms and conditions likely to be encountered in ballast water and to extend the initial range of options and designs for future extension and implementation of this technology.

Background and introduction

Mandatory reporting and regulations now exist in many parts of the world for the management and control of ballast water to minimize the risks of translocating harmful organisms around the world (Rigby and Taylor 1993). The International Maritime Organisation's (IMO) Maritime Environmental Protection Committee (MEPC) Ballast Water Management Convention is in its final stagers of being drafted and is scheduled for submission to a Diplomatic Conference in February or March 2004 for the signing of the 'Final Act' of this Convention.

These regulations require each ship to have on board and implement a Ballast Water Management Plan (BWMP) that uses an approved management procedure. At the present time this generally involves the use of an accepted form of Ballast Water Exchange (BWE). In addition to BWE most Guidelines/Regulations (including the new IMO Draft Convention) have provision for the use of an alternative treatment option that complies with the approved standard for efficacy (the latter are yet to be defined and agreed in detail at the Diplomatic Conference).

BWE significantly reduces the number of organisms from the ballasting port being discharged into the receiving environment and hence is a step in the right direction in reducing the risk of the establishment of new inoculations establishing. In general, the BWE regulations stipulate that a water

exchange replacement efficiency of at least 95% be achieved. However for many ships and/or voyages, although this level of water exchange is achieved (or exceeded) the biological replacement efficiency for e.g. zooplankton may be considerably less than 95%. Furthermore, for some voyages, BWE can significantly increase the risk of possible establishments of harmful aquatic organisms as a result of taking on new organisms during the exchange process that may be more detrimental than those in the originally ballasted water (Rigby, 2001).

Even though insufficient information is currently available to estimate with certainty what constitutes a minimal viable inoculum for a biological establishment, it is widely recognized that the ultimate long term goal for ballast water treatment should be a 100% removal or inactivation of harmful organisms.

A variety of alternative technologies have been tested (Rigby & Taylor, 2001) and new options are continually being proposed as possible candidates. However at the present time, only limited success has been achieved in achieving superior performance to that available from BWE.

One of the difficulties in comparing the performance of alternative technologies arises from the fact that no standard for biological efficiency currently exists. A Standards Workshop organized by the Global Ballast Water Management Programme developed some suggestions in 2001 that were reviewed and modified at the subsequent meetings. However efforts to refine the standard have been hampered by the complexities involved in combining a practically achievable as well as a scientifically acceptable outcome both for the short term and long term and have only been partly successful to date using currently available best technology. To obtain an achievable starting point an initial standard might be based on an "equivalent" biological standard to that currently prescribed for BWE, i.e. 95% removal, kill or inactivation.

The issue of definition of "organisms" is yet another difficulty and the discussion in this paper will be restricted to more general comments based on currently available data, but will be primarily focused on zooplankton and phytoplankton observations. Although some concerns about possible risks from viruses and bacteria in ballast water have been expressed, it has generally been considered that these are of secondary concern in overall international operations and consequently research on treatment technologies has not included these organisms.

The most promising treatment option identified by the US National Research Council review for successful shipboard treatment was constant backwash filtration (NRC, 1996). Extensive research and demonstration studies have been undertaken internationally using this and other filtration systems to assess the effectiveness of this option. From work carried out so far, mean particle size count efficiencies of 91% have been achieved for particles above 50 μm (using a screen filter) and 91.6% for particles above 100 μm (disk filter) with wide variations in removal efficiencies for organisms with a mean of 90% for zooplankton (50 μm filter) and 50%-around 95% for phytoplankton (Parsons & Harkins, 2002; Cangelosi, 2002).

Like BWE, filtration, which is based on a physical separation process, is not directly linked to biological destruction but rather relies on the efficiency of size separation and the relationship between size and organism species for removal. Clearly this option has limitations in achieving what may be regarded as an acceptable level of biological efficiency. Likewise very few other treatment options have demonstrated an ability to achieve desirable results, especially at the scale of operations that will be required for many vessels (2000 to 20,000 m^3/h ballast water-or an equivalent total quantity of 25,000 to 200,000 m^3).

Heating ballast water to kill or inactivate ballast water organisms, although not yet formally accepted by IMO or any National Authority as an approved treatment option has been demonstrated in some full on-board at sea trials to be capable of destroying virtually all of the phytoplankton and zooplankton present in the ballast water, and as such offers a superior treatment option in cases where it can be used. This presentation reviews the current status of heat treatment research and development and recommends its acceptance as one of the superior options for future implementation.

Research methods and review of studies to date

The biological basis of heat to kill or inactivate marine organisms.

High temperatures induce denaturation of key proteins and compromise cell membrane structures through increased mobility of molecules, thereby inactivating metabolic processes vital to all known living organisms. As a general rule, the smallest organisms such as bacteria tend to be most heat resistant, because their minute protoplasm volume allows for less damage from heat-induced mobility of molecules.

Enterobacteria such as *Salmonella, Campylobacter* and *Escherichia*, which are adapted to living within warm blooded animals, require heat treatments of 60-70°C for complete inactivation. It has been well established that effective heat treatment is a probability function of both temperature and treatment time, e.g. milk pasteurisation can equally be achieved by 15 seconds at 72°C ("flash" pasteurisation) or 30 min at 63-66°C ("holding method"). There is no evidence that heat treatment has any cumulative effect on cells (Brock & Madigan, 1994). Among the enterobacteria, species that produce highly resistant endospores (e.g. *Clostridium botulinum*) are the most heat resistant. Autoclaving procedures widely used to sterilise laboratory and hospital equipment utilize heat treatment of 10-15 min at 121°C.

Table 1 lists lethal temperatures for a wide range of marine organisms, from bacteria, microalgae, seaweed spores, molluscs, starfish, brineshrimp to rotifers. A striking conclusion (Figure 1) is that most marine organisms, at least in a hydrated stage, can be killed at temperatures of 40-45°C, that is well below temperatures used in food treatment technology. The only exceptions are marine bacteria (commonly requiring 45-55°C), the smallest (<5 micron) diatoms and dehydrated brineshrimp cysts or rotifer eggs. Longer treatment times (hours to days) are generally more effective in achieving heat transfer into the interior of organisms than using short treatments at higher temperatures. An example of this is spraying of thick-walled oysters for 40 sec with 70°C water killed associated boring polychaetes, but did not sufficiently raise the core temperature of the oysters to kill them (Nel et al, 1996).

Concerns that heating ballast water to temperatures of 40-45°C would stimulate the growth of harmful bacteria have not been substantiated by simulated laboratory experiments (Desmarchelier & Wong, 1996). Bacterial growth at those temperatures would only be stimulated when contained in food products or nutrient broth, but *not* in nutrient starved seawater.

Table 2 summarises the studies and nature and observations from experimental studies that have been undertaken to date.

The fact that lower temperatures are generally required for longer treatment times means that appropriate temperatures can be selected for specific shipboard designs based on the nature and availability of heat from the ship's main engine or auxiliary sources together with the ballast water temperatures, pump and tank designs. These facets are explored in more detail in the design case studies that are included in this paper.

The original heat treatment proposals for use on ships (Rigby, 1994) recommended the use of waste heat from the ship's main engine cooling water system. The quantity of heat required to heat the total quantity of water on a large ship (50,000 to 100,000 tonnes) is large and to provide this from a stand alone independent heat source would be impractical and expensive. As an example, heating the 50,000 tonnes of ballast water on the *Iron Whyalla* on a once through basis (from 30°C to 45°C) during ballasting or deballasting) without any heat recovery would require approximately 70 MW power, which well exceeds the main engine power of 13.7 MW.

Table 1. *Summary of Lethal Temperatures for Marine Organisms.*

Organism	Acute (secs-mins)	Chronic (hrs-days)	Reference
MARINE BACTERIA			
Vibrio cholerae	≥55°C	45°C, 2-3 hrs in seawater but survived in nutrient broth	McCarthy 1996 Desmarchelier & Wong 1998
MICROALGAE			
Diatoms *Skeletonema costatum , Detonula pumila,Pseudo-nitzschia cuspidata, Thalassiosira rotula*	35°C, 30-60 min		Marshall & Hallegraeff (original data); Forbes & Hallegraeff 2001
Small diatoms *Amphora, Navicula jeffreyi*	35°C, 5 hr (*Nitzschia paleaceae* survived)		Forbes & Hallegraeff 2002
Raphidophyte *Heterosigma akashiwo*	35°C, 5 hr		Marshall & Hallegraeff (original data)
Picoplankton Nannochloropsis oculata	42.5°C, 3 hr		Marshall & Hallegraeff (original data)
Chlorophyte *Dunaliella tertiolecta*	42.5°C, 24 hr		Marshall & Hallegraeff (original data)
Dinoflagellate *Amphidinium carterae*	35°C, 30 min		Marshall & Hallegraeff (original data)
Dinoflagellate *Alexandrium*	45°C, 3 min		Montani et al. 1995
Alexandrium catenella dinocysts	42°C, 30 min	38°C, 4.5hr	Hallegraeff et al.1997
Gymnodinium catenatum dinocysts	40-45°C, 30-60 sec	35-37.5°C, 1-2 hr	Hallegraeff et al.1997
SEAWEED			
Undaria pinnatifida spores	35-40°C, 0.9-42 min		Mountfort et al.1999
MOLLUSCS			
Dreissena polymorpha (adult)	36°C, 10 min	32°C , 3hr 33°C,1.5hr	Jenner & Janssen-Mommen 1992
Crassostrea gigas (larvae)	40-48°C, 6-97 min		Mountfort et al.1999
Crassostrea virginica	48.5°C		Sellers & Stanley 1989
Mytilus edulis	40°C, 0,33 hr		Johnson et al. 1983
Corbicula fluminea	44°C (instantaneous)		Graney et al. 1983
Perna viridis	43°C, 30 min		
STARFISH			
Coscinasterias calamaria (larvae)	39-44°C, 1-35 min		Mountfort et al.1999
CRUSTACEAN			
Artemia salina (hydrated eggs)	42.5°C, 48 h (dry eggs survive)		Marshall & Hallegraeff (original data)
ROTIFER			
Brachionus	42.5°C, 1h (eggs survive)		Marshall & Hallegraeff (original data)

Table 2. *Summary of heat treatment studies undertaken to date.*

Research Group	Nature of studies	Summary of results and observations
Bolch and Hallegraeff 1993 Rigby and Hallegraeff 1994 Rigby 1994, Hallegraeff et al. 1997 Rigby et al.1998, 1999	Laboratory studies to evaluate the effects of heat on dinoflagellate cysts Biological observations of organisms in heated ocean engine cooling water Design evaluation for heating ballast tank water on *Iron Whyalla* –further laboratory tests for effect of extended times on temperature thresholds Full scale trials on *Iron Whyalla*	*Gymnodinium catenatum* cysts killed at 40-45°C for 90-30 s, lower temperatures less effective No survival of phytoplankton and zooplankton Identified sufficient waste heat from main engine to heat all ballast water to 38°C - most phytoplankton algae tested in vegetative stage killed at 35°C for 30m-several h; total mortality of *G. catenatum* and *A. catanella* cysts at 38°C after 4.5 h. All zooplankton and almost all phytoplankton destroyed-original organisms reduced to amorphous flocculent detritus. Combined actions of flushing and heating give dual treatment in single operation
Sobol et al., 1995	Suggested shipboard design using engine hot water and steam to heat ballast water to 70°C with three additional heat exchangers	Not tested on board ship, but identified feasibility using design details provided
Thornton, 2000	Shipboard design using additional heat exchanger and holding tank to heat ballast water to 65°C	Small scale system (20m^3/h) tested on MV *Sandra Marie*. Plankton mortality of 80-90% achieved-rough seas caused problems and tank mixing not monitored
Mountfort et al., 1999, 2000, 2001	Laboratory and shipboard studies with model organisms including larval mollusks, starfish and seaweed spores	Temperature/time regimes identified for mortality; long (≥16h at ≤36°C), medium (10 min to 16h at 36-45°C, short (≤10min at ≥46°C). Trials on *Union Rotama* at 38°C resulted in all organisms being killed. Trials on the M/T *Iver Stream* identified need for effective mixing in tanks
Zhou, 2002 and MARTOB, 2003	Laboratory and crude oil tanker shipboard design for rapid heating ballast water to 65°C	Ship design using waste heat from steam discharged from cargo pumps identified effective heating can be achieved during ballast water discharge-design not tested yet –laboratory studies using model organisms suggest a treatment temperature of 50-55°C should be suitable

However 21% of the main engine power (5.71 MW) is discharged in the form of waste heat imparted to ocean water used to cool the main engine. It was on the basis that this waste energy is available without the use of additional fuel, that the original concepts of water heating were developed. Energy balances and engine thermal efficiencies vary widely for different ships based on heat recovery and utilization, sea water temperatures, ballast water pump capacities and drive arrangements as well as operational requirements. Consequently the nature and feasibility of using this mode of ballast water treatment requires a detailed analysis of the specific requirements and ship design features. A number of these aspects are explored in the case studies below.

Case Study 1

Heating/flushing on the Iron Whyalla

In this study, in addition to achieving a practical design suited to the normal operation of this ship, two shipboard trials were undertaken in one of the sets of ballast tanks (topside, trunk and double bottom, containing 6350 tonnes water) on the BHP owned bulk carrier, *Iron Whyalla* – loaded DWT 141,475 tonnes (Rigby et al, 1998). Analysis of the waste energy available from the main engine cooling system, together with the ship's usual voyage schedule, and ballast water temperature history and laboratory investigations to identify the desirable temperature/time conditions required to kill the major organisms likely to be of concern, identified that flushing the heated engine cooling ocean water through the tanks and allowing the excess to overflow through the breather pipes would be the best option (Figure 2).

In these trials heated water at approximately 41°C was flushed through the tank at a flowrate of 520 tonnes per hour. Figure 3 shows how the temperatures in various parts of the treatment tank increased and at the end of the first trial (after 30 hours and 2.5 tank volumes of flushing) the entire tank contents has exceeded temperatures of 38°C (Rigby et al, 1998).

On board biological observations and subsequent culturing showed that none of the zooplankton present (mainly chaetognaths and copepods) and only very limited original phytoplankton (mainly dinoflagellates) survived the heat treatment. The original organisms were all essentially reduced to flocculent amorphous detritus. Subsequent culturing on samples only produced growth of some small (5 μm) diatoms and colourless ciliates which are considered likely to be of little consequence.

Another very significant aspect of this mode of heating is that the flushing (especially with ocean water that had been heated to some 42°C) in itself is very effective in exchanging the original water. In the above trial, 90-99% of the original plankton was removed by flushing.

Only minor modifications were necessary on the ship to allow the heating operation to be carried out. The installation of an additional piece of pipework allowed the overflow water to be pumped via the existing general services pump. This modification and the operating procedures were approved by the ship's Classification Society. The estimated total cost of carrying out this treatment (including the capital cost for the additional pipe installation) has been estimated as $5.56^{c}/m^3$ (capital $0.9^{c}/m^3$, operating $4.66^{c}/m^3$). The equivalent cost for ballast exchange using continuous flushing with three tank volumes would be $3.74^{c}/m^3$ (Rigby & Taylor, 2001).

Based on the successful outcome of this trial together with the quite acceptable cost involved in this form of ballast treatment, it would be potentially feasible to apply this mode of treatment with a highly superior biological efficiency (compared to BWE) to most of the international ballast water (≈120 million tones annually, Kerr 1994) transported to Australian ports in bulk carriers.

In addition to the added feature of flushing with biologically deficient water, this mode of heating ensures that all of the water in the tank reaches the final minimum temperature of 38-40°C. Some of the other options (discussed below and referred to in Table 2) involve recycling water from the ballast tanks and in these cases mixing becomes an important issue in achieving treatment of all the water (and organisms) in the tank. Another feature of the flushing mode is that the temperatures in the lower sections of the tank reach a much higher temperature than the overall final minimum temperature. This means that the sediment (and any contained biological organisms) are heated to a temperature approaching that of the inlet water thereby enhancing the effect of destroying organisms in accumulated sediments.

Other requirements for this form of flushing are sufficient voyage time to allow all tanks to be heated to the desired temperature (approximately 8 days for the *Iron Whyalla*) and a temperature differential between the initial ballast water and desired final temperature compatible with the amount of energy available in the heated engine cooling water (approximately 14.5°C for the *Iron Whyalla*). Where these conditions are not met, such as in colder seas or short voyages, an alternative form of heating (as detailed below) would be required.

Case Study 2

Heating/recycling on the Iron Whyalla

Although this design has not been tested on the ship, it illustrates an alternative to that used above which would permit the water to be treated over a shorter voyage time and would be compatible with lower ocean temperatures. A higher final temperature is also included to demonstrate this possibility.

In this case, it is assumed that the starting water temperature is 20°C and is heated to 45-50°C. Ballast water is recirculated from the ballast tanks through an additional preheater where it is heated to 35°C before entering the main jacket water coolers where it reaches a temperature of 45-48°C. This heated water is then returned to the top of the ballast tank (either via the appropriate length of pipe or via a tank depending on the biological requirements for time/temperature) after passing through the preheater where the water is cooled to approximately 30°C (Figure 4).

Although some small scale trials (Thornton, 2000; Mountfort et al, 1999, 2000, 2001) have attempted to test this basic arrangement, equipment or trial conditions have not allowed the full concept to be proven. One of the main areas to be explored is the mixing of the treated water within the ballast tank after recirculation. Further trials are necessary to identify the specific requirements, however it is expected that 50,000 tonnes could be treated successfully over a period of approximately 4-5 days. Shorter times could be achieved by utilizing additional heat to allow higher recirculation rates.

This design also has the ability to treat ballast water at significantly lower starting temperatures, simply by cooling the treated water to a lower end temperature. For example if the initial temperature was 10°C, the end temperature before recycling back to the ballast tank would be 20°C (compared to 30°C for the earlier example).

The estimated cost of treating the water on the *Iron Whyalla* using this system has been estimated (Rigby and Taylor, 2001) as 9.13 $^{c}/m^{3}$ (capital 6.6 $^{c}/m^{3}$, operating 2.53 $^{c}/m^{3}$). This compares with an estimated total cost of 28 $^{c}/m^{3}$ for the combined use of filtration and ultraviolet irradiation using similar cost estimation parameters (capital 27.14 $^{c}/m^{3}$, operating 0.86 $^{c}/m^{3}$).

Case Study 3

Heating ballast water during discharge on an oil tanker

Zhou (2002) has examined this case for an "Aframax" 107,000 DWT oil tanker owned by Neptune Orient Lines. The tanker has a total ballast water capacity of 41,262 m^{3}. The vessel uses steam driven cargo pumps to discharge the oil product. Waste heat from the condensed steam used to drive these pumps can be used to heat the ballast water as it is discharged (Figure 5). In this study it has been assumed that the water needs to be heated to 65°C and this requires additional heat (over that available from the condenser) which can be obtained from an auxiliary boiler. Using this system the ballast water can be discharged at its normal capacity of 2,580 t/h over a total pumping tome of approximately 16 hours.

Using a similar cost basis to that used for the *Iron Whyalla* analysis (Rigby and Taylor, 2001), the estimated total cost for heating the water on this tanker would be approximately 22.44 $^{c}/m^{3}$ (capital 16.9 $^{c}/m^{3}$, operating (for additional steam cost only 5.54 $^{c}/m^{3}$).

Based on the information contained in Table 2 related to temperatures required for effective biological control, the temperature of 65°C chosen for this study is considered to be excessive and it is likely that the costs would be lower if a lower temperature (45°C) were used.

Case Study 4

Container ship

In the case of container ships, only small amounts of ballast water are involved when compared to bulk oil or ore carriers. The ballast water is usually carried in a large number of tanks (27 ballast tanks carrying 12,300 tonnes for a 3,950 TEU container ship, for example, fitted with two 550 m^{3}/h ballast pumps powered by a 47,520 BHP main engine). Container ships are designed to never be empty in service and therefore only small amounts of ballast water may be loaded or unloaded at any one time to ensure trim, stability, propeller immersion and visibility over the bow. They also use ballast water to maintain the ship in a vertical envelope to allow the container to be slotted into the guides and clearance under the gantry cranes whilst loading and discharging.

This heating application would also be ideally suited to passenger ships which also carry a small quantity of ballast water.

These design and operational arrangements for ballast water mean that main engine cooling water heating is an ideal method for treatment since the process can be carried out at low flow rates utilizing

only partial quantities of the heated water. This operation can be used over a short period or extended periods of time to ensure that "biologically acceptable" water is available for discharge when it is required. A number of options based on the above cases could be adopted, although the flushing option has many advantages due to the lower capital costs of additional equipment that may be required.

Case Study 5

Use of heated engine cooling water as a preferred method of ballast exchange

This case offers a biologically superior treatment option for vessels that have sufficient strength to permit the empty-refill mode of ballast water exchange to be used.

The option would involve firstly pumping the ballast water from a particular tank until it is empty (loss of pump suction). At this stage hot water from the engine cooling system (at a temperature of around 45°C and already biologically deficient as a result of being heated to this temperature) is then used to refill the tank. The process is continued in a sequential pattern until all the original ballast water has been replaced. In general this process would require longer times than the normal refill operation but offers a superior option in cases where the safety of the ship can be guaranteed.

This method would be ideally suited to container and passenger ships that carry small quantities of ballast water in a large number of tanks. The most suitable method would be to undertake this type of treatment in matched port and starboard tanks, mindful of the bending moment, shear forces and stability of the vessels.

Conclusions and Recommendations

Ballast water organisms that have the potential to initiate new invasions can be effectively killed or inactivated by heating them to a temperature sufficient to inactivate the metabolic processes. The lethal temperature required varies for different organisms, however as a general rule, for most marine organisms of concern in ballast water, a temperature of 40-45°C is sufficient to achieve mortality. Longer periods at lower temperatures are generally more effective than using short treatments at higher temperatures.

Heating of ballast water using waste heat from the ship's main engine cooling system, high and low temperature centralised cooling water system, auxiliary steam condenser cooling water auxiliary boiler or other heat sources available can achieve the required conditions for a large proportion of ships operating on both domestic and international voyages. A variety of designs are possible for a wide range of ships to optimize the heat availability, voyage duration, sea temperatures and other operating parameters. A series of case studies have illustrated a number of possible options, however specific designs need to be considered for each ship based on the criteria outlined above.

Full scale shipboard trials using a combined flushing and heating design have demonstrated high levels of biological and cost effectiveness with a superior performance to typical ballast water exchange and other treatment options currently available. Other heating designs suitable for different voyage conditions and ship energy balances require further exploration and trials to demonstrate and confirm effectiveness.

Heating offers a potential ballast water treatment option and can make a significant contribution to the future elimination of biological threats from ballast water discharges.

References

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

Brock, T.D. and Madigan, M.T. (1994). *Biology of microorganisms*. 6th edition.Prentice Hall, USA.

Cangelosi, A. 2002. Filtration as a ballast water treatment measure. In *Invasive Aquatic Species of Europe. Distribution, Impacts and Management*. Leppakoski, E., Gollasch, S., & Olenin, S. (Ed.) Kluwer Academic Publishers, Dordrecht, pp.511-519.

Desmarchelier P. and Wong, F. 1998. *The potential for Vibrio cholerae to translocate and establish in Australian waters*. AQIS Ballast water Research Series, Report No. 10. 45pp.

Forbes, E. & Hallegraeff, G.M. 2002. Transport of potentially toxic *Pseudo-nitzschia* diatom species via ships' ballast water. In: *Proceedings from the 15th International Diatom Symposium, Perth 1998 (J.John, ed.)*. Gantner Verlag. pp. 509-520.

Graney, R.L., Cherry, D.S. & Cairns, J. 1983. Heavy metal indicator potential of the Asiatic clam (Corbula fluminea) in artificial stream systems. *Hydrobiologia* 102, pp. 81-88.

Hallegraeff, G.M., Vallentine, J.P., Marshall, J.A. & Bolch, C.J. 1997. Temperature tolerances of toxic dinoflagellate cysts: application to the treatment of ships' ballast water. *Aquatic Ecology* 31, pp. 47-52.

Hallegraeff, G.M. 1998. Transport of toxic dinoflagellates via ships' ballast water: bioeconomic risk assessment and efficacy of possible ballast water management strategies. *Mar. Ecol. Prog. Ser*. 168: pp. 297-309.

Jenner, H.A. & Janssen-Mommen, J.P.M. 1993. Monitoring and control of *Dreissena polymorpha* and other macrofouling bivalves in the Netherlands. In: Nalepa, T.F. & Schloesser, P.W. (eds), *Zebra Mussels: Biology, Impacts and Control*, pp. 537-554. Lewis Pubs.

Johnson, G., Foerth, J., Keser, M. and Johnson, B. (1983). Thermal backwash as a method of macrofouling control at Millstone Nuclear Power Station, Waterford, Connecticut, USA. In: Dias-Tous, I.A., Miller, M.J .& Mussalli, Y.G. (ed), *Symposium on condensor macrofouling control technologies: The state of the art, CS-3343, Electric Power Research Institute, Palo Alto, CA*, 25-1-25-15.

Kerr, S. 1994. *Ballast water ports and shipping study.* Agriculture, Fisheries and Forestry – Australia Ballast Water Research Series, Report No. 5, Feb.

McCarthy, S.A. 1996. Effects of temperature and salinity on survival of toxigenic *Vibrio cholerae* O1 in seawater. *Microbial Ecology* 31, pp. 167-175.

MARTOB. 2003. On board treatment of ballast water (technologies development and applications) and application of low-sulphur marine fuel. Work Package 3 Completion Report. DTR-3.11-VTT-03.03. www.marinetech.ncl.ac.uk/research/martob.

Montani, S., Meksumpun, S & Ichimi, K. 1995. Chemical and physical treatments for destruction of phytoflagellate cysts. *Journal of Marine Biotechnology*. 2: pp. 179-181.

Mountfort, D., Dodgshun, T & Taylor, M. 2001. Ballast water treatment by heat-New Zealand laboratory and shipboard trials. *Proc. 1st International Ballast Water Treatment R&D Symposium. IMO, London, 26-27 March*, pp. 45-50.

Mountfort, D.O., Dodgshun, T., Gibbs, W. and McCallin, B. 1999. *Towards a feasible heat treatment system for ships' ballast water. Proc. Workshop on Ballast Water Problem-Where to from here?* Ports Corp. of Qld. EcoPorts Monograph Ser. No. 19. July.

Mountfort, D.O., Hay, C., Taylor, M., Buchanan, S. & Gibbs, W. 2000. Heat treatment of ship's ballast water: development of a model based on laboratory studies. *J. Marine Env. Engg*. 5, pp. 193-206.

Nel, R., Coetzee, P.S. & Vanniekerk, G. 1996. The evaluation of two treatments to reduce mud worm (Polydora hoplura Claparede) infestation in commercially reared oysters (Crassostrea gigas Thunberg). *Aquaculture* 141, pp. 31-39.

NRC 1996. *Stemming the tide. Controlling introductions of nonindigenous species by ships' ballast water*. National Academy Press, Washington, DC USA. 141pp.

Parsons, M.G. & Harkins, R.W. 2002. Full-scale particle removal performance of three types of mechanical separation devices for the primary treatment of ballast water. *Marine Technology*, 39, 4, pp. 211-222.

Rigby, G.R. 2001. Ocean exchange as a means of mitigating the risks of translocating ballast water organisms – a review of progress ten years down the line. *J. Marine. Env. Engg.* 6, pp. 153-173.

Rigby, G.R. & Taylor, A.H. 2001. *Ballast water treatment to minimise the risks of introducing nonindigenous marine organisms into Australian ports. Review of current technologies and comparative costs of practical options*. Agriculture, Fisheries and Forestry – Australia Ballast Water Research Series, Report No. 13, Jan.

Rigby, G.R. 1994. Possible solutions to the ballast water problem, *AQIS Ballast Water Symposium Proceedings, Canberra 11-13 May*.

Rigby, G.R. & Hallegraeff, G.M. 1994. The transfer and control of harmful marine organisms in shipping ballast water: behaviour of marine plankton and ballast water exchange on the MV "Iron Whyalla". *J. Marine Env. Engg*., 1: pp. 91-110.

Rigby, G.R., Hallegraeff, G.M & Sutton, C.A. 1998. *Novel ballast water heating and sampling trials on the BHP ship MV Iron Whyalla.* AQIS Ballast Water Research Series, Report No.11. Oct.

Rigby, G.R., Hallegraeff, G.M. & Sutton, C.A. 1999 Novel ballast water heating technique offers cost-effective treatment to reduce the risk of global transport of harmful marine organisms. *Mar. Ecol. Prog. Ser*. 191: pp. 289-293.

Sellers, M.A. & Stanley, J.G. 1989. *Species profiles: Life histories and environmental requirements of coastal fishes and invertebrates (North Atlantic). American oyster*. FWS/OBS-82/11.23, US Fish.and Wildlife Service, Washington, DC. and US Army Engineering Waterways Experiment Station.

Sobol, Z., Wladyslaw, K. & Bohdan, W. 1995. *System for destruction of microorganisms occurring in ballast waters*. Paper presented at IMO MEPC 38.

Zhou, P. 2002. A rapid thermal ballast water treatment system for oil tankers. *Proc. RECSO/IMO Joint Regional Seminar on Tanker Ballast Water Management & Technologies, Burj Al Arab, Dubai, U.A.E.* pp. 107-114.

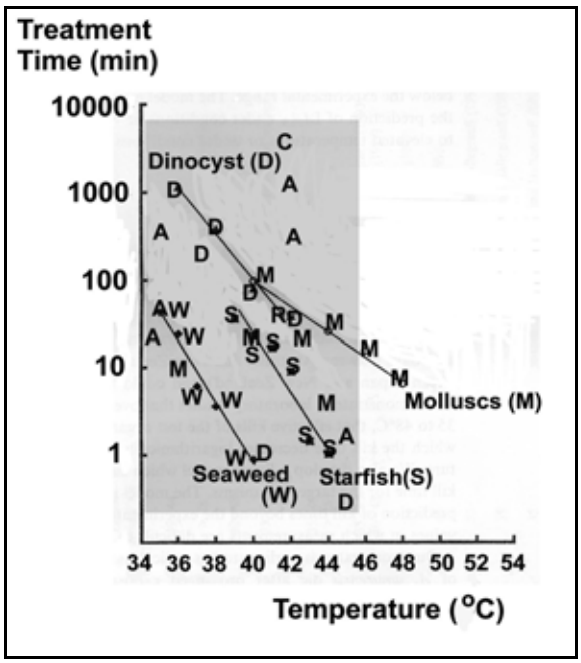


Figure 1. *Relationship between treatment time (plotted on a logarithmic scale; in minutes) and lethal temperatures (°C) for a wide range of marine organisms. The solid lines for dinoflagellate cysts (D), seaweeds (W) , starfish (S) and molluscs (M) are based on Mountfort et al. (1999) supplemented by data for vegetative stages of microalgae (A), crustaceans (C) and rotifers (R) as specified in Table 1. The overwhelming majority of marine organisms can be killed utilising temperatures of 40-45°C in combination with treatment times of 100-1000 mins.*

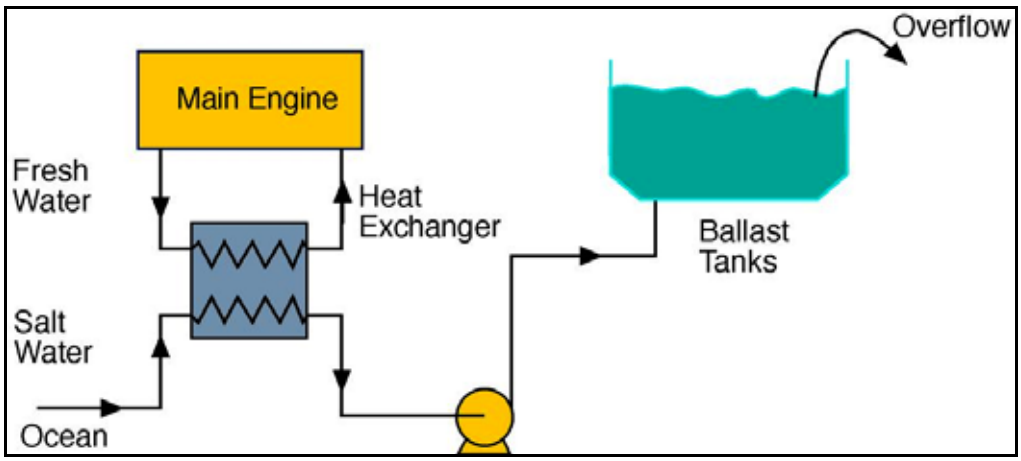


Figure 2. *Heating circuit used to simultaneously flush and heat ballast water on the* Iron Whyalla *(Rigby et al. 1999).*

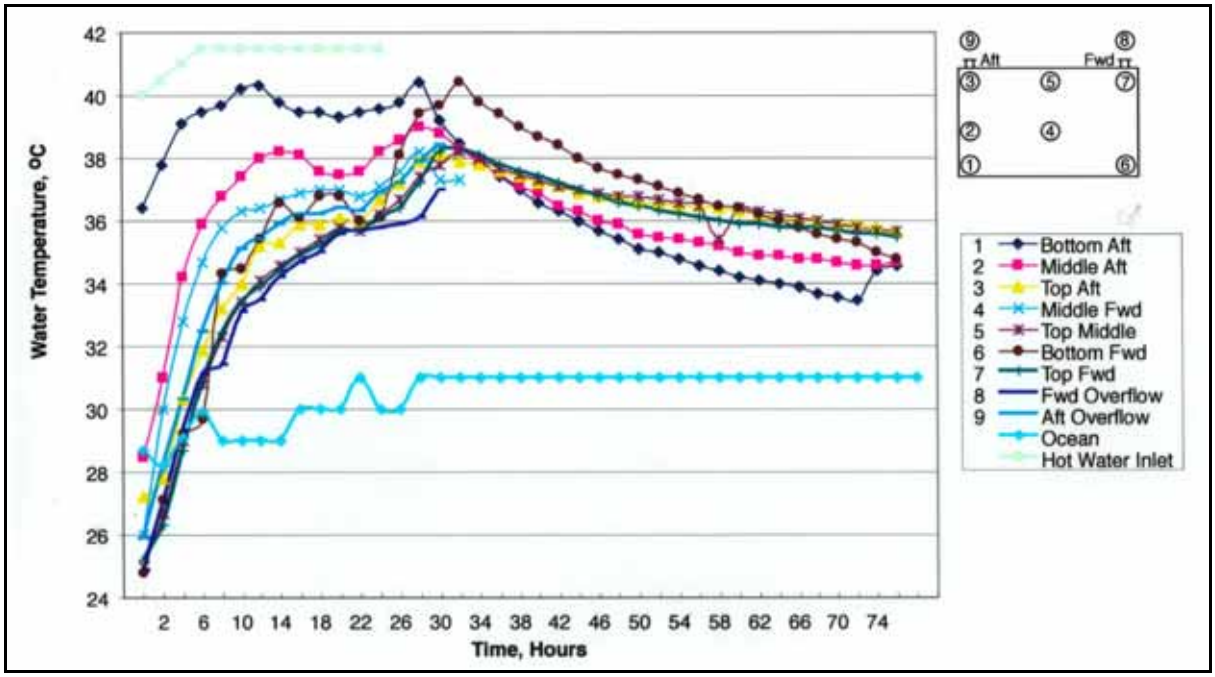


Figure 3. *Tank temperatures during one of the heat treatment trials on the* Iron Whyalla.

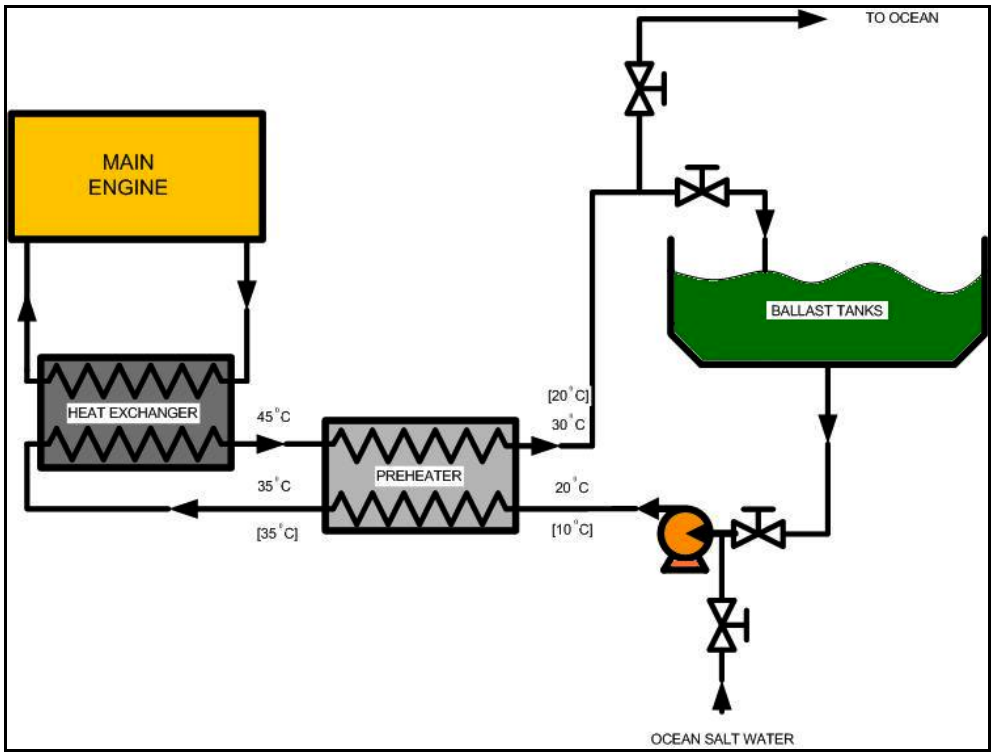


Figure 4. *Heating system involving recirculation of ballast water from the ballast tanks and recovery of heat using an additional heat exchanger.*

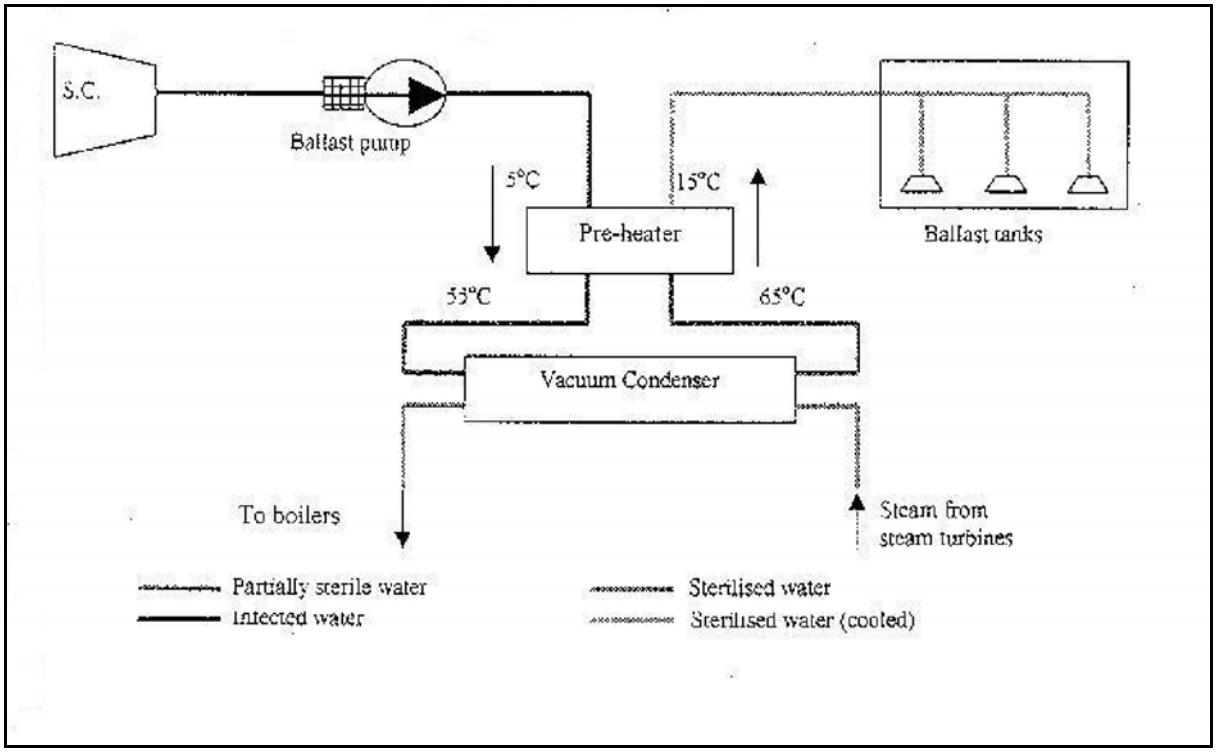


Figure 5. *System proposed by Zhou (2002) for heating ballast water during deballasting.*

Treatment of residual ballast water in the NOBOB ship using heat

D.T. Stocks[1], M. O'Reilly[2], & W. McCracken[3]

[1]*BMT Fleet Technology Ltd, Canada*
dstocks@fleetech.com

[2]*ESG Stantec Consulting Inc, Canada*

[3]*Consultant, USA*

Introduction

The majority of ships entering and leaving the Great Lakes do so loaded with cargo and therefore report a "no ballast on board" condition. However, as a result of ballast tank design, residual materials (ballast water, sediment, and biota) still remain in the bottom of the tanks when emptied. During their visit to the Great Lakes, NOBOB ships invariably take on ballast water during cargo discharge and loading operations. This exposes the tank residuals, which may contain invasive biota, to discharge through re-suspension in the outgoing ballast water.

Background

Numerous treatment technologies for the control of invasive species via the ballast water vector are presently being evaluated, including heat treatment. Present heat treatment system designs make use of the waste heat generated by the propulsion engines to increase the temperature of the ballast water to a point where IAS are reduced or inactivated. To date these studies have been limited to large ships, with treatments being carried out over relatively long distances and time periods, and in relatively warm climates. Significant success has been demonstrated in some Australian sponsored projects and several other waste heat-generating treatment systems have been proposed for study. The systems may offer significant advantages in that they are relatively simple, do not produce significant disinfection by-products (DBPs), and are effective against a majority of flora and fauna found in ballast water.

In general, the water to sediment ratio in the NOBOB condition is considerably lower and more variable than in full ballast tanks and this presents numerous difficulties when attempting to treat the tank residuals. Pumping the residuals through any treatment system is made difficult due to the limitations of the ballast tanks design, the location of the pump intakes in the tank, and proximity of the pump intakes to the bottom of the tank. More importantly, the high sediment content of the residual ballast water makes treatment using filtration and Ultra Violet (UV) light methods difficult, and settled material can act as a refuge to protect certain organisms from treatment by chemical methods.

The treatment limitations resulting from the conditions within a NOBOB ballast tank mean that direct treatment of the tank residuals is necessary. The demonstrated heating capacity of portable boiler systems makes this possible.

Objective

The objective of the study is to examine the use of heat as a treatment to reduce invasive aquatic species (IAS) in the ballast tanks of NOBOB ships entering the Great Lakes. The study explores issues such as the:

- thermal tolerance of typical ballast water organisms;
- energy requirements to achieve target treatment temperatures in a NOBOB ship; and
- development of a thermal model to predict heat transfer and dissipation within a typical ballast tank.

Approach

NOBOB ballast tanks are expected to contain residual water and sediment associated with normal ballasting operations. The amount and types of aquatic species present in a ballast tank will depend on numerous factors including transit routes, management practices, and ship design. Effective treatment of ballast tank residuals will require that a majority of the organisms (and lifestages of those organisms) be inactivated prior to discharge.

Thermo toxicity tests will be used to determine Lethal Temperature to 90% mortality (LTm90) and Lethal Time to 90% Mortality (LT90) values for organisms and resting stages representative of those found in ballast water and their associated sediments.

Heat dissipation models have been developed based on a variational finite difference methodology. The models assume heat loss through all modes, i.e. conduction, convection and radiation, and in order to calibrate the heat transfer coefficients a full scale trial was conducted on a ship in Toronto Harbor, Canada. These trials had a second purpose, to demonstrate the practicality of using relatively low energy input requirements to heat treat the residual contents of the NOBOB ballast tank typical of ships entering the Great Lakes.

Thermo toxicity tests

Objectives

The purpose of this portion of the study is to determine the LTm90 and LT90 values for typical ballast water organisms. This is being achieved in the laboratory through controlled thermo toxicity tests using the organisms listed in Table X. These organisms were selected for testing because;

- the organism represents an organism/lifestage expected to be found in ballast water;
- the organism is considered to be reasonably tolerant to treatment, and;
- the organisms ease of culture.

The thermo toxicity tests are designed to determine the upper treatment temperature required to inactivate each species/lifestage, expected in the NOBOB ballast tank.

Table 1 summarizes the organisms that will be used in the thermo-toxicity tests.

Table 1. *Summary of organisms selected for thermo-toxicity testing.*

Organism Group	Species	Lifestage	Media	Measure
Bacteria	E. coli	Vegetative	Freshwater	Viability
Bacteria	Bacillus subtilis	Spore	Freshwater	Viability
Copepod	Cyclops spp.	Adult	Freshwater	Survival
Rotifer	Brachionus	Egg	Freshwater	% Hatch
Crustacean	Daphnia magna	Neonate	Freshwater	Survival
Crustacean	*Daphnia magna*	Ephippia	Freshwater	% Hatch
Shrimp	Americamysis bahia	Adult	Marine	Survival
Shrimp	Artemia salina	Cyst	Marine	% Hatch
Bivalve	Dreissena polymorpha	Veliger	Freshwater	Survival
Algae	Selenastrum capricornutum	Vegetative	Freshwater	Growth
Diatom	Skeletonema costatum	Vegetative	Marine	Growth

Thermotoxicity data will be compared to ballast tank thermal distribution models and energy requirements to evaluate the efficacy of the heat treatment and determine target treatment temperatures.

Ship board heat treatments

A thermal gradient model was developed to analyze heat dissipation through the steel structure of a ballast tank to the water. This model represents the steel structure of the tank, its residual content and the surrounding environment and uses finite difference techniques to establish a heat balance such that thermal energy input balance heat dissipation to maintain a given temperature in the portion of ballast water remaining in the bottom of the ballast tank.

This model can be exercised for the anticipated temperature of the operational environment using standard coefficients of heat transfer for water and steel and both conduction and convection components of heat transfer.

There is a significant uncertainty in the model in the dissipation of heat through convection of water up and around the outer hull as heat is lost to the environment. Ballast tanks, being the part of ship's structure, are inherently heavily subdivided by girders, floors and other elements. These structural elements act as baffles and cooling fins and affect both heat losses and temperature distribution within the tank. Furthermore, heat transfer is affected by the presence of sediment at the tank bottom of a NOBOB ship and coefficients of thermal conductivity for such case are unknown. It is these factors that are the primary target of calibration data to be recovered from the experiment.

Upon recovery of temperature and energy data from the experiment the model will be calibrated to replicate the steady state energy temperature distribution.

Experimental model calibration

The experiments were conducted in Toronto Harbor on-board the ULS ship *Canadian Provider* in May and June 2003. This ship is a typical Great Lakes bulk carrier. Ballast is carried in 6 sets of port and starboard tanks which are integral side and bottom tanks. The tanks do not extend vertically to the upper deck and for the entire length of the ship there is an access tunnel along the ship side, this provided an ideal location for the data acquisition system.

The *Canadian Provider* is currently active carrying grain from Lake Superior ports to St. Lawrence River terminals and iron ore on the return trips. The typical voyages are thus of short duration, across lakes were ballast operations are frequent and often in shallow draft high sediment areas, consequently the amount of sediment build up is significantly higher that in the typical trans ocean bulk carrier. This afforded the opportunity to perform the experiment in a tank with significant sediment and after cleaning, a sediment free tank.

Starboard ballast tank No. 6 is available for the experiment.

Equipment and materials

Name:	Canadian Provider
Type:	Bulk Carrier
Built	(as Murray Bay) in 1963 by Collingwood Shipyards, Collingwood, ON
Loa =	222.5 m
B =	22.86 m
T =	8.35 m (7.92 m)
H =	11.94 m
Capacity	27450 t (25600 t) in 6 holds

V = 15 kn.
Powered: By a single 9,000 HP John Inglis steam turbine with 2 water tube boilers
Owner: Upper Lakes Group, Toronto, ON

Measuring equipment

Equipment used for temperature measurements consisted of Cambbell Scientific's 107B thermistors connected to Campbell Scientific CR10 datalogger via AM 416 multiplexer and CR10WP Wiring Panel (Figure 1).

Ambient temperatures were measured by hand-held thermometer. Since the harbour water temperature is not subject to quick changes, it was measured only before and after each test. Air temperature was measured and recorded at the same intervals the internal tank temperatures are sampled.

The update frequency required was low (between 5 and 15 min reading interval) temperatures were scanned and recorded manually via CR10KD Keyboard Display unit.

Heat (steam) source

Steam for tank heating was provided by 50 HP oil-fired firetube boiler.

The Boiler was located on shore, just by the ship's side, and positioned between superstructure and aft hold (No. 6).

Water supply for the boiler was provided by a pump submerged into the lake. Electricity supply and fuel was provided by the ship.

Steam distribution system

Steam from the boiler was transported via 2 in. flexible pipe vertically to the deck where the pipe entered the tank vent, routed downwards to the side ballast tank bottom and into the double bottom tank. Inside the bottom tank the pipe ran transversely towards the ship's centre line and at 3 points in between girders, longitudinal branches were attached to main pipe. Each of the branches consists of short piece of 25mm flexible pipe and 1.5 m of heavy perforated steel pipe. These pipes were submerged into the sediment or water at the bottom of the tank. No fastening were provided since the weight of the pipes is sufficient to keep them submerged.

Circulating pump

A small pneumatic diaphragm pump was installed close to forward tank bulkhead and centrally between girders to circulate the tank contents. Pump discharge were routed via appropriate hose to a place near the middle steam exhaust pipe.

Test procedures

Initial Conditions (water depth in tank, air/water temperatures)

The experiment was designed to resemble the reality of the NOBOB as close as possible and therefore modifications to initial conditions were kept to a minimum. However, some additional ballast water was added in order to facilitate steam flow from the perforated pipes. The maximum depth of water in the ballast tank did not exceed the depth of the bottom longitudinal stiffeners.

Transducer locations

15 107B-type thermistors were located at three longitudinal positions and five across the section. These thermocouples were placed at the very bottom of the tank, touching the bottom plating.

Three additional probes were located 10 cm above the tank bottom in the NOBOB water, between longitudinal girders.

One thermistor probe was placed in air in the tank center.

One thermistor was located in the cargo hold, touching the inner bottom plate directly above the middle steam exhaust pipe.

Cables running from transducers located within the tank were routed via the forward manhole, then vertically to the tunnel deck to a small platform within a cargo hold.

The thermometer used for outside air temperature measurements was located at the main deck, in the shaded area near the superstructure.

Temperature sampling

Temperatures were recorded at 5 min sampling intervals

Results

Thermotoxicity tests.

Preliminary results from range-finding experiments are nearly completed for most species. The definitive thermotoxicity experiments will take place in July and August of 2003. A report detailing results and methodologies will be available at project completion.

Ship-board heat treatment studies

Experiments were conducted in both mud laden and clean tanks with and without the aid of water circulating pumps. Results from the experiments demonstrate that the temperature rises from around 15 degrees centigrade to 40 degrees centigrade can be achieved with a 50 HP boiler system over a 4-hour period. Data from each thermistor are shown in Figure 2. These data also demonstrate the long cool down period required to get back to ambient temperatures, i.e. in excess of 14 hours.

The temperature distribution throughout the tank with and without the circulating pump operating are shown in the following figures, These presentations demonstrate that the heat input at one end of a tank does not generate heat transfer through the tank sufficient to raise the temperature at the forward end of the tank without the aid of a circulating pump. It is also evident that the large amount of sediment in these particular tanks enabled higher temperatures to be achieved.

These data will be used to calibrate the heat models and provide a methodology to establish the heat input necessary to achieve the thermotoxicity levels currently under development.

The heat experiment demonstrates that it is possible to heat the residual content of a NOBOB tank effectively with a small external power source.

Figure 1. *Equipment used for temperature measurements.*

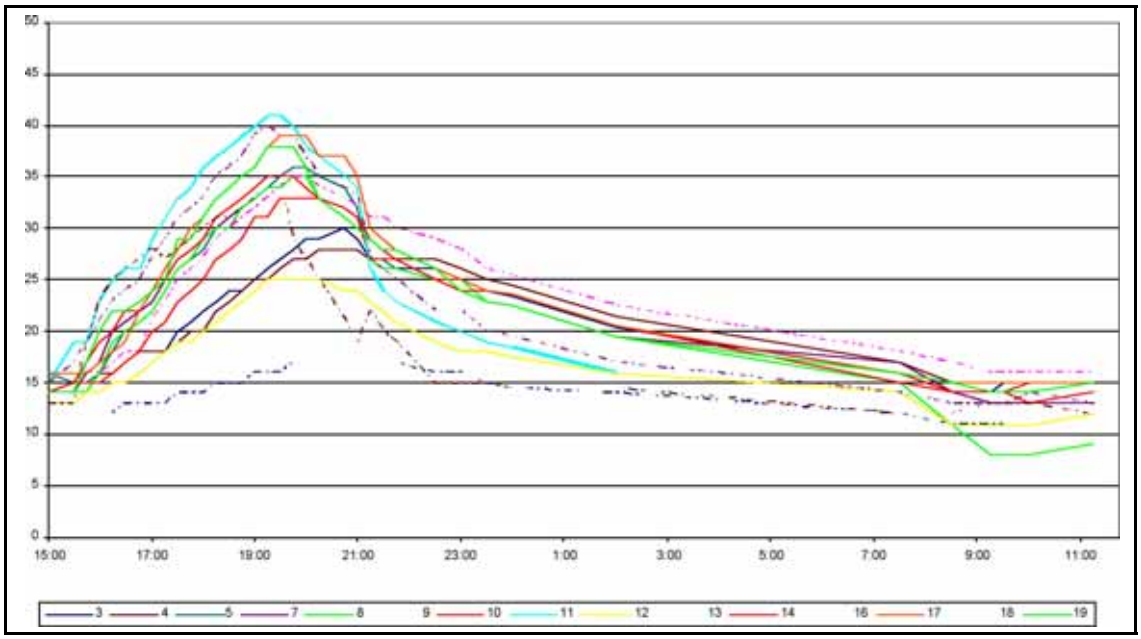


Figure 2. *Data from each thermistor.*

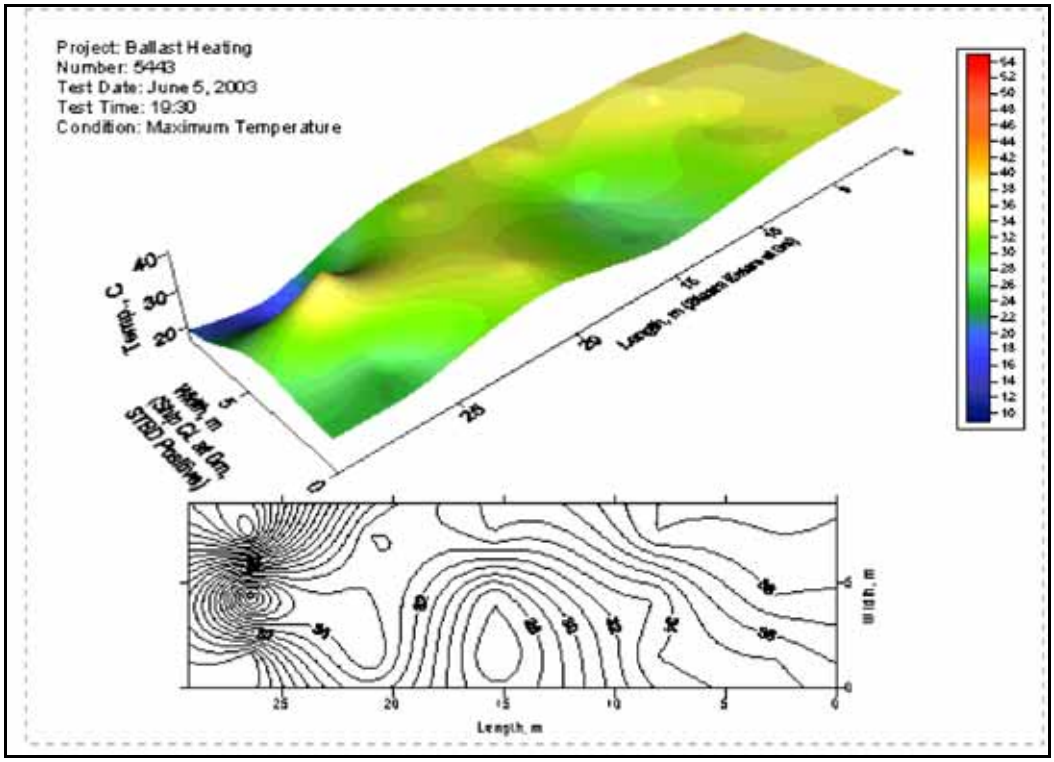


Figure 3. *Clean tank + circulating pump after 4 hours heat input.*

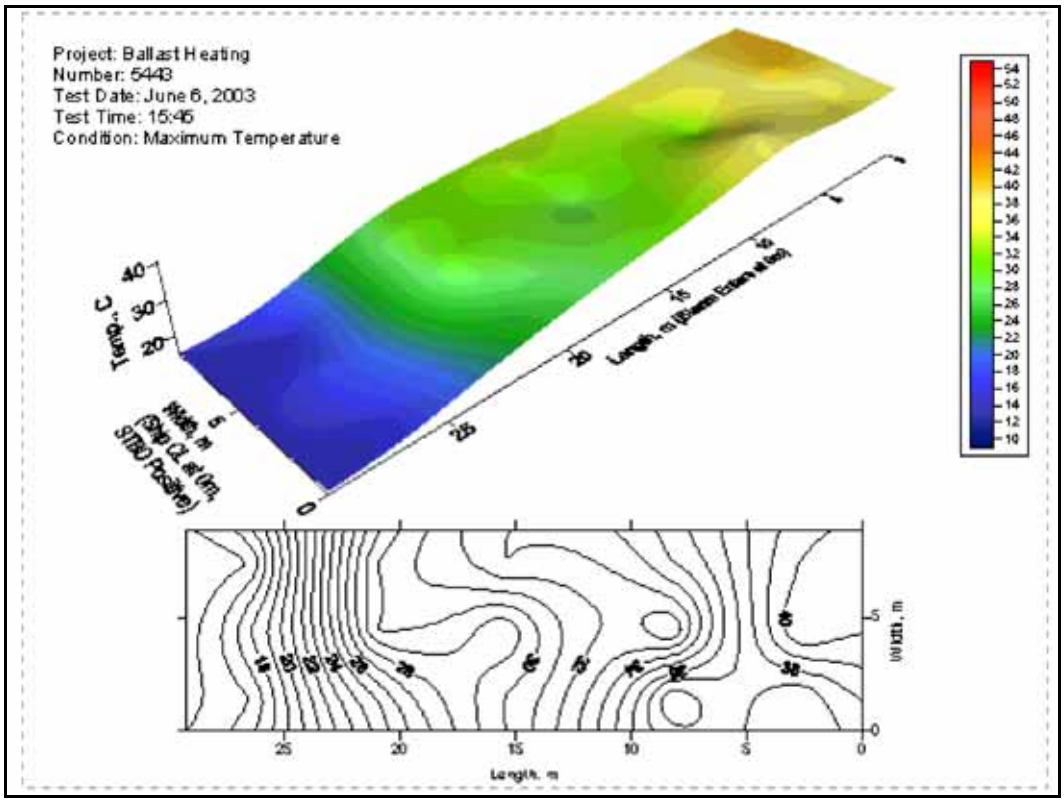


Figure 4. *Clean tank no circulation.*

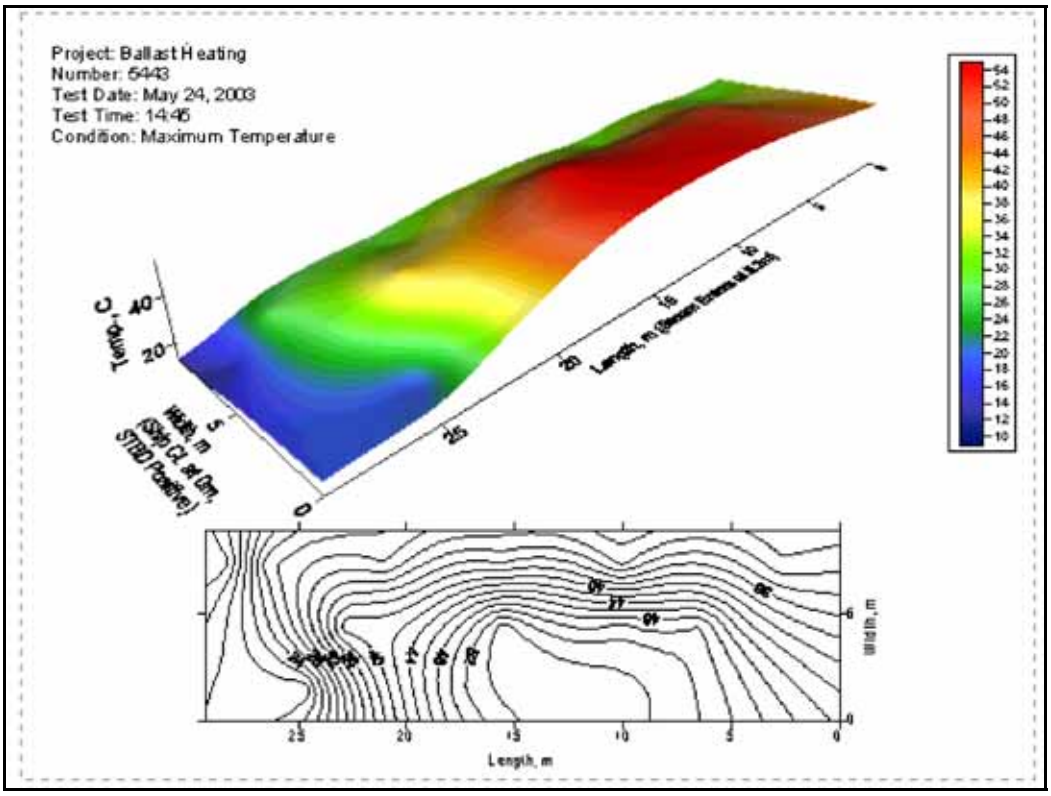


Figure 5. *Mud laden tank no circulation.*

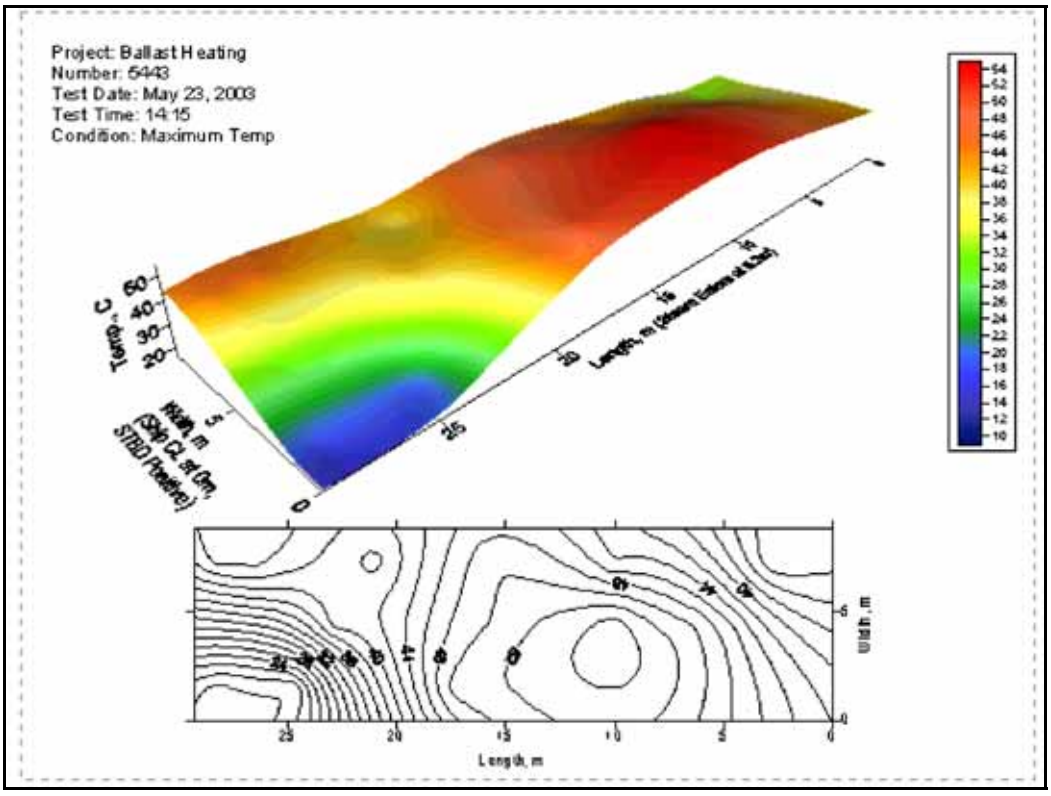


Figure 6. *Mud laden tank + circulating pump.*

The use of heat for ballast water disinfection - the AquaTherm method

G. A. Thornton & J. E. Chapman

Hi Tech Marine Pty. Ltd.
Australia
gthornton@htmarine.com.au

Treatment method

Physical - heat.

Project timeframe

1995 - 2003

Project aims

When commenced in 1996, the Heat Disinfection (AquaTherm, originally 'WaterSafe') Project was an offshoot of our On-board (SeaSafe-3) system. It was realised that a majority of ballast water could be treated off the ship, giving a greater efficacy of treatment and diminishing the risks of exotic organisms invading a marine area.

The project was commenced in 1995 with the aim of killing the Toxic Dinoflagellate Cyst, which is regarded as a difficult organism to kill. In 1997 the treatment temperature and dwell-times were raised to include the destruction of V*ibrio cholerae* which is inactivated at 73°C/30 seconds or 65°c/120 seconds (Australian Quarantine and Inspection Service (AQIS) 1997). In 1999 the treatment temperature and dwell-time were raised again to include other human pathogens including Hepatitis A virus which is inactivated at 90°C/60 seconds – in order to treat ballast water in the Great Lakes area (Northeast-Midwest Institute (NEMWI) 1999). We have always aimed at >95% mortality for all of the organisms on the Australian Ballast Water Management Advisory Council - Marine Target Species List (Table 2) which may be contained in the ballast water, with on-board treatment, and 100% mortality of all discharged organisms, for shore based treatment.

Our original concept looked at the overall picture and we realised that with the number and types of ocean-going ships there would be no single answer to the problem and certainly the logistics of fitting and retrofitting equipment would be an immense undertaking, taxing the capabilities of any one company.

We determined that there are three basic ways to resolve the problem:

1. Load clean ballast water – for ships that trade on a regular route. The modification of the ship is straightforward and the ship uses it's own ballast pumps and trimming system. This system requires the initial removal of all sediment from the ballast tanks, and depending on the biota to be killed, may require the addition of a residual disinfectant.
2. Treat the ballast water en-route – suitable for vessels on longer voyages. The problem with this method is that it is not possible to eliminate all organisms; some may remain in the sediments and in out of the way areas of the ballast tanks.
3. Disinfect the ballast water at the port/point of discharge. This ensures that 100% of all of the organisms being discharged are killed, prior to the re-use or disposal of the Ballast Water.

Project objectives

The objective of the project is to provide an environmentally acceptable, commercially viable, safe, ballast water disinfection system. The system would be able to kill/inactivate all pathogens contained or likely to be contained in ballast water, would be able to operate from suitable existing sources of waste heat, where available, and would be able to operate either on-board a ship or on shore as either a fixed installation or transportable system.

Research methods

HTM conducted research on Ballast Water (1991–1993) with the assistance of a Research and Development laboratory using Ultrasonics, Biocides (in conjunction with Rohm and Haas), chemicals, ultra violet, and microwaves. In 1995, after further research, it was concluded that the most cost-effective, user friendly and environmentally acceptable process would be heat treatment.

When the temperature of a body of water containing the target organism is elevated to a temperature above the thermal-threshold of the target organism, the target organism is killed. The thermal threshold is the point at which an organism is instantly killed due to either denaturing of cellular proteins or increasing the organism's metabolism beyond sustainable levels.

This thermal threshold is variable among different species, as is a species' ability to endure periods of high temperatures that are below their thermal threshold. In general, temperatures close to an organism's thermal threshold can be tolerated for short periods with little non-reversible damage, and temperatures sufficiently cooler than the thermal threshold organisms can be survived for longer periods.

The organisms requiring destruction were sourced by way of requests from various organizations (AQIS and NEMWI). Thermal-threshold temperature/times have been provided privately (Hallegraeff and Appendix) or are from published sources (AQIS, 1994). By taking the thermal-threshold value of the most thermo-tolerant organism requiring destruction, and allowing for a margin of safety above that value, we assume that organisms of lesser thermo-tolerance will succumb at the higher temperature.

Test protocols

Testing was carried out with AquaTherm systems of variously, 250, 360, and 1,000 litres per hour capacity.

Analysis has been independently carried out by Testing Laboratories accredited by the National Association of Testing Authorities – Australia (NATA) to the relevant International or National Standard. The ramp-up (25 to 30 seconds), ramp-down (25 to 30 seconds), and residence (2 minutes) times of the AquaTherm system precludes accurate laboratory replication.

Experimental design

The AquaTherm (and SeaSafe-3) system is based on holding a body of water at a given temperature for a given period of time, which will be fatal to a given organism and all organisms with a lower thermo tolerance.

AquaTherm system design

The design of the AquaTherm disinfection system is technologically simple and based on pasteurisation techniques. AquaTherm uses many off-the-shelf components.

Water to be treated is pumped through a series of heat exchangers into the water heater circuit heat exchanger, raised to the desired temperature for the required time, and then discharged through the heat exchanger series into the ballast tank (uptake) or local waters (discharge) after being cooled by pre-heating the incoming water (Figure 1).

The AquaTherm system is controlled by a Programmable Logic Controller (PLC) and consists of four stages.

Stage 1: Raw product is transferred from the source through a transfer pump into intake of the preheat heat exchanger (primary circuit), which is recovering the heat from the disinfected product of Stage 4.

Stage 2: Preheated raw product is then passed through a second heat exchanger (secondary circuit) to be heated to a temperature of 85°C via a water heater.

Stage 3: Heated product then passes into a holdover tank for a specified time of 2 minutes at 85°C, allowing disinfection to occur.

Stage 4: Disinfected product is then passed through the preheat heat exchanger (primary circuit) to recover the heat of the disinfected product, allowing it to be used for preheating the raw product as part of stage 1 process. The disinfected product on exit from the AquaTherm can be within as little as 2°C of inlet temperature.

The temperature difference between the inlet and discharge water (referred to as Delta T- ΔT , Actual Temperature Difference – ATD, or, Approach Temperature) is the heat required (minus losses) to raise the water to disinfection temperature – whatever the disinfection temperature may be (Table 1).

Table 1. *Energy calculations.*

Given:
- Flow in kilograms
- Temperature change in °C
- Heat Exchanger area in metres^2
- 1 Kg of water raised 1°C = 1 kilocalorie (Changes marginally with salinity & temperature)

∴ Flow in kg per Hour x Temperature change °C = Heat load in kilocalories
∴ A smaller change in temperature requires a proportional increase in flow
(also requires a greater heat exchanger area)

So: 1,000 kg/hr x 10°C change = 10,000 kilocalories/hr
as does: 2,000kKg/hr x 5°C change = 10,000 kilocalories/hr

There are of course practical limits

kilocalories/hr ÷ 860 = kilowatts/hour

Given the target organism's kill temperature (i.e., water temperature at which target organisms succumb), AquaTherm will give known exposure time and known disinfection temperature. The source of energy for the water heater(s) is flexible and can vary with what is available. Industrial water heaters for our ballast water applications can use several sources of fuel. Other sources of heat energy are Industrial Processes (Thornton 2000), Central Cooling Systems, Oil Refineries, Power Stations, and Co-Generation Systems.

Energy requirements

Energy requirements are proportional to the incoming water volume, and ATD (ΔT) of the AquaTherm (only pumping is required if using a source of waste heat). Hot water flow requirements are approximately $^1/_3$ of disinfection flow rate.

Biota

The organisms listed in the **Australian Ballast Water Management Advisory Council - Marine Target Species List (**ABWMAC) (Table 2) are killed by a disinfection temperature of 50°C for 30 seconds, which includes a margin of safety. The best time-series temperature data for an aquatic organism known to be carried in ballast water is for *Gymnodinium catenatum* and *Alexndrium tamarense* cysts (red-tide Dinoflagellate). Bolch and Hallegraeff (1993) report that 0% of *G. catenatum* and *A. tamarense* cysts exposed to 45°C water were able to germinate (100% mortality).

Table 2. *ABWMAC Marine Target Species List.**

Species Name	**Common Name**	**Native and Introduced Regions**
Organisms that are already in Australia		
Sabella spallanzanii	Mediterranean fanworm	Mediterranean
Carcinus maenas	European shore crab	Europe
Asterias amurensis	Northern Pacific seastar	Japan, Russia, Korea
Corbula gibba	Asian bivalve	Asia
Crassostrea gigas* (FERAL)	Pacific oyster	Japan
Musculista senhousia	Asian date mussel	China, Taiwan, Philippines
Undaria pinnatifida	Japanese seaweed	Japan
Alexandrium catenella	Dinoflagellate	
Alexandrium minutum	Dinoflagellate	
Alexandrium tamarense	Dinoflagellate	
Gymnodinium catenatum	Dinoflagellate	
Organisms that have not yet arrived in Australia but pose a significant threat **		
Eriocheir sinensis	Chinese mitten crab	China, Taiwan Japan, Europe, North America
Hemigrapsus sanguineus	Asian crab	China, Taiwan, Japan, West Atlantic
Caulerpa taxifolia spp	(Aquarium hybrid)	Mediterranean
Mnemiopsis leidyi	Comb jellyfish	West Atlantic, Black and Azov Seas, Eastern Mediterranean
Potamocorbula amurensis	Asian bivalve	China, Taiwan, North America
Dreissena bugensis	Quagga mussel	Europe, North America
Philline aurioformis	New Zealand sea slug	New Zealand, North America
Sargassum muticum	Japanese seaweed	China, Taiwan, Japan, Eastern Pacific, Atlantic Europe

**All species listed here have been assessed as having either a severe economic and/or ecological impact. The list was developed using an Impact Assessments Score Sheet developed by the CSIRO Centre for Research into Introduced Marine Pests (CRIMP) and the results of the process of listing species were subsequently endorsed by the Australian Ballast Water Management Advisory Council's Research Advisory Group (RAG) and agreed by ABWMAC.*

In addition, in their evaluation of exposure period verses effectiveness, Bolch and Hallegraeff found that whilst 45°C water could reduce germination to 0% with a 30-second exposure time, exposure to 40°C water required 90 seconds to achieve 0% germination. Thus, if a Ballast Water treatment system were designed for only *G. catenatum* and *A. tamarense* cysts (relatively hardy micro-organisms of concern), 45°C water with a 30 second exposure period in the system would be adequate.

The temperature/dwell times required for *G. catenatum* and *A. tamarense* cysts' mortality are *not* adequate for the destruction of *V. cholerae*, which requires 65°C for 2 minutes, or, 73°C for 30 seconds for complete mortality this is exceeded with the AquaTherm system.

The NEMWI required a number of organisms to be killed or inactivated (Table 3) for the *Great Lakes Ballast Water Program*. To kill the most thermo-tolerant organism, *Hepatitis A virus* and excluding *Clostridium refringens* (Appendix), a temperature of 90°C for 60 seconds (or equivalent) is adequate.

Organisms used for testing were known to occur in the water being tested and were not introduced. As will be discussed in the safety aspects of the AquaTherm, the attainment of the required kill temperature is incorporated as a function of design, as is the residence time. That is, once the AquaTherm is at operating temperature the target organisms are killed or pedantically, in the case of viruses, inactivated, without the need for hands-on process control or adjustment.

Table 3. *Great Lakes Ballast Water Program: Northeast-Midwest Institute organisms required to be killed or inactivated.*

	Cyanobacteria	**Phytoplankton**	
Faecal coliforms	*Microcystis elebans*	*Skelatomina*	*Zebra mussel veligers*
Faecal streptococci	*Spirulina subsalsa*	*Thalassiosira eccentria*	*Adult calanoid copepods,*
Clostridium perfringens	*Chroococcus limneticus*	*Cryptomonas pseudobaltica,*	*Various crab & shrimp zoea*
Salmonella spp		*Chroomonas amphoxera*	*Starfish (Asterias rubins) larvae*
E. coli		*Euglena proxima*	*Infectious pancreatic necrosis (fish related),*
Vibrio cholerae		*Pfiesteria*	*Amphidinium sp ate alga*)
Cryptosporidium spp		*Gymnodinium catenatum*	
Giardia spp		*Gonyalaux*	
Hepatitis A virus			
Enteroviruses			
Aphanomyces			
Infectious Hepatitis			
Chlorella Vulgaris			
Pseudomonas			
Myxosporeans			
Staphylococcus aureas			
Poliovirus,			
Nematode eggs – Ascaris			

Effectiveness of the AquaTherm was determined as mortality/inactivation by independent laboratories.

Results of Testing

AquaTherm has been tested on 14-day old Pig effluent containing greater than 15% solids, Secondary-treated human effluent, and estuarine river water.

Queensland (QLD) Department of Primary Industries – Centre for Food Technology, analysed samples from the AquaTherm 360 – Estuarine water, Burnett River, QLD (for non-potable industrial use) (Table 4).

Silliker Microtech Pty Ltd analysed samples from an AquaTherm 250 – 14-day old untreated Pig effluent (Table 5).

ECOWISE Environmental Pty Ltd were commissioned to monitor the performance of an AquaTherm 250 – connected to an AWTS (secondary treated human effluent), and AquaTherm 1000 – Estuarine water, Hawkesbury River, NSW (non-potable human use). (Tables 6-8, 10)

Environmental Pathogens performed the analysis of samples for viruses using in-house methods. (Table 9)

Estuarine river water:

1. Burnett River, QLD:

Coliforms from 35 to <1 CFU/100ml (method AS4276.4 – 1995)

E. Coli from 3 to <1 CFU/100ml (method AS4276.6 – 1995)

Table 4. *Test Results for AquaTherm 360: Analysis for pre and post-disinfection samples – Burnett River estuarine water (Queensland Department of Primary Industries – Centre for Food Technology).*

Description:	Sampling Date:	Sampling Time:	Aerobic Plate Count per mL (at 21°C for 72 ± 2hrs)	Aerobic Plate Count per mL (at 37°C for 48 ± 2hrs)	Coliforms Per 100mL	E. coli Per 100mL
Raw water	22.02.99	13:05	86	190	11	1
Raw water	22.02.99	13:05	240	410	35	3
Treated water	22.02.99	13:05	250	2200	<1	<1
Treated water	22.02.99	13:05	150	460	<1	<1

2. Hawkesbury River, NSW – with aggregate and activated Carbon pre-AquaTherm filtration:

Total Coliform from 19,000 to 0 CFU/100ml (method 540.06)

Faecal Coliforms from 11 to 0 CFU/100ml (method 610.04)

E. coli from 11 to 0 CFU/100ml (method 610.04)

Pig effluent

The AquaTherm unit was found to reduce:

Thermo-tolerant Coliforms from CFU/100ml >16,000 to <2 (method M16.2)

E. coli from CFU/100ml >16,000 to <2 (method M16.3)

At 4 Days, the Thermo-tolerant Coliforms were CFU/100 ml <2 (method M16.2)

E. coli CFU/100ml <2 (method M16.3)

Table 5. *Test Results for AquaTherm 250: Analysis for pre and post-disinfection samples - 14-day old raw Pig Effluent (Silliker Microtech Pty Ltd.).*

Description:	**Sampling Date:**	**Sampling Time:**	**E. coli**	**Thermotolerant Coliforms**	**Salmonella**	**Salmonella Stage 2**
Pre-disinfection	13.08.02	NA	>16,000	> 16,000	Further Testing required	Not Detected
Post-disinfection	13.08.02	15.30	<2	< 2	Further Testing required	Not Detected
Post-disinfection at 4 Days	17.08.02	NA	<2	<2	Further Testing required	Not Detected

Secondary-treated human effluent

Daily and re-growth testing on 7-days, over a period of 3 months indicated a 100% kill of::

Total Coliform – pre-disinfection <1,000 to 40,000 CFU/100ml (method 540.06)

Faecal Coliforms – pre-disinfection 650 to 7,100 CFU/100ml (method 610.04)

E. coli - (pre-disinfection 180 to 5,900 CFU/100ml (method 610.04)

Total Plate Count – pre-disinfection 650 to 31,000 CFU/100ml (method 520.06)

P. aeruginosa pre-disinfection 150 to 44,000 CFU/100ml (method APHA 9213 E)

Reovirus*
Enterovirus*
Norwalk virus*
Adenovirus reduced from 8550 to 22 units/L*
(*Environmental Pathogens – in house method)

Table 6. *Summary of methods used by ECOWISE for all samples.*

Analysis	Units	Detection Limit	Method Reference	NATA	Method Summary
NH3	mg/L	0.002	APHA 4500-NH3-H	Yes	Salicylate method – Colorimetric FIA
BOD	mg/L	1	APHA 5210 B	Yes	Probe Method – 5 day incubation at 20'C
COD	mg/L	3	APHA 5220 C	Yes	Dichromate reflux – Spectrophotometric UV/VIS
E. coli	cfu/100mL	0	APHA 9222	Yes	Confirmed from Faecal Coliforms
Faecal Coliforms	cfu/100mL	0	APHA 9222	Yes	Membrane Filtration -
Pseudomonas aeruginosa	cfu/100mL	0	APHA 9213 E	No	Membrane Filtration -
SS	mg/L	0.1	APHA 2450	Yes	Gravimetric analysis
TOC	mg/L	1	APHA 5310	Yes	Determined as non-purgeable organic carbon measured by non dispersive infra-red
Total Coliforms	cfu/100mL	0	APHA 9222	Yes	Membrane Filtration -
N	mgN/L	0.1	APHA 4500-N B	Yes	Cadmium reduction method – Colorimetric FIA
P	mgP/L	0.07	APHA 4500-P I	Yes	Ascorbic acid – Colorimetric UV/VIS
Total Plate Count	cfu/1mL	0	APHA 9215 B	Yes	Pour plate method

Table 7. *ECOWISE Test Results for AquaTherm 250/AWTS: Physical and Chemical analysis for pre and post-disinfection samples.*

Description:	Sampling Date:	Sampling Time:	Temperature	pH	Free Cl2	SS	TOC	COD	NH3	N	P
			°C	pH Units	mg/L	mg/L	mg/L	mg/L	mgN/L	mgN/L	mgP/L
Pre-disinfection	16.12.02	10:00	29	6.6	0.2	2.6	7	13	0.13	15	6.5
Post-disinfection	16.12.02	10:00	33	6.6	0.1	2.3	8	10	0.12	15	6.6
Pre-disinfection	18.12.02	9:00	26	6.4	Na	2	7	16	0.08	18	7.7
Pre-disinfection duplicate	18.12.02	9:00	26	6.4	Na	2.2	7	16	0.08	18	7.8
Post-disinfection	18.12.02	9:00	29	6.3	Na	2.2	7	15	0.08	18	7.8
Field Blank	18.12.02	9:00	24	7.1	Na	0.6	<2	<1	<0.01	<0.01	<0.01
Pre-disinfection	23.12.02	9:00	26	6.4	Na	1.3	8	20	0.05	21	9.7
Post-disinfection	23.12.02	9:00	31	6.3	Na	1	8	22	0.05	21	9.7
Post-disinfection Day 4	28.12.02	9:00	Na	Na	Na	Na	Na	Na	Na	Na	Na
Field Blank	22.12.02	9:00	Na	Na	Na	Na	Na	Na	Na	Na	Na

Table 8. *ECOWISE Test Results for AquaTherm 250/AWTS: Biological analysis for pre and post-disinfection samples.*

Description:	Sampling Date:	Sampling Time:	BOD	Total Coliforms	Faecal Coliforms	E. coli	P. aeruginosa	Total Plate Count
			mg/L	cfu/100mL	cfu/100mL	cfu/100mL	cfu/100mL	cfu/100mL
Pre-disinfection	16.12.02	10:00	1.9	39000	2500	2500	720	31000
Post-disinfection	16.12.02	10:00	1.6	0	0	0	25	3400
Pre-disinfection	16.12.02	12:00	1.6	20000	650	430	280	29000
Post-disinfection	16.12.02	12:00	1.3	0	0	0	8	1400
Pre-disinfection	16.12.02	14:00	1.2	40000	720	180	300	27000
Post-disinfection	16.12.02	14:00	<1.0	0	0	0	4	840
Pre-disinfection	18.12.02	9:00	2.1	<1000	7100	5900	44000	680
Pre-disinfection duplicate	18.12.02	9:00	1.6	<10000	2800	2100	52000	650
Post-disinfection	18.12.02	9:00	<1.0	0	0	0	200	100
Field Blank	18.12.02	9:00	<1.0	26	0	0	0	610
Pre-disinfection	23.12.02	9:00	2.3	11000	2300	2300	8800	3400
Post-disinfection	23.12.02	9:00	<1.0	<100	0	0	1300	2200
Post-disinfection Day 4	28.12.02	9:00	Na	0	0	0	1600000	1900000
Field Blank	22.12.02	9:00	Na	0	0	0	11	88
Post-disinfection Day 4	31.01.03	9:00	Na	Na	Na	Na	0	2
Trip Blank	31.01.03	9:00	Na	Na	Na	Na	0	2300
Post-disinfection	3.02.03	9:00	Na	Na	Na	Na	160	9
Trip Blank	3.02.03	9:00	Na	Na	Na	Na	0	150
Post-disinfection Day 4	8.02.03	9:00	Na	Na	Na	Na	210000	17000
Post-disinfection Point 1	18.02.03	15:00	Na	Na	Na	Na	60	1
Post-disinfection Point 2	18.02.03	15:00	Na	Na	Na	Na	88	2
Pre-disinfection	22.02.03	15:00	Na	Na	Na	Na	150	1200
Post-disinfection Point 1	22.02.03	15:00	Na	Na	Na	Na	300	16
Post-disinfection Point 2	22.02.03	15:00	Na	Na	Na	Na	11	2
Trip Blank	22.02.03	15:00	Na	Na	Na	Na	0	0

Table 9. *Environmental Pathogens Test Results for AquaTherm 250/AWTS: Viral analysis for pre and post-disinfection samples.*

Description:	Sampling Date:	Sampling Time:	Reovirus	Adenovirus	Enterovirus	Hepatitis A virus	Norwalk virus
			units/L	units/L	units/L	units/L	units/L
Pre-disinfection	18.12.02	9:00	485	8550	7250	Negative	Positive
Post-disinfection	18.12.02	9:00	<1	22	<1	Negative	Negative

Table 10. *ECOWISE Test Results for AquaTherm 1000/Hawkesbury River estuarine water: Biological analysis for pre and post-disinfection samples.*

Description:	Sampling Date:	Sampling Time:	Total Coliforms	Total Coliforms	Faecal Coliforms	Faecal Coliforms	E. coli	Bio ID	Plate Count
			Pres Count CFU/100ml	Conf Count CFU/100ml	Pres Count CFU/100ml	Conf Count CFU/100ml	CFU/100ml		35°C 48 Hr CFU/100ml
Pre-disinfection	07.04.03	11:30	19000	20	11	11	11	Flagellates	1100
Post-disinfection	07.04.03	11:30	0	0	0	0	0	No Flagellates	160

Practicability/utility

Heat disinfection technology is well established and is an effective application. The principal limitations for rapid disinfection of incoming or discharging ballast water are engineering/design and limits on energy-consumption.

The AquaTherm and SeaSafe-3 systems are two potential systems for ballast water treatment (Thornton 1997), (Thornton 2000),(Rigby and Taylor 2001). Of the two systems, we regard the AquaTherm as the better of the two in that all of the water is disinfected. The SeaSafe-3 system is generally limited to the disinfection temperature of 65°C and residence time of 2 minutes, which is adequate for *V. cholerae* as previously discussed. Another inherent problem with any on-board system is to guarantee the treatment of all of the ballast water – in that there are dead pockets within ballast tanks, and there will always be some sediment. As was demonstrated in the AquaTherm 250/AWTS

tests, disinfected water presents an opportunity for a viable organism to expand exponentially – as there are no other organisms to conflict with or counteract it.

Using the AquaTherm system requires little alteration to the ship. It would be connected to the outboard side of the ship's ballast pumps, and this would require moving the ship's ballast discharge pipe to above the waterline if need be. We are led to believe that an electromagnetic coupling has already been developed which would enable a seamless connection between the ship and the shore piping. It may also be practical in some instances to fit a pipe from the engine room to the main deck with a 'T' head and discharge the Ballast Water through it.

The SeaSafe-3 system was designed to be easily fitted whilst building or retrofitted to a ship without the ship being withdrawn from service. Allowance was also made so that the system could be easily removed from a ship and fitted to another ship of similar engine capacity.

Cost effectiveness

The cost-effectiveness figures are calculated on a 515-m^3/h capacity on-board and 6,000-m^3/h shore-based systems. Certain operating parameters have been assumed.

On-board

Cape size Bulk Carrier – ballast water capacity 55,000 m^3.

Twelve voyages per year.

Useful life of ship 15 years.

Life of system 40+ years.

Indicated price of SeaSafe-3 system US$ 200,000 plus say, US$ 91,000 for pipe work.

Amortised over life of ship × voyages = US$ 1616 per voyage.

Therefore cost per m^3 of ballast water carried = 2.9381 cents.

N.B. The SeaSafe-3 system uses the engine-cooling pump, as the Ballast Water is substituted for the engine cooling water during the disinfection process. Should the pressure drop on the Engine-Cooling Pump be too great to return the disinfected water to the ballast tank, the Auxiliary-Fire or General Service pump would be used to assist.

This would add the following costs:

Total pumping time required = 128 hours (ballast water x 1.2 volumes) per voyage

Diesel fuel required (80 kW pump power) = 2893 kg

Fuel cost per cubic metre of ballast water on ship = 1.97 cents/m^3.

Estimated maintenance cost for pump and generator = 0.56 cents/m^3.

Total capital and operating cost = 5.43 cents/m^3 [7].

Shore-based

AquaTherm systems are a modular design and are manufactured in 316 stainless steel, Titanium, or other specialised materials as required. Nominally, for marine work, Titanium is the preferred material. The smallest system available will treat 250 Litres/hour. The largest module will treat 6,000 m^3/hour; modules and can be combined to suit any greater flow requirements.

AquaTherm system capable of 6,000 m^3/h with 1°C Delta T Starting Temperature 15°C Disinfection Temperature 80°C for 2 minutes.

Life of system 40+ years.

Indicated price of AquaTherm system US$ 40,000,000

Amortised over life of system = US$ 2739.73 per day

Per cu m of ballast water = 0.0190 cents/m^3.

Energy required for Delta T of 1°C = 6,978 kW/h

Fuel (light fuel oil) required per hour (calculated at 1kg/kW/h) = 6,978 kg.

At assumed price of 20 cents/kg = US$ 1395.60

= 0.2326 cents/m^3.

Total capital and operating cost = 0.2516 cents/m^3.

AquaTherm system capable of 6,000 m^3/h with 2°C Delta T Starting Temperature 15°C Disinfection Temperature 80°C for 2 minutes.

Life of system 40+ years.

Indicated price of AquaTherm system US$ 30,000,000

Amortised over life of system = US$ 2053.38 per day

Per cu m of ballast water = 0.0142 cents/m3.

Energy required for Delta T of 2°C = 13,956 kW/h

Fuel (light fuel oil) required per hour (calculated at 1kg/kW/h) = 13,956 kg.

At assumed price of 20 cents/kg = US$ 2791.20

= 0.4652/m^3.

Total capital and operating cost = 0.4794 cents/m^3.

AquaTherm system capable of 6,000 m^3/h with 5°C Delta T Starting Temperature 15°C Disinfection Temperature 80°C for 2 minutes.

Life of system 40+ years.

Indicated price of AquaTherm system US$ 26,000,000

Amortised over life of system = US$ 1788.05 per day

Per cu m of ballast water = 0.0124 cents/m^3.

Energy required for Delta T of 5°C = 34,890 kW/h

Fuel (light fuel oil) required per hour (calculated at 1kg/kW/h) = 34,890 kg.

At assumed price of 20 cents/kg = US$ 6977.60

= 1.1629 cents/m^3.

Total capital and operating cost = 1.1753 cents/m^3.

The costings for the AquaTherm shore-based systems as set out above illustrate the advantage of a lower Delta T when considering the balance between equipment costs and operating costs, and also the quantity of water able to be processed from any available waste heat source. The energy required in the costings does not include the running of pumps as the piping distances, and thus the pump capacity cannot be determined.

The comparison between on-board and shore-based systems is weighted towards the AquaTherm shore-based system over the on-board system. Shore-based disinfection is even more cost effective if

there is a local source of waste heat available. Environmentally, the balance is weighted towards shore-based treatment, as the disinfection temperature can be higher and all of the pathogens in the discharging ballast water are killed.

Safety

The use of an AquaTherm or SeaSafe heat disinfection system cannot create safety concerns. The use of heat to treat Ballast Water will not create a hot-water hazard.

As almost all of the operating heat is recovered in our system, there are very few safety concerns for the ship, which would otherwise be associated with filling ships' ballast tanks with hot water.

Routing Ballast Water to or from topside or side-of-ship connection points, or to other parts of the ship, will not alter its stability. The ship takes on or discharges ballast water in a *normal* manner as determined by the ship's computer system. The associated shipboard ballast water management piping may need minor alterations.

AquaTherm - safety

AquaTherm is controlled by two PLCs, one for the system and one for the Hot Water Service (HWS).

System PLC inputs:

HWS temperature – heater failure
Heater Plate Heat Exchanger (PHE) return water temperature – PHE is at operating temperature
Raw water feed pump flow – pump failure, strainer blockage
Raw water Low-level float switch – turns raw water feed pump off
Raw water High-level float switch – turns raw water feed pump on
Recirculating hot water pump flow – pump failure

System PLC outputs:

Raw water feed pump – flow control to ensure correct operating temperature
Raw water feed pump - from Low-level and High-level float switches
Chlorine dosing equipment (where applicable)
Pump failure alarm
HWS failure alarm
Digital readout of operational failure
Digital readout of Heater PHE return water temperature – this temperature will always equal the disinfection temperature.
The HWS PLC ensures that the correct operating temperature is maintained to within 1°C. In the event of any component failing, the AquaTherm system instantaneously shuts down and or reverts to a bypass mode.

SeaSafe-3 - safety

Lloyds Register and Australian Maritime Safety Authority (AMSA) approved the SeaSafe system in 1997.

The system is designed utilising normally closed electro-valves to ensure that in the event of a malfunction or fire the system shuts down instantaneously.

Ship stability and hull stresses are not affected by the SeaSafe system as water is drawn from the bottom of the ballast tank and returned to the top of the same ballast tank in a continuous loop until all of the water (plus 20%) in the tank is disinfected (Figure 3).

In 1997, a sea-trial was conducted on the small Australian bulk carrier 'Sandra Marie' primarily to prove that the water in the Ballast tank would remain stratified. Gale force winds and big seas proved the stratification would remain (Table 11).

Conclusion

The AquaTherm system exceeds the following guidelines for the destruction of pathogens in potable (drinking) water, and sewage effluent - for water re-use: NSW Department of Health; South Australia Department of Human Services; Australian National Health and Medical Research Council (NHMRC); Australian and New Zealand Environment and Conservation Council (ANZECC); Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ); U.S. EPA; World Health Organisation.

The AquaTherm system is able to operate at 121°C with a 4 minute dwell-time, which yields sterile water and when used for the treatment of discharging Ballast Water, will destroy all pathogens likely to be found in Ballast Water, excepting Infectious Pancreatic Necrosis Virus (IPNV), and possibly, Salmonid herpeviruses, *Renebacterium salmoinarum, Myxosoma cerebralis,* and resting spores of fungus *ichthyophonus* (AQIS 1994).

AquaTherm and SeaSafe-3 are fully developed water disinfection systems that have the potential for ballast water applications. AquaTherm is used commercially and is being considered for a number of applications in the food, potable water, agricultural, water re-use, and sewage effluent re-use areas, with some major sites requiring up to 22,000 tonnes per hour disinfection flows. Testing has shown that AquaTherm is able to kill or inactivate 99.9% of all pathogens likely to be carried in ballast water.

Recommendations

HTM's AquaTherm and SeaSafe-3 systems already exist, and show the potential to be commercially and environmentally viable, as may be the case with certain other systems.

The Regulators should set an arbitrary Standard for Ballast Water Treatment and at least stop the further daily introduction of alien, exotic organisms and biota into the world's fragile native environments.

The Scientific Community have a wealth of knowledge about Ballast Water-transported, non-indigenous life forms, and should be given the opportunity to apply that knowledge in rectifying these known, existing, problems.

With such a wide variety of ships and operational variations to be found in the world, it is improbable that one, single, universally adopted method of treating ship's Ballast Water will emerge. There will be scope for the use of a variety of systems in various applications, especially in the case of non-standard vessels engaged in non-mainstream work.

We have demonstrated that for the world's large commercial fleets plying between the world's large commercial ports, treating Ballast Water by means of heat, whether on-shore or on-board, may be one of the economical and environment-friendly systems of choice.

A strong case has been put for the preference for on-shore over on-board treatment of Ballast Water. The logistics of building and installing equipment on approximately 80,000 ships are daunting, as is the potential time frame of the task.

The sooner we start to take *real action* the sooner the problem will be solved!

References

Hallegraeff G.M. Department of Plant Science, University of Tasmania, Hobart, Australia. (personal communication).

Hoffman, G.L. 1975. *An Epidemiological Review of Possible Introductions of Fish Diseases, Northern Pacific Seastar and Japanese Kelp Through Ship's Ballast Water* AQIS Ballast Water Research Series, Report No.3, January 1994 - pp. 172-173. (*)

Agriculture Forestry & Fisheries Australia - Ballast Water Research Series Report No. 13, January 2001: *Ballast Water Treatment to Minimise the Risks of Introducing Nonindigenous Marine Organisms into Australian Ports*. 75.

Bolch, C.J. & Hallegraeff, G.M. 1993. Chemical and Physical options to kill toxic dinoflagellate cysts in ships' ballast water. *Journal of Marine Environmental Engineering.* 1: pp. 23-29.

American Public Health Association 1998, *Standard Methods for the Examination of Water and Wastewater*, 20th Edition.

Agriculture Forestry & Fisheries Australia - Ballast Water Research Series Report No. 13, January 2001: *Ballast Water Treatment to Minimise the Risks of Introducing Nonindigenous Marine Organisms into Australian Ports*. 33 – 34; pp. 67.

Agriculture Forestry & Fisheries Australia - Ballast Water Research Series Report No. 13, January 2001: *Ballast Water Treatment to Minimise the Risks of Introducing Nonindigenous Marine Organisms into Australian Ports*. 67.

Thornton, G.A. 1997. Ballast Water Heat Treatment. *Maritime Pollution Control Seminar*, Australian Defence Industries, Operations Group, Marine. Sydney, Australia.

Thornton, G.A. 1997. Ballast Water Heat Treatment. *Marine Engineers Review*. October 1997, London.

Thornton, G.A. 2000. Ballast Water Decontamination – Using Heat as a Biocide. *Sea Australia 2000*. Sydney, Australia.

(*) Also see - Whirling Disease (*Myxosoma cerebralis*): Control with ultraviolet irradiation and effect on fish. *Journal of Wildlife Diseases* 11: pp. 505-507.

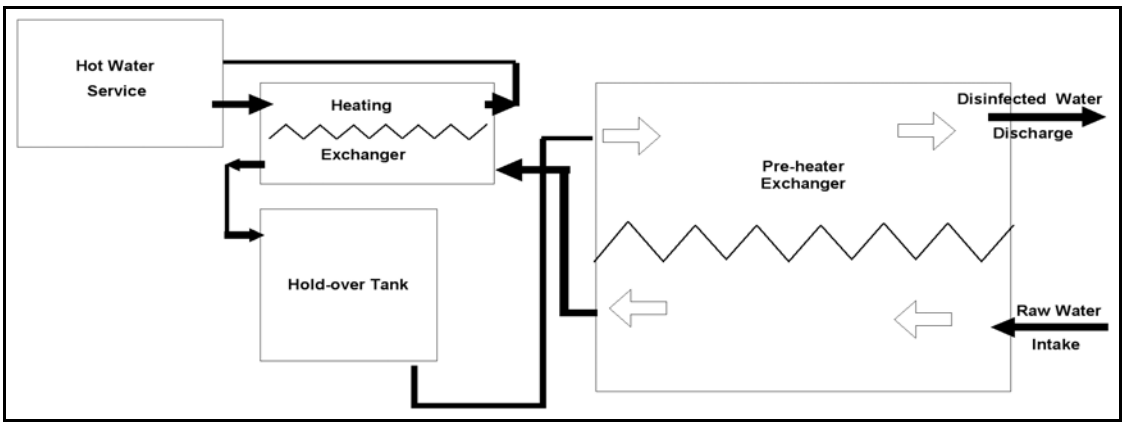


Figure 1. *Diagram of AquaTherm system.*

Appendix

Scientific report re: WaterSafe 250 water treatment program

Prepared for:

Mr Robert Prentice
Hi Tech Marine Pty Ltd
P.O. Box 524, Newport, Sydney, Australia 2106.

By:

Dr B.J. Hudson MBBS.DTPH.FAFPHM.FACTM.FRACP.FRCPA
Physician & Microbiologist,
Infectious Diseases & Public Health.
Department of Microbiology, Royal North Shore Hospital (Sydney University),
St Leonards, Sydney, Australia 2065.
November 11, 1999

Introduction

A water treatment program is required to kill a number of microbial species, viruses and plankton. The treatment process is a heat treatment that can elevate water temperature to (or above) the thermal threshold of the target organisms. This report tabulates the thermal thresholds for the target organisms, and makes recommendations on the required temperature and contact times.

Required Temperatures

The thermal thresholds vary for the target organisms. The most resistant of the target organisms are spores of *Clostridium perfringens*. The spore stage requires high temperatures of steam at pressure for inactivation. In reality, however, illness caused by this organism is related to errors in food preparation that permit proliferation of the vegetative stage of the organism. A thermal process effective against the vegetative stage of the organism is a more appropriate goal. Apart from vegetative bacteria, the highest thermal threshold is that for hepatitis A (see table). Any process used, therefore, should inactivate hepatitis A virus. Additionally, a margin of safety must be provided by the process. This would be provided by at least 5-10°C above the thermal thresholds outlined in the table.

Conclusion

A temperature of water at 90°C for 1 minute would provide a treatment that offers inactivation of the target organisms with an acceptable safety margin.

Dr B.J. Hudson

Appendix table. *Thermal inactivation data of known water organisms.*

Class of organism	Examples of most heat resistant organisms in class	Temperature required for contact time of 1 minute or less to inactivate the microorganism	Temperature required for contact time of > 1 minute to inactivate the microorganism	Comment
Vegetative Bacteria are Most rapidly killed at 65°C-100°C. These include: *E.coli*, coliforms, *Vibrio spp*, faecal streptococci, (*Enterococcus spp*), *Staphylococcus aureus*, Fungi	Legionella pneumophila *Salmonella enteritidis* PT4	80°C for 0.3 to 0.7 minutes 71.5°C for 15 seconds	70°C for 0.7 to 2.6 minutes Tailing occurs at 60°C for 5mins in food studies	Quoted times are D values (see reference 1) References 1, 2
Enteric Viruses	Hepatitis A virus	85°C for 1 minute achieves complete inactivation	60.6°C for 19 minutes achieves partial inactivation	Reference 3
Protozoa	*Cryptosporidium parvum*	72.4°C or higher for 1 minute	Oocysts remain infectious at 67.5°C for 1 minute	Reference 4
Marine organisms including Cyanobacteria, Phytoplankton	*Gymnodinium catenatum* cysts	45°C for 30 seconds	Generally not required	Reference 5 Temperature of 65.5°C is considered above the thermal threshold for all aquatic organisms of concern
Spore forming bacteria (non-vegetative forms)	*Clostridium perfringens*	Not recommended for inactivation of bacterial spores	121°C for 15 minutes	*C.perfringens* spores are the most susceptible to heat among the pathogenic spore-forming bacteria

Appendix references

Gardner J.F., Peel M.M. 1991. *Introduction to sterilization, disinfection and infection control*. Churchill Livingstone. (2nd edition). 49 pp.

Humpheson L., Adams M.R., Anderson W.A. et al. 1998. Biphasic thermal inactivation kinetics in *Salmonella enteritidis* PT4. *Appl. Environm Microbiol*. 64 : pp. 459-464.

Scheid R., Deinhardt F., Frosner G. et al. 1982. Inactivation of hepatitis A and B viruses and risk of iatrogenic transmission. In *Viral Hepatitis, 1981 International Symposium, Philadelphia*. Franklin Institute Press,. 1982. pp. 627-628.

Harp J.A., Fayer R., Pesch B.A. et al. 1996. Effect of pasteurization on infectivity of Cryptosporidium parvum oocysts in water and milk. *Appl. Environm Microbiol*. 62 : pp. 459-464.

Hallegraeff GM, Department of Plant Science, University of Tasmania, Hobart, Australia (personal communication).

Application study of ballast water treatment by electrolysing seawater

K. Dang[1] ,P. Yin[2], P. Sun, J. Xiao & Y. Song

[1] *Dalian Maritime University*
P.R. China
david_dangkun@hotmail.com

[2] *Dalian Maritime University*
P.R. China
phyin@dlmu.edu.cn

Treatment options being researched

The treatment method employed in this paper is the electrolysis of seawater. The raw seawater from Xinghai bay was used as ballast water and treated by this means.

Timeframe of the project

First phase: experimental study. This phase includes the design and building of an experimental system as well as test experiments to verify the effectiveness of this method (2002-2003).

Second phase: on board trial. The electrolysing unit is going to be installed on board a cargo ship and operational trials will be carried out (2003-2004).

Aims and objectives of the project

To develop a model of a ballast water treatment unit that is used to treat ballast water by means of electrolysing seawater. The capacity can meet the requirements of IMO conventions and the requirements of ship survey. The unit will be made up of:

- seawater electro-chlorinator;
- control system for the regulating concentration of chlorine;
- piping system; and
- auxiliary equipment.

The system can regulate the chlorine concentration produced according to the content of harmful organisms in the seawater and the temperature of the seawater. This then is used to kill all harmful organisms and pathogens with free residual chlorine kept in a minimum level.

To make a blue print for the installation of the system on board.

Research methods

Experimental system

The experimental system has been built as shown in Figure 1. Figure 2 shows a schematic diagram of the same. The experimental system mainly consists of:

- one storage tank 2.0 m × 1.0 m × 1.0 m;
- one electrolytic unit. 440 V, 50 A, throughput 2.5 m^3/h

- one portable submerged pump, centrifugal type, with a rated capacity of 3.0 m^3/h and a rated water head of 2.5 m;
- one floater type flow meter with a measurement scale of 0-3.0 m^3/h;
- large barrels, 6 × 90 L;
- sample receivers; 4 × 10 L;

Experimental procedures and testing methods

Experimental procedures

1. **Natural seawater electrolysing**. The raw seawater from Xinghai bay was simulated as ships' ballast water and treated by electrolysis.
2. **Electrolysing seawater with different concentrations of *Artemia salina*.** *Artemia salina* (hatched in seawater for 24-48 hrs) is used as target species to verify the effectiveness of the process. Then the sample, which is either the hatching seawater or a mixture of the hatching seawater and natural seawater, is treated by electrolysis. All of the samples flow through the electrolytic cell and different electrolysing voltages are applied, but the control samples are not treated in any way.

Testing methods:

Zooplankton: conducted in according with GB 17378.7-98 (NBS 1998) and counting under a microscope.

Phytoplankton: conducted in according with GB 17378.7-98 (NBS 1998) and counting under a microscope.

Bacteria: see Table 2.

Residual chlorine: measured with the residual chlorine indicator (colour comparison).

Live/dead *Artemia salina* counting: Three samples for each treated group or control group to be taken and put into 3 Petri dishes (D = 90 mm). These samples are subjected to visual inspection under a special light lamp or under an optical microscope.

Results

Tables 1 to 4 are the results of natural seawater electrolysing, where C stands for control group and T stands for treated group.

Table 1. *Electrolysing condition and initial residual chlorine (natural seawater electrolysing).*

Sample	*Voltage V*	*Current A*	*Temperature °C*	*Flowrate m^3/h*	*Initial residual chlorine ppm*
C	Control group				
T	1.8	13	15	2.03	4.0

Table 2. *Quantitative analysis of bacteria (natural seawater electrolysing).*

Group/Item	*Culture medium*	*Inoculating method*	*Sample volume cm^3*	*Total cfu*	*Final cfu*
C	2216	Plate isolation	0.1	838	8.38×10^{3}/cm^3
T	2216	Membrane filtration	10	1	1/10 cm^3
	2216	Membrane filtration	100	1	1/100 cm^3

Table 3. *Quantitative analysis of phytoplankton (natural seawater electrolysing).*

Name	***C*** ***Individual/L***	***T*** ***Individual/L***
Thalassiosira.sp	21,600	18,200
Cyclotella.sp	200	200
Navicula.sp	200	200
Navicula.spp	200	Nil found
Nitzschia.sp	200	200
Cocconis.sp	Nil found	Nil found
Hemiaulus.sp	Nil found	Nil found
coscinodiscus.sp	Nil found	Nil found
Gyrosigma.sp	Nil found	Nil found
Melosiea sulcala	Nil found	Nil found
Leptocylindrus danicus	5,200	3,400
Gomphonema sp	Nil found	Nil found
R.logiseta	600	200
Synedra sp	Nil found	Nil found
C.vulgaris	1,056,853	593,851
C.ellipsoidea	322,089	120,783
T.minimum	Nil found	Nil found
Scenedesmus	Nil found	Nil found
Dunaliella sp	191,241	60,392
Dunaliella salina	200	Nil found
Chroococcus tenas	Nil found	Nil found
Gloeothece linearis	1,157,506	503,263
Oscillatotia sp	3,000	Nil found
Dactlococcopsis rhaphidioides	Nil found	Nil found
Synechococcus sp	3,583,235	422,741
p.tenue	543,524	201,305
Chamaesiphon sp	400	Nil found
Glenodinium sp	5,200	2,600
Trachelomonas	200	1,800
Diatom cysts	Nil found	Nil found
Total	6,891,648	1,929,135

From the table it can be drawn out that 4 kinds of alga are destroyed and the total mortality is (6,891,648-1,929,135)/6,891,648 = 72.00%

Table 4. *Quantitative analysis of protozoa (natural seawater electrolysing).*

Name	C Individual/L	T Individual/L
Euciliata sp	200	Nil found
Strombidium	Nil found	Nil found
Larvae of seashell	Nil found	Nil found
Difflugia sp	Nil found	Nil found
Euplotes	Nil found	Nil found
B.calyciflorus	Nil found	Nil found
Total	200	0

Tables 5 to 7 illustrate the results of electrolysing seawater with different contents of *Artemia salina*. Sample O1 is natural seawater without *Artemia salina*. A10, A20 and B0 are control groups and A1, A2, B1, B2, B3 are treated groups.

Table 5 *Electrolysing condition and initial residual chlorine.*

Sample	Voltage V	Current A	Temperature °C	Flowrate m3/h	Initial residual chlorine ppm
O1	2.0	15	22	2.07	4.5
A1	1.9	13	22	2.07	3.5
A2	1.9	13	22	2.07	3.0
B1	1.9	12	23	2.025	4.0
B2	2.2	28	23	2.025	8
B3	2.5	47	23	2.025	15

Table 6 *Results of group A.*

Contact time	5min	0.5h	2h	4h	8h	12h	24h	36h	48h
Sample	*Residual chlorine ppm*								
O1	*4.00*	*4.00*	*3.50*	*3.25*	*3.00*	*2.00*	*2.00*	*1.00*	*0.75*
A1	*3.50*	*3.00*	*1.75*	*1.25*	*0.90*	*0.50*	*0.20*	*0.15*	*0.10*
A2	*3.00*	*2.50*	*2.00*	*1.50*	*1.00*	*0.75*	*0.45*	*0.15*	*0.10*
	Total live individual number in 6 ml								
A10	*19*	*20*	*20*	*39*	*42*	*42*	*54*	*43*	*48*
A1	*19*	*19*	*18*	*20*	*10*	*11*	*7*	*8*	*1*
A20	*11*	*14*	*11*	*17*	*21*	*18*	*21*	*25*	*28*
A2	*9*	*12*	*7*	*7*	*9*	*1*	*2*	*1*	*1*
	Mortality percentage								
A1	*0%*	*5%*	*10%*	*43.50%*	*76.19%*	*73.80%*	*87.04%*	*81.40%*	*97.92%*
A2	*18.18%*	*14.29%*	*36%*	*58.82%*	*57.14%*	*94.44%*	*90.48%*	*96.00%*	*96.43%*

Note: Test samples of A10, A1, A20, A2 are taken as 3 × 2ml. The average live individual is 6,056 per litre in A10 and 2,704 per litre in A20.

The variation of residual chlorine and mortality as time changes are shown in Figures 3 and 4**.**

Table 7 *Results of group B.*

Contact time	***5min***	***0.5h***	***2h***	***4h***	***8h***	***12h***	***24h***	***36h***	***48h***
Sample	*Residual chlorine ppm*								
B1	*4.0*	*3.5*	*2.5*	*1.8*	*1.6*	*0.6*	*0.05*	*0*	*0*
B2	*8*	*7.5*	*7.3*	*7.2*	*6.5*	*5*	*3*	*2.5*	*1.5*
B3	*15*	*13*	*13*	*13*	*12.5*	*7.5*	*7.5*	*6*	*5.5*
	Total live individual number in 15 ml								
B0	*32*	*25*	*32*	*31*	*23*	*35*	*31*	*29*	*21*
B1	*25*	*19*	*17*	*11*	*2*	*1*	*-*	*-*	*1*
B2	*18*	*14*	*15*	*5*	*-*	*1*	*-*	*-*	*-*
B3	*24*	*15*	*9*	*4*	*1*	*-*	*-*	*-*	*-*
	Mortality percentage								
B1	*21.88%*	*24%*	*46.88%*	*64.52%*	*91.30%*	*97.14%*	*99.99%*	*99.99%*	*95.23%*
B2	*43.75%*	*44%*	*63.13%*	*83.87%*	*99.99%*	*97.14%*	*99.99%*	*99.99%*	*99.99%*
B3	*25%*	*36%*	*71.88%*	*87.10%*	*95.65%*	*99.99%*	*99.99%*	*99.99%*	*99.99%*

Note: Test samples of B0, B1, B2, B3 are taken as 3 × 5 ml. The average live individual is 1,919 per litre in B0.
The sign - stands for Nil found.

The variation of residual chlorine and mortality of group B as time changes are shown in Figures 5 and 6**.**

AC power consumption and cost

If ships' ballast water is treated by direct electrolysis of seawater, there will be no cost for salt consumption. The DC power consumption is about 4.5-6.5 kWh/kg active chlorine and the AC power consumption is only about 6.0-10 kWh/kg active chlorine (NBS 1990). Supposing the secondary electrolytic cell is employed on shipboard and the cost can be calculated in the following manner:

Assuming the AC power consumption 7.0kWh/kg active chlorine, i.e. 0.007kWh/g (NBS 1990).

Diesel oil consumption rate: 200-230g/kWh. Taking account other cost factors, such as lube oil consumption use 270g/kWh as an assumed rate (1.25 × [200-230] = [250-287.5]g/kWh).

Diesel oil price: 365 US$/t = 0.365 US$/kg = 0.000365 US$/g.

Cost of 1kWh: 270 × 0.000365=0.09855 US$/kWh ≈ 0.10 US$/kWh.

The power cost for 1000 m^3 ballast water treatment will be:

Applied chlorine concentration	5ppm	10ppm	15ppm	20ppm
AC power consumption (kWh)	35	70	105	140
Cost US$/1000t	3.5	7.0	10.5	14.0

Note: The cost just refers to the electrolytic cell power consumption and it does not include other costs such as equipment purchase, pump operation etc.

Conclusions and recommendations

- If the raw seawater is treated by electrolysis, it can kill 4 kinds of alga from 18 kinds with an initial chlorine concentration of 4.0 ppm. The total mortality of phytoplankton can be up to72% and the mortality of bacteria is 99.99%. *Euciliata sp* in the seawater can be killed immediately.

- If the seawater with an *Artemia salina* density increased from 2 individual/ml to 6 individual/ml is treated by electrolysing with an initial chlorine concentration of 4.0 ppm, the mortality of *Artemia salin* is more than 95% after 48 hours of contact.

- If the seawater with an *Artemia salina* density of not more than 2 individual/ml is treated by electrolysing with an initial chlorine concentration of 8.0 ppm, the mortality of *Artemia salina* is more than 95% after 24 hours of contact. With an initial chlorine concentration of 15 ppm, 99.99% of *Artemia salin*a is killed after 12 hours of contact.

- If the residual chlorine in the treated seawater is less than 0.5 ppm, the chlorine will have no effect on *Artemia salina*.

It is recommended that the target species used to verify the performance of any new ballast water treatment unit or system should be selected and standardized as soon as possible.

Acknowledgements

This project is one (1B4c) of China's activities as part of the GloBallast programme. It is financially supported by the GloBallast programme and China Ocean Shipping Company (COSCO). We would like to express our appreciation to the GloBallast Programme Coordination Unit (PCU), GEF, UNDP, COSCO and China SMA. We are grateful to Mr. Zhao Dianrong for his coordination between PCU and the implementation team for this project, and further for his contribution and valuable suggestions to the project.

References

NBS 1998: *China National Bureau of standards, Coastal pollution biological measurement and ecological survey*, GB 17378.7-98.

NBS 1990: *China National Bureau of standards, sodium hypochlorite generator*, GB 12176-90.

Figure 1. *The picture of the experimental system.*

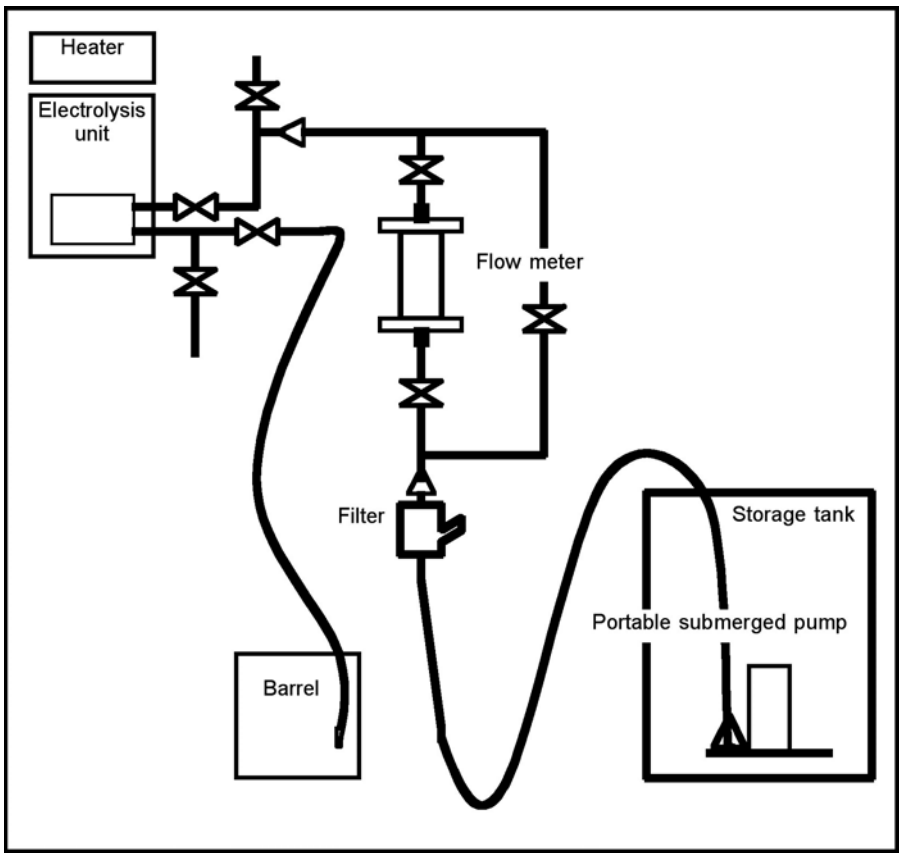


Figure 2. *Schematic diagram of the experimental system.*

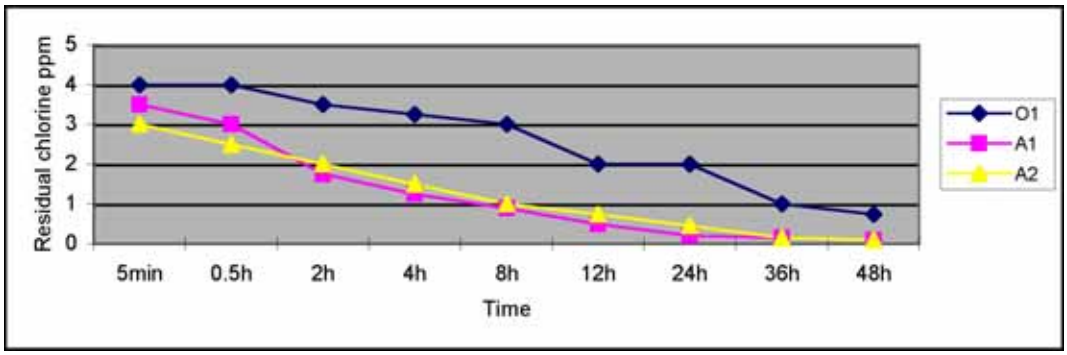


Figure 3. *Changes in residual chlorine (Group A).*

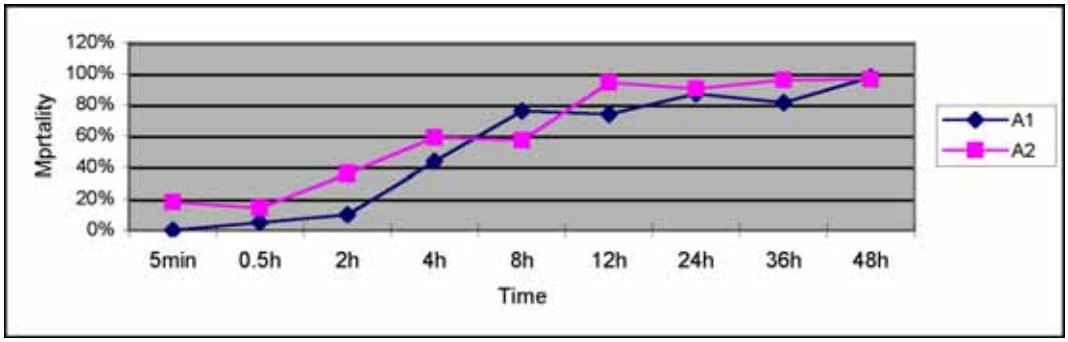


Figure 4. *Changes in mortality (Group A).*

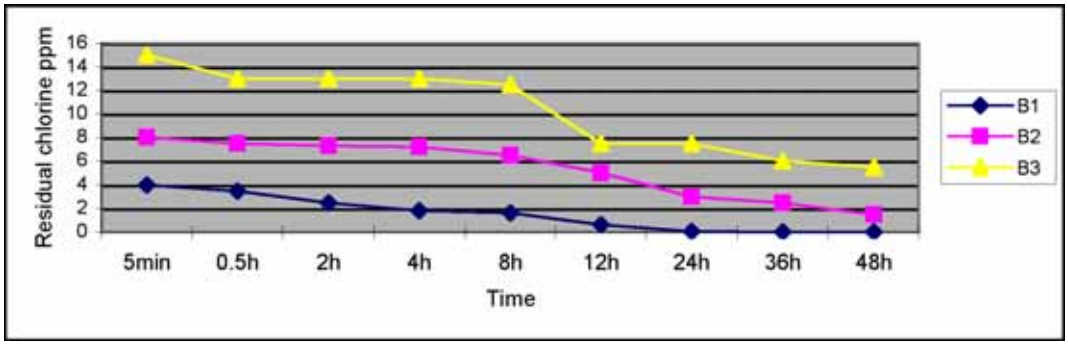


Figure 5. *Changes in residual chlorine (Group B).*

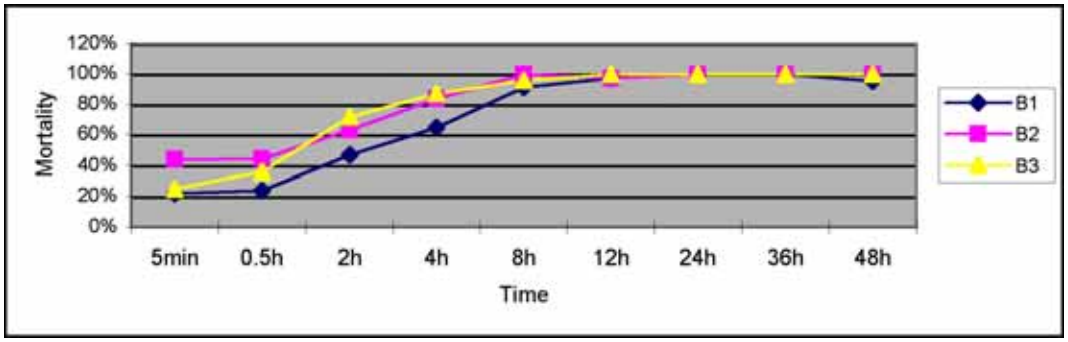


Figure 6. *Changes in mortality (Group B).*

Electro-sanitization of ballast water

C.E. Leffler[1], A. Rogerson[2], W. Paul[1], G. Germaine[1], M. Elliot[1], V. Antonelli[3], S. Grubs[2], C. Campbell[2], G. Beall[4] & A. Salamone[1]

[1]*Marine Environmental Partners, Inc. (MEP)*
USA
bud@mepi.net

[2] *Oceanographic Center of Nova Southeastern University (NSU), USA*

[3]*ISIR, Genoa, Italy*

[4]*Nanospec Company, USA*

Treatment options being researched

MEP's continued development of a ballast water treatment system based on electro-ionization is the subject of this paper. Design criteria include achieving a > 95% kill of marine biota (bacteria and protists) found in ballast tanks and an ecologically safe discharge effluent while maintaining engineering standards and cost effectiveness.

Research began three years ago by examining the strengths and limitations of other technologies being considered: chemical additives, ultraviolet light, heat treatment, and others. Investigation, through a series of laboratory, pilot, and on-board experiments, produced MEP's current version of an electro-ionization system for treatment of ballast water. This system in its nascent form was reported on at the 1st International Ballast Water Treatment R&D Symposium 2001 (Aliotta et al, 2001).

Timeframe of the project

This paper reports on research and development occurring between Spring 2002 and May 2003.

Objectives of the project

1. Refine laboratory and shipboard electro-ionization systems for ballast water sanitization.
2. Apply biological and chemical tests to evaluate performance and safety of treatment.
3. Design a scalable system to treat ballast on diverse ship types.

Biological and chemical test protocols

Electro-ionization treatment systems

On-Board Pilot Treatment System

A pilot system was installed in Spring 2002 aboard the Carnival Cruise ship the M.V. *Elation* ("*Elation*") that operated out of Long Beach, California traveling south to Mexico on a 7-day itinerary. The treatment system was installed as a flow-through system re-circulating ballast water at approximately 350 gallons per minute (Figure 1). This pilot system consisted of the electro-ionization technology, comprising an air ionization module and seawater electrolysis generator. The ionized air and the electrolyzed seawater mixture were delivered into the bulk of the ballast water flow via a mixing manifold.

1/20th Scale Model Treatment System

At Nova Southeastern University, a 1/20th scale model of the 2003 Carnival *Elation* single-pass system was built for equipment and treatment development. The three components of the system are undergoing testing and refinement: seawater electrolysis generator, ionized air module, and the filtering system. Mixing of the ionized air and electrolyzed seawater with the bulk of the ballast water is accomplished with an inline static mixer.

Current On-Board Treatment System

The electro-ionization system currently being installed on the Carnival *Elation* is a full-scale single-pass system with a flow rate of approximately 1000 gallons per minute. It was designed based on the results to date from the 1/20th scale model system and the 2002 *Elation* pilot system.

Sample collection and handling

Collection of ballast water samples from the ballast tank during on-board *Elation* tests (2002) was effected by suction withdrawal of ballast water from a sampling tube one meter below the ballast water surface. Sampling at discharge occurred post the discharge pump and the ORP sensor. To collect water from the pre- and post- treatment ports, samples were collected from sampling taps (*Figure 1, a and b*). In all cases, equipment and sampling bottles were sterilized prior to use. Samples were processed after one hour of collection (except those set aside for re-growth; these were left at room temperature for 24 h before counting). EPA method 9060A was followed for sample collection.
Baseline samples were taken from seawater alongside shipboard, Los Angeles, Port of San Pedro, California.

Laboratory procedures

Enumeration of organisms

Since reactive chemicals were generated in the treated ballast water, collected samples were degassed by shaking them briefly and then allowing them to stand for one hour before processing for biota.

A. Bacteria

Total culturable bacteria were counted using standard plate counting and/or membrane filtration methods. For plate counting, samples were processed by serial dilution and aliquots (0.1 ml) were spread on the surface of a Marine Agar (Difco) plate (EPA method 9215C). The heterotrophic plate count (HPC), formerly known as the standard plate count, is a procedure for estimating the number of live heterotrophic bacteria in water. All counting was replicated three times. After treatment, when bacterial counts were significantly reduced, samples were processed by membrane filtration counting (EPA method 9215D). Aliquots of treated water (10, 50 and 100 ml) were filtered through a sterile 0.45 μm filter to collect bacteria. Filters were placed on Marine Agar plates and incubated. All incubations were at room temperature (around 23°C) for five days. Thereafter, the number of colony forming units (cfu's) was recorded for both untreated and treated water.

B. Protists (algae and protozoa)

Protists span a wide diversity of forms including naked amoebae, heterotrophic flagellates, ciliates, diatoms, autotrophic flagellates, dinoflagellates and non-motile algae. Consequently, the protists represent an important diverse array of eukaryotic microbes that are useful for verification testing when dealing with "indigenous" organisms. Some of these protists form resistant resting stages (cysts), such as those of dinoflagellates. Depending on native populations in the water column, the protistan count included trophic and resistant stages.

The aliquot method has routinely been used for the enumeration of heterotrophic protozoa, but is also appropriate for autotrophic protists if inoculated dishes are incubated in light. Small samples of water withdrawn from the ballast tanks (ca 50 ml) were vortexed to randomly distribute protists

in the sample (often, protists are located on suspended flocs). To count protists, aliquots (10 to 40 µl) of water were micropipetted into the wells of tissue culture plates. For each of the five replicates from each sample, 48 tissue culture wells were inoculated. Each well also contained one ml of sterile seawater and a one cm^3 bloc of malt-yeast agar. Nutrients diffusing from the agar nourished attendant bacteria that in turn were grazed by protozoa present in the inoculums. Plates were incubated at 20°C in the dark and were examined after seven days for the presence of protozoa (amoebae, flagellates, and ciliates). An inverted phase contrast microscope was used to examine the base of wells. It was assumed that a well with positive growth originated from a single cell added in the inoculums. In this way, the total number of protozoa in the total volume inoculated (48 × inoculation volume) was calculated and expressed as density per ml.

The number of autotrophic protists in the sample was estimated in a similar manner as above. In addition, seawater was enriched with a dilute soil extract solution to supply trace nutrients essential for the growth of algae. Cultures were incubated in the light to promote the growth of autotrophs in the wells.

Chemical and Physical Evaluation

Chemical and physical parameters were monitored to provide baseline information on the pre- and post- treated ballast water. This monitoring provided information on changes resulting from the ballast water treatment. In particular, due to potential chlorine or bromine residuals in the treated water, trihalomethanes (THM) were analyzed by mass spectroscopy at Spectrum Laboratories, Ft Lauderdale, Florida, using EPA method 8260. This method is capable of detecting 58 common organic compounds. Triplicate samples were collected and monitored for the following (all protocols in Eaton, et al. 1995; the EPA method reference number for each is indicated in parenthesis):

a) Dissolved oxygen (4500-0 G. Membrane Electrode Method)

b) pH (4500-H+)

c) Temperature (2550)

d) Conductivity/Salinity (2520 B. Electrical Conductivity Method)

e) Turbidity (2130 B, Nephelometric Method)

f) Chlorinated/Brominated organics (Mass Spectroscopy Method 8260)
   - conducted by Spectrum Laboratories

g) Chlorine/Bromine (4500-ClF. DPD Ferrous Titrimetric Method)

h) Oxidative Reduction Potential (ORP) (2580 Oxidation-Reduction Potential)

i) Reduction Potential Analysis
   - conducted by Nanospec Company

Acute and Chronic Toxicity

The effluent from the on-board testing was not subjected to acute and chronic toxicity testing, however, a $1/20^{th}$ scale model, located at the Oceanographic Center of NSU, was used to generate treated water for testing. The pilot system is a modified single-pass system similar to the system currently being installed on Carnival *Elation*.

Toxicity tests were carried out by Toxikon Corporation, Jupiter, Florida, to determine the acute toxicity of treated effluents to the mysid shrimp, *Mysidopsis bahia*. The methodologies used for the 96-hour acute static definitive studies were based on those described in EPA/600/4-90/027F "Methods for Measuring the Acute Toxicology of Effluents and Receiving Waters to Freshwater and Marine Organisms". The tests consisted of exposure of *Mysidopsis bahia* to nominal

concentrations of 6.25, 12.5, 25, 50 and 100% treated effluent. The effluents were produced by treatment per the electro-ionization process of this paper. Samples of the effluent were collected at discharge in sealed containers and transported for testing in an ice-filled container. Reactive halogens were measured within four hours (0.04 ppm – 0.12 ppm) of sample collection and toxicity testing was begun within a 24-hour period. A dilution water control of filtered laboratory saltwater, as well as a raw seawater control (reactive halogen-containing chemicals – 0.00 ppm) from the NSU boat basin were run concurrently.

Seven-day definitive chronic toxicity testing, by Toxikon Corporation, was conducted on electro-ionization treated effluent containing two times the maximum normally produced residual chlorine, 1.2 ppm, to simulate extreme conditions. Methods for the seven-day static-renewal definitive test followed "Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Marine and Estuarine Organisms" (EPA/600/4-91/003 - U.S. EPA, 1994). The test consisted of exposure of mysid shrimp to 100% (undiluted), 50%, 25%, 12.5% and 6.25% test effluent, as well as a laboratory saltwater control and de-chlorinated effluent (100% only). The endpoints observed in this study were survival, growth (via dry weight), and fecundity (ability of the females to reproduce).

A subsequent seven-day definitive chronic test was also conducted using effluent containing residual halogens produced at normal operating levels (0.04 ppm).

All statistical analyses for chronic tests were conducted following the decision tree for analysis of survival or growth (via dry weight) utilizing the statistical program Toxcalc, Version 5.0. The survival data was transformed using the one-tailed arcsine-square root transformation. Statistical comparison of each effluent testing concentration was made to the control replicates tested concurrently with the effluent testing concentrations.

The statistical comparisons for survival data used in this study include Shapiro-Wilk's Test for normal distribution. Additionally, Dunnett's Test was used for the Hypothesis Test of survival data and Trimmed Spearman-Karber for the LC_{50} calculation.

The statistical comparisons for the growth via dry weight data used in this study include Shapiro-Wilk's Test for normal distribution and Barlett's Test for the equality of variances. Additionally, Dunnett's Test was used for the Hypothesis Test of growth data.

Results

Marine Environmental Partners Inc. (MEP) (with C. E. Bud Leffler as the lead technical investigator) and the Oceanographic Center of Nova Southeastern University (NSU), (with Dr. Andrew Rogerson as the lead independent investigator in biological testing) have evaluated multiple processes for sanitizing ballast water and found electro-ionization technology to be a promising option. Electro-ionization is a treatment method which has been used to disinfect freshwater effluents that MEP modified and applied to treat marine and estuarine waters.

Data on various treatment configurations employing electro-ionization technology was collected over the last two years. Generally, the results show the technology, generating halogen residues of around 0.5 ppm, to be capable of killing (or inactivating) approximately 95% of indigenous (i.e. native), culturable bacteria in water from Port Everglades, Florida. On one occasion, up to 99% of bacteria were killed or inactivated. Trials conducted on indigenous protist (algae and protozoa) indicate a kill efficiency of around 90%. These promising results guided the evolution of the treatment system to its present configuration.

Pilot system tests on board the Carnival M/S Elation

In January 2002, MEP installed a pilot system on the Carnival cruise ship *Elation*. The pilot electro-ionization system on the Carnival *Elation* was tested on one 200 m^3 ballast tank at a flow rate of

350 gpm. This pilot system was installed to function as a re-circulating system providing continuous electro-ionization (sanitization) of the ballast water.

Based on prior laboratory tests, the shipboard pilot system was designed in such a manner that a slipstream was diverted from the main ballast to feed several electrolysis cells for generation of primary disinfectants. Each electrolysis cell (three in total) was 1.5" in diameter with an output of 158 oz of halogens/24 hours/cell. This slipstream and the airflow from the gas ion generators were then introduced via a mixing module, known on the ship as "the octopus", for combining the ionized air (gas) and halogen species, in tandem, with the ballast water to kill biota. The shipboard prototype system utilized air compressors so that a precise amount of ionized gases was injected into the system.

Using the continuous recycling system, bacteria and protists were reduced by over 95% during the first 20 h of treatment (Figures 2 and 3). In these runs, starting bacterial counts were close to 120×10^3 bacteria per ml and total protists were around 20 per ml. Of course, these counts are significant underestimates of the true numbers of bacteria and protists in the ballast water, since not all were amenable to laboratory cultivation (in the enrichment counting methods used). However, they give a representative 'index' of kill rate and it is expected that these underestimates reflect actual die-offs in the treated water. However, in the next 20 h, numbers of biota in the tanks recovered and reached levels equivalent to the starting concentration. This was probably due the fact that the system did not run continuously on-board ship. Although continuous treatment had been planned over the course of the voyage, ship-operating procedures required the use of the ballast pump resulting in frequent shut-downs of the system (Figure 4). Hence, the dramatic recoveries in counts probably resulted from the lengthy down-times around the 35 to 70 hour times. This recovery after treatment is an example of re-growth. This was investigated further by storing treated samples for 24 hours prior to counting bacterial levels. Figure 5 shows that immediately after treatment (in the case of the samples at 24 h, 48 h, 72h, and 96 h), the numbers of bacteria were low but that there was a rapid population increase over the next 24 h as surviving bacteria quickly became re-established because of high nutrient loads (from lysed biota) and reduced competition. To attain the densities observed, bacteria were replicating in a few hours. For example, the 72 h data showed that bacteria increased from 94×10^3 bacteria per ml to 930×10^3 bacteria per ml, which indicated the bacteria were dividing approximately every eight hours. The scale of recovery in these incubation bottles was comparable to the recoveries observed in the ballast tank treatments.

Mass spectrometry was used to determine the chemical species generated by this system. The seawater electrolysis cell module was found to generate reactive bromine ions (Spectrum Laboratories, Ft. Lauderdale, FL). Concurrently, atmospheric air was ionized into various (undefined) species of oxygen and nitrogen in the air ionization module. These ionized species probably included various singlet molecular oxygen species, ionized nitrogen, and peroxyl ions (e.g. O_2^-, O_2^{--}, N_2^+, e^-, H_2O_2, OH^-). The ionized air (gas) stream was fed into the electrolyzed seawater stream where reaction occurred with the previously electrolyzed bromine, thereby enhancing biota termination.

Utilizing the mass spectrometry data along with reduction potential analysis, the electro-ionization system was theorized to utilize a combination of hydrogen peroxide, oxygen species, and bromine species as disinfectants (Nanospec Company, San Marcos, TX). Ozone did not appear to be a factor in the chemical reactants. This was consistent with the analytical data where bromo species (40–54 ppb bromoform and 2-11 ppb dibromochloromethane) were the main trace contaminants left in the seawater (Spectrum Laboratories). Both oxygen and hydrogen peroxide are expected to dissipate rapidly in oceans to environmental levels. In summary, the net result of the treatment system was the disinfection of the ballast water using trace amounts of bromoform and even smaller amounts of dibromochloromethane, with no persistent disinfectant species released to the marine environment. It must be recognized that even the bromoform concentration was below levels normally applied to drinking water.

Notably, the use of chlorine in potable water is known to react with organic materials in water and form a variety of carcinogenic trihalomethanes (THMs) and other molecular species. Therefore, the

U.S. Environmental Protection Agency (EPA) set an absolute limit of 100 ppb for THMs in any potable water system. As existing discharge standards do not address the presence of THMs, MEP tested its shipboard ballast water for THMs utilizing EPA drinking water standards and found it to be well within the EPA drinking water standards [bromoform (80-100 ppb), dibromochloromethane (0.5-3.1 ppb), and dibromoethane (1-4 ppb)]. Furthermore, no detectable THMs were present at the point of discharge. MEP confirmed ballast water processed in its recirculating system remains within EPA's parameter even when fluid is circulated for several days during the electro-ionization process (Spectrum Laboratories).

The Carnival *Elation* tests demonstrated that 0.5 ppm of halogen (0.35 ppm free and 0.15 ppm combined) produced effective kills in the greater than 95% range.

1/20 scale model single pass system

Because of re-growth issues during idle treatment periods with the recirculating system, constant treatment of ballast water during passage was deemed undesirable. Therefore, although results from the recirculating pilot system were promising, it was concluded that sanitization treatment should occur at de-ballasting to ensure the highest flexibility for on-board operation. Hence, the transition to the single-pass system is presently being made.

In preparation for installation of the current system on the *Elation* and to provide a testing platform for new methodologies and equipment, MEP installed a 1/20-scale model single-pass electro-sanitization ballast water system at the Oceanographic Center of Nova Southeastern University. To date, the system has primarily been run to provide treated water for toxicity tests.

Acute exposure results on discharged ballast water indicate no surrogate organism (mysid shrimp) death at electro-ionization treatment levels required for 95% on-ship ballast water biota kill (0.04 – 0.12 ppm residual halogens). Chronic static exposure (seven days) testing of discharged ballast water on mysid shrimp, at treatment levels required for 95% on-ship ballast water biota kill (0.04 ppm residual halogens), also indicated no-impact to growth or ability to reproduce. All chronic and acute toxicity testing is being performed at Toxikon Corporation. A critical element of this ballast water system is its lack of environmental impact upon discharge.

After 96 hours of acute exposure, there was 0% mortality in all test controls and all test effluents produced by treatment per the electro-ionization process utilizing a full capacity system and even at 1.2 ppm residual halogen if neutralized prior to discharge. The LC_{50} cannot be calculated due to the lack of significant mortality during the 96-hour exposure when compared to the controls. Therefore, the LC_{50} value is greater than the highest test concentration or > 100% effluent and the NOEC (no observable effects concentration) can be stated to be 100% effluent.

After seven days of chronic exposure to treated ballast water containing 0.04 ppm of total residual halogen, mysid mortality was zero percent in testing concentrations of 6.25%, 25%, 50%, and 100% test effluent in seawater. Testing concentration 12.5% yielded 5% mortality. The LOEC value (lowest observable effects concentration) for survival was 100% test effluent. The LC_{50} is calculated to be 100% test effluent – the treated ballast water at discharge does not kill mysid shrimp even upon seven days of full exposure.

The discharged treated ballast water (0.04 ppm total residual halogen) was found to have no affect on the mysid growth. At test termination, mysid growth (as average dry weight per mysid in each replicate) ranged from 0.39 mg to 1.1 mg for surviving mysids exposed to treated effluent. The average dry weight of the laboratory control animals was 0.69 mg; and was 0.55 mg in raw seawater. There was no statistical difference in dry weight between the treated tests and the controls. Therefore, again the LOEC was calculated to be > 100% effluent and the NOEC value was 100% effluent. In summary, the mysid shrimp grew to the same size whether living in discharged treated ballast or raw seawater.

Also the discharged treated ballast water (0.04 ppm total residual halogen) did not affect fecundity, the ability to produce offspring. Mysid fecundity is expressed as the percentage of gravid and/or ovigerous females bearing eggs observed at the termination of the study. With treated effluent containing 0.04 ppm residual halogen, the fecundity of female mysids was 100% in each testing concentration that contained identifiable females. Laboratory and seawater controls produced 100% fecundity. Therefore, the LOEC value for fecundity was >100% effluent, while the NOEC value was 100% effluent.

In order to test an extreme situation, seven-day chronic exposure tests with treated effluent containing 1.2 ppm residual halogen (two times the level required for treatment) produced mysid mortality of zero percent at 6.25% and 12.5% test effluent. Testing concentrations 25% and 50% yielded three percent mortality. The 100% test treatment yielded one hundred percent mortality. Mortality was zero percent in 100% de-chlorinated effluent and in the laboratory saltwater control. The LOEC value for survival was 100% test effluent and the NOEC value for survival was 50% test effluent. The LC_{50} was calculated to be 68% test effluent. With this testing series, the mysid shrimp exposed to 50% effluent or less, demonstrated no statistically significant difference in dry weight when compared to the laboratory controls or raw seawater controls. Therefore, based upon growth via dry weight, the LOEC value was calculated at > 50% effluent and the NOEC value was 50% effluent.

Summary of electro-ionization system testing results

***Elation* pilot recirculating system**		**1/20 scale single-pass system**
Biological testing		
Bacteria kill	> 95%	> 95%
Protists kill	> 90%	>90%
Effluent toxicology – electro-ionization system at full capacity (95% biota kill or higher)		
- 96-hr acute		NOEC = 100% effluent LD_{50} > 100% effluent
- 7-dy chronic mortality		NOCE = 100% effluent LOEC > 100% effluent LD_{50} > 100% effluent
- 7-dy chronic growth		No effect
- 7-dy chronic fecundity		No effect
Chemical analysis at full capacity (95% biota kill or higher)		
- treatment halogen	0.4 - 0.5 ppm	0.4 - 0.5 ppm
- halogen residuals		0.04 – 0.12 ppm
- THM residuals on ship	80 – 100 ppb bromoform 0.5 – 3.1 ppb dibromochloromethane 1 – 4 ppb dibromoethane	
at discharge	not detectable	

System currently being installed on-board the *Elation*

The most effective ballast water treatment system found to date utilizes three technologies - solids removal, electrolysis and ionization - in a single pass system. This system will continue to develop over its five-year testing plan on the Carnival *Elation*. As the ship changes routing and encompasses various silt loads and other variables, MEP expects to develop a database of information to refine engineering of future systems.

Currently, at intake, the ballast water is filtered to remove solids larger than 50 microns. During transit the ballast water is left without treatment. Just prior to de-ballasting, the ballast water is re-filtered to remove any large particles or biota formed during transit. This filtrate is handled as required

by management. The filtered ballast water is then sanitized as it flows through a static mixer with reactive chemicals formed from electrolysis of the ballast water and ionization of ambient air. Discharge occurs immediately following sanitization.

MEP has built a 1000 gpm unit, which is being installed on the Carnival *Elation*. Each of the system modules will meet class certification and is built to perform over the life of the ship. The system is designed with integrated power and control systems driven by a PLC (programmable logic controller) module, which monitors and controls over 300 points. This system, to be tested over a five-year period, is designed to operate at a cost of $0.005 or $^1/_2$ cent per metric ton based on $0.16/kW hr energy charge as estimated by Carnival Cruise Lines.

Solids removal

After testing alternative means of solids removal, filtration modules were selected and are deployed based on the quality of the seawater influent anticipated aboard a given ship as determined by its proposed routing.

Based on anticipated regulatory action and system efficiency, MEP is using a self-cleaning 50 micron filtration module (Figure 6) controlled by a PLC (programmable logic controller). When taking on ballast, the discharge of the filtrate can be returned overboard, as only local species should be present during ballast intake.

When de-ballasting begins the PLC initiates the filtration process utilizing the same filter on the ballast water held during transit. Since a ship is normally in port at this stage, the filtrate must be managed onboard per ship management requirements.

Electrolysis and ionization

The original pilot electro-ionization system on the Carnival *Elation* was tested on one 200 m^3 ballast tank at a flow rate of 350 gpm. The current electro-ionization system, which is being installed in May/June 2003, processes 1000 gpm of ballast water with a single pass system. This increase in treatment rate from 350 gpm to 1000 gpm was accomplished by the addition of parallel electrolysis and ionization modules as well as module design efficiencies.

The pilot ionization gas-generating cylinders were 30” long by 4” in diameter. Two of these cylinders generate 1.25 cfm of airflow; four generate 2.5 cfm of airflow, the number used on the pilot Carnival *Elation* tests *(*Figure 7*)*. By doubling the length of the cylinders to 60” and increasing the diameter to 8”, MEP effected another quadrupling of output while reducing the equipment footprint and cost. In other improvements, the original ionization unit was water jacketed for cooling; air-cooling has been found to be preferable.

The current units are rack-mounted onboard the *Elation (*Figure 8*)*. They may be remote mounted to a bulkhead or elsewhere in other applications. The ionization generator rack is monitored for flow from each cylinder as well as temperature, pressure, etc**.** Photocopies are included of both the pilot and the current ionization gas generators.

Following pilot testing on the Carnival *Elation* and on MEP’s 1/20-scale model at Nova Southeastern University, it was determined to not use a ballast water slipstream for electrolysis of ballast water. Instead the ballast water, in its entirety, flows through the electrolysis cell as shown in *Figure 9*. The current module contains 10 cells for a combined capability of 1,580 oz of halogens/24 hours, which was designed to treat ballast water pumping at 1000 gpm while being discharged. The halogens which are sanitizing the ballast water are > 99% bromine species (as detected by mass spectrometry).

Electrolysis cell diameter and parallel electrolysis modules are planned to increase capacity to 6,500 gpm for cargo ship requirements. Further design modifications are planned to reduce sensor costs for controlling the electrolysis module and to decrease the number of parts.

Effective mixing of the sanitizing agents within seawater held in the reaction vessel is a key research area, which has resulted in the engineering of a unique mixing module.

Static mixing

Prior to shipboard installation, MEP designed mock ballast water tanks to simulate the transmissive qualities of the ionized gases and electrolyzed seawater into the ballast water. In order to expose all of the ballast water in a tank to the treatment process, the reactants had to be distributed in a manner where virtually all fluids would come into contact with the sterilizing ionized gases and electrolyzed bromine species.

In the earlier shipboard pilot testing, the electrolyzed ballast water slipstream and the airflow from the gas ion generators were introduced to each other via a mixing module known on the ship as "the octopus" (Figure 10).

With the current electro-ionization system, the "octopus" has been replaced by a mix manifold module, which provides thorough mixing of the ionized air and electrolyzed seawater with the bulk of the ballast water for disinfection, while stabilizing the water chemistry in preparation for discharge (Figure 11).

The controls

The ballast water treatment system is controlled and monitored by an electronic control system. The controls are installed in four cabinets that start with a stabilized and conditioned power supply to the PLC, which monitors and drives the entire system (Figure 12). The PLC monitors the system and can self- repair by turning on additional back-up units if it senses a problem, and is designed to self-report and generate information for remote troubleshooting.

The testing of the control system was designed to integrate the modules and determine the least amount of equipment/energy required to fully sanitize the biota. MEP uses periodic biological plate counts to validate the control system operation.

Conclusions and recommendations

MEP's electro-ionization system shows promise for use in sanitizing ballast water. The system, as tested on Carnival's *Elation* and in the 1/20-scale model, disinfected seawater (California coast, Pacific Ocean, and Florida coast, Atlantic Ocean) to at least a 95% kill of bacteria.

The effluent's safety also appears promising. No detectable trihalomethanes were present at de-ballast from the *Elation* pilot trials. The concentrations of reactive halogens present at ballast discharge from the $1/20^{th}$ scale model preliminary tests were ecologically non-toxic producing no mysid shrimp mortality and no effect on mysid shrimp growth or fecundity.

Chemical and biological research methods that were tested provided useful information for system improvements and for determining efficacy and safety. Further development of an ATP rapid detection protocol for living biota is planned, as well as further protocol development for effluent toxicity.

Formal testing, for the California Lands Commission, of the system currently being installed on the Carnival *Elation* is expected to begin in Summer 2003. In the meantime, equipment refinements are now concentrating on defining the least concentration of bromine species required to effect a high elimination of biota. This concentration, as determined from the $1/20^{th}$ scale model, will become the starting point for the upcoming on-ship system testing.

References

Aliotta, J, Rogerson, A., Campbell, C. & Yonge, M. 2001. Electro-ionization treatment for ballast water; assessment of effectiveness against marine microbiota typical of those in ballast water. *IMarEST 1st International Ballast Water Treatment R& D Symposium*.

Nanospec Company, Gary W. Beall, Director of Southwest Texas State University, Center for Nanophase Research, Institute for Environmental and Industrial Science, 601 University Drive, San Marcos, TX 78666-4616, USA.

Spectrum Laboratories, 1460 W. McNab Road, Ft. Lauderdale, FL 33309, USA.

Toxikon Corporation, 106 Coastal Way, Jupiter, FL 33477, USA.

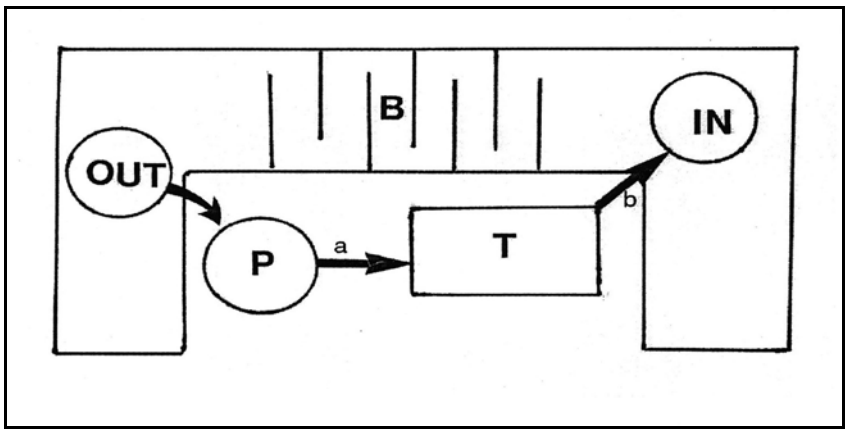


Figure 1. *Diagram of ballast tank with re-circulating pilot treatment system (T) on Carnival* Elation*. Tank was baffled (B). Water was taken from an entry hatch (OUT), pumped through the treatment system with the ballast pump (P), and returned into another entry hatch (IN). Sampling ports (a and b) are indicated. Diagram not to scale.*

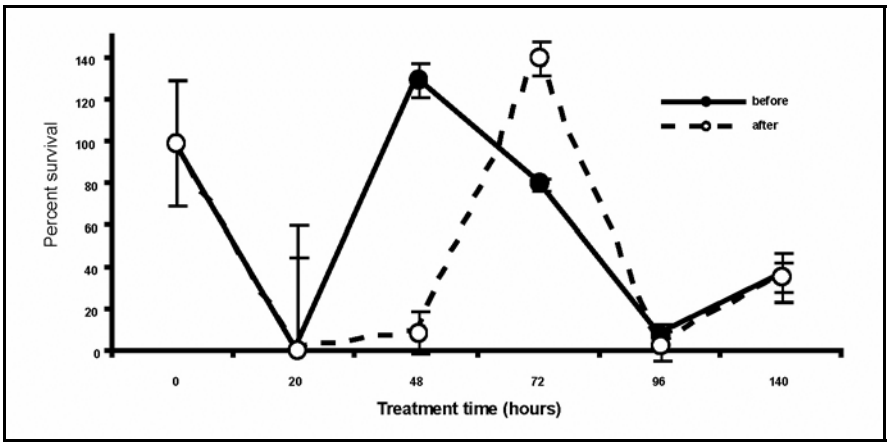


Figure 2. *Percent survival of bacteria in the pilot ballast tank as a function of treatment time. Samples were collected from the sample port 'a' located before the treatment system and at port 'b' located after the treatment system. Means of 5 replicate runs with standard errors.*

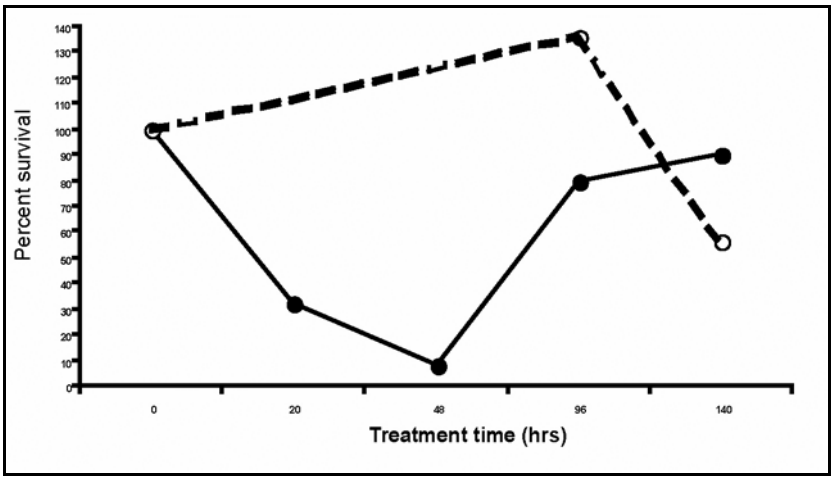


Figure 3. *Percent survival of total protists in the treated tank (solid line) and the control tank (dotted line). Samples were collected from the 'before' sample port.*

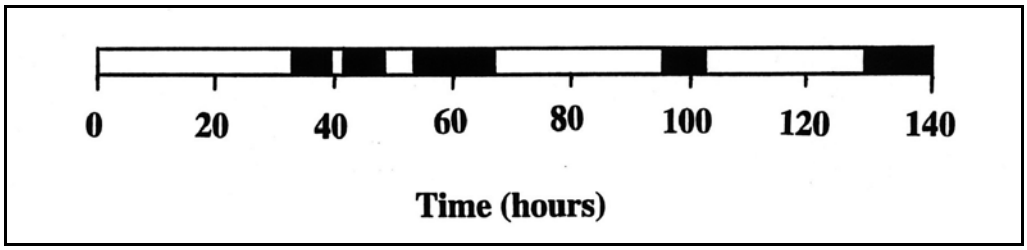


Figure 4. *Time line showing functioning treatment times (white) and treatment down-times (black) of the on-board recirculating treatment system.*

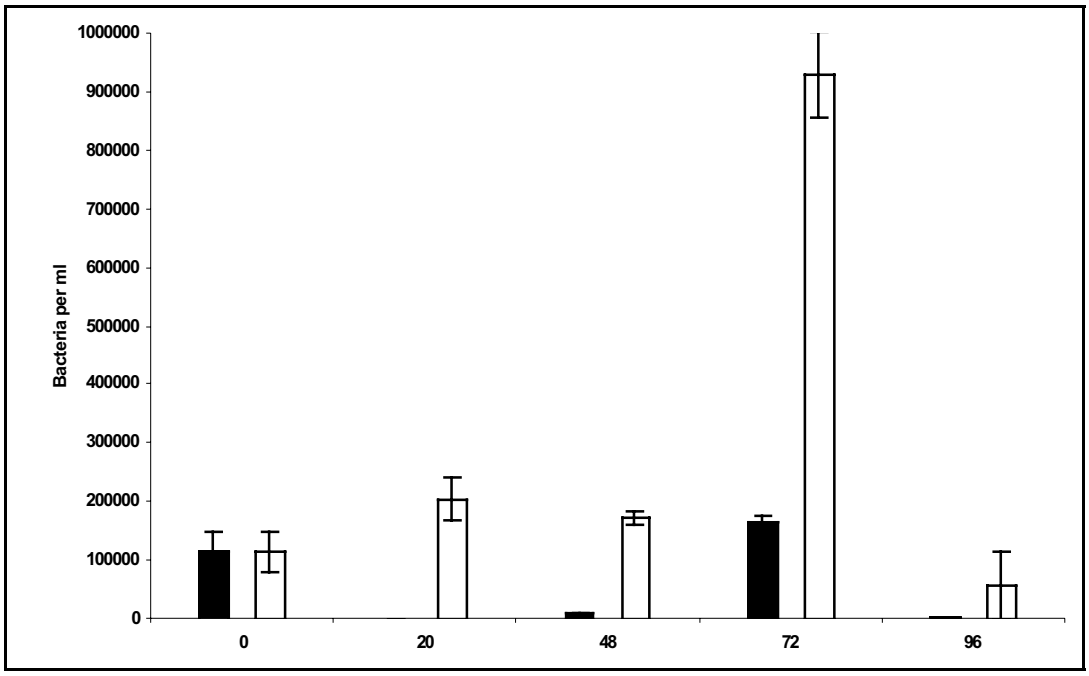


Figure 5. *Bacteria per ml in treated samples (collected from sample port 'b' at 0 h. 20 h, 72 h, and 96 h) after a 24 h incubation period at room temperature. Data as means of 5 replicates with standard errors. Black bars = numbers before incubation: open bars = numbers of bacteria after incubation. Note, the time 0 bars are similar since there was no treatment and therefore no regrowth.*

Figure 6. *Self-cleaning filter for Carnival* Elation *current system.*

Figure 7. *Racks of ionization generators (30) on Carnival* Elation *pilot project.*

Figure 8. *Ionization generator rack module for Carnival* Elation *current system.*

Figure 9. *Electrolysis module for Carnival* Elation *current system.*

Figure 10. *The "octopus" onboard the Carnival* Elation *pilot project.*

Figure 11. *Shear mix manifold module for Carnival* Elation *current system.*

Figure 12. *Electrolysis module power cabinet - one of four power and control cabinets.*

Superconducting magnetic separator for ballast-water treatment

N. Saho, H. Isogami, T. Mizumori & N. Nishijima

Mechanical Engineering Research
Laboratory of Hitachi Ltd.
Japan
saho@merl.hitachi.co.jp

Treatment options being research

Mechanical (filtration and magnetic separation).

Timeframe of the project

Phase 1: 2003

Basic research on superconducting magnetic separation system for ballast water treatment.

Phase 2: 2004

Detailed design of superconducting magnetic separation system on board.

Phase 3: 2005

On board testing of the superconducting magnetic separation system

Aims and objectives of the project

The aim is to develop a ballast water treatment system that is suitable for rapidly purifying ballast water on board.

Research methods, test protocols and experimental design

A prototype water treatment system using a superconducting magnet to clean the ballast water discharged from ship was developed. The system is capable of treating 100 cubic meters of contaminated water a day through the following process sequence: mixing contaminated water with magnetic powder and a flocculant, stirring the mixture to make magnetic flocs, filtering the flocs, transferring them to a rotary magnetic shell, and dumping them in a sludge tank. The system was evaluated in experiments on two types of contaminated water samples, one containing kaolin particles and the other crude oil.

Prototype structure

As the name implies, the new water-treatment system (Saho N., 2000) combines filtration and magnetic separation. As Figure 1 shows, the treatment process is divided into three steps. First, a pre-application treatment unit gathers the targeted contaminants in the influent into magnetic flocs. Second, a filtration unit filters these magnetic flocs through a rotating filter to purify the water. Third, a magnetic separator unit attracts the flocs deposited on the surface of the filter, washes the surface for reuse, and recovers the magnetic flocs as highly concentrated sludge.

In the pre-application-treatment step, ferromagnetic magnetic particles (Fe_3O_4), a flocculant ($Fe_2(SO_4)_3$-nH_2O), and a polymer are introduced into the influent. They are then stirred and mixed into the influent to produce magnetic flocs (containing contaminant particulates and ferromagnetic particles) to magnetize nonmagnetic contaminants, such as fine organic matter. Three to four minutes is an adequate time for this stirring and mixing.

Since most of the particulates in the generated magnetic flocs have a diameter of several hundred microns, we considered a single filter would be sufficient to trap and filter these flocs if it had a micropore diameter of several tens of microns. The filter unit with a frame and a wire net is shown in Figure 2. A stainless-steel wire net with a pore diameter of 43 μm is used as the filter, and the width of the aperture inside the frame is 200 mm. Twelve filter units, forming a rotating micro-pore filter, are located on the outer circumference of a rotating shell with an outer diameter of 400 mm (see Figure 1).

To enable continuous treatment, the system has a configuration with a rotating filter fitted to the outer circumference of a rotating drum, and the pre-treated water is passed from the outside to the inside of the filter. The magnetic flocs are trapped and accumulated on the surface of the rotating filter, the influent is purified and flows to the inside of the drum, and the purified water is discharged from the system. The magnetic flocs accumulated on the filter in the water migrate from the rotating filter toward the high-temperature superconducting (HTS) bulk magnet positioned near the surface of the pre-treated water. They are separated from the filter by a shower of water from inside the filter near the surface, so the filter is continuously cleaned and is thus always ready for reuse.

In the magnetic separator, the HTS bulk magnet, magnetized in advance and chilled by a cooler inside a vacuum adiabatic chamber, is fixed inside a nonmagnetic rotating cylinder. The separated magnetic flocs adrift in the magnetic field near the surface migrate swiftly, drawn by the strong attraction of the HTS bulk magnet. The migrating magnetic flocs adhere to the surface of the cylinder and are then ejected into the atmosphere above the surface of the water by the rotation of the cylinder. At this point, the surplus water in the magnetic flocs falls out owing to gravity and its magnetic concentration increases, resulting in a highly concentrated sludge. This sludge is continuously stripped from the surface of the cylinder by a claw and dropped under its own weight into a sludge tank. The surface of the cylinder is continuously scraped for reuse by the claw. This series of operations continuously purifies the influent, and the by-product is highly concentrated sludge.

Since magnetic flocs may be magnetically drawn to the surface of the cylinder at high speed by the strong magnetism of the HTS bulk magnet, a large volume of sludge can be separated per unit time. If the number of revolutions is increased, the new water-treatment system can therefore clean large volumes of pre-treated water even with a small rotating filter, so even a small treatment system can process vast amounts of contaminated water.

Configuration of the HTS bulk magnet system

Figure 3 is a photograph of the 33-mm-square, 20-mm-thick $YBa_2Cu_3O_7$ high-temperature superconducting bulk superconductor impregnated with epoxy resin (Tomita, M. et al, 2000) used in the system. Eleven such bulk magnets were used to build a 387-mm-long trial HTS bulk-magnet system. Figure 4 shows the configuration of the magnetization system. A small, single-stage Gifford-McMahon helium cryocooler cools the inside of the adiabatic vacuum chamber containing the HTS bulk superconductorsto a temperature of approximately 35 K. To allow connection to the magnetizing unit, the HTS bulk superconductors are embedded in the tip of a copper, thermal-conductive bar. The other end of the thermal-conductive bar is joined to the cold station of the cooler by a flange via an indium sheet. The low-temperature unit is wrapped with several layers of laminated heat-insulating material to prevent radiation heat for penetrating it.

Split-solenoid superconducting magnets are used to magnetize the HTS bulks. The magnetic field in the tunnel between the split magnets is 70 mm in diameter and approximately 100 mm long with a maximum field of 5.0 T. As the configuration for the magnetizing system in Figure 3 shows, the HTS

bulk section of the magnet system is inserted into the tunnel between the split superconducting magnets before excitation. After cooling the bulk superconductors to a temperature of approximately 100 K, i.e., just above its critical temperature Tc, the split superconducting magnets are excited and emit a specified magnetic field. Since the bulk superconductor do not reach a state of superconductivity, the magnetic field penetrates the bulk superconductor unassisted. When the bulk superconductor is cooled further, the temperature falls below its critical temperature Tc, and the internal magnetic flux gradually begins to be trapped. The split superconducting magnets are demagnetised at a few degrees above the lowest temperature, and the temperature of the bulk superconductor then drops to the lowest temperature. Finally, the HTS bulk-magnet system is extracted from the solenoid magnets (with the cooler still running) and mounted in the sludge-cylinder of the prototype filtration-magnetic separator.

The magnetized superconductors retain their strong magnetism for good, as long as they are kept appropriately cooled by the cryocooler. The experimental superconductor-bulk-magnet system is shown in Figure 5, and a photo of the 1,380-mm-high magnetic separator is shown in Figure 6.

Results

Magnetization of HTS bulk magnets

Figures 7(b) and (c) show the magnetization characteristic of the superconductor bulk magnets under a 5.0-T magnetic field. As the coordinates show, the upper wall of the vacuum adiabatic chamber has been assumed to be the x-y plane. Figure 7(a) shows there are 11 bulk superconductors arranged in a row, and the centre of the sixth from either end of the row meets the zero point of the x-y coordinates. The symbol Bz stands for the distribution of magnet field intensity along the z-axis (vertical). The intensity is 3.2 T at the centre on the surface of the chamber, which is the maximum distribution, and a nearly uniform intensity distribution exists in the range from –50 mm to +50 mm along the x-axis; that is, the magnet at the centre and the two magnets on either side have nearly the same magnetic field intensity. Outside this range, the intensity decreases in proportion to the magnetizer's distribution of magnetism. [no clear meaning] And a magnetic field of 1.6 T to 3.2 T was produced within a 200-mm range (–100 to +100 mm). The cooling temperature for the bulk magnets is about 35 K, and the power consumption of the cryocooler is 2.8 kW. (See Table 1). Graph (c) in Figure 7 shows the maximum intensity along the z-axis, which is inversely proportional to the distance from the chamber-wall surface, in other words, the further away, the lower the intensity. At 6 mm from the surface at x=0 mm and y=0 mm, the intensity is 1.0 T; this means the bulk magnet generates a stronger magnet field than that of an ordinary rare-earth metal permanent magnet.

Table 1. *Performance of bulk-superconductor cooling system*

bulks temperature	34 K
cool-down time	4 hours
electric power consumption	2.8 kW

Treatment of kaolin-contaminated water

The contaminated sample for the treatment experiment was obtained by adding kaolin particles to tap water. The grain size of the particles was 0.5 μm at a concentration in the water of 92 mg/L. In the experiment, 100 m^3 of sample water were processed per day. The water was mixed with magnetic powder and a flocculant and stirred to form flocs. The flocs were trapped on the rotary filter and transferred to the magnet separator, where they accumulated as sludge on the rotary shell. The sludge was scraped off the shell's surface and dumped into the sludge tank after the water had dripped and drained off.

Table 2 lists the results of the experiment. The system removed 93% of the suspended particles ("suspended solids"), which means that it can purify plankton-contaminated water (because the

diameter of plankton is similar to that of kaolin particles or even larger). The concentration of sludge immediately after magnet separation was 90,000 mg/L, and it was further concentrated as a result of water dripping and draining into the atmosphere. However, this concentration would be lower in plankton-contaminated water because the contaminant concentration in the original seawater is a little lower than that of kaolin in this experiment (i.e., several ten-thousand milligrams per litre). The new water-treatment system is a continuous one, but the complete purification process takes about five minutes from when contaminated sample water is input into the flocculation vessel to when it is dumped in the sludge tank.

Table 2. *Treatment test results for kaolin-polluted water at flow rate of 100m^3/day.*

Item	Influent	Effluent	Removal efficiency (%)
Suspended solids (mg/L)	92	6.8	93
Concentration of solids in recovered sludge (mg/L)	-	90,000	-

Figure 8 is a photo of the water before and after the treatment process. The processed water is more transparent, which proves the new treatment technology is effective. Figure 9 is a photo of the rotary filter and magnetic separator in operation. It clearly shows how the suspended solids are captured by the cage, magnetically transferred to the rotary shell, and scraped off and dumped in the sludge tank. The scraping position is about 100 mm from the magnetic separator, and magnetic field intensity there is about 0.05 T, which means magnetic force barely influences the sludge, so scraping is easy.

In the past, we carried out an experiment on a batch-type system using superconductor coil magnets to remove plankton from red tide (Saho, N. et al., 1999), and the results are listed in Table 3. The phytoplanktons treated were *Chattonella antiqua,* and *Heterocapsa circularisquama*. We made magnetic flocs of the planktons in the same way as described above for kaolin. The flocs were magnetically captured on a metal net. The removal rate was 92% or better, which is satisfactory for water treatment. Although the filter-magnet separation differs from the batch-type system in regards to the separation of the magnetic flocs, the authors believe that it will have comparable performance.

Table 3. *Treatment test results for three kinds of red phytoplanktons (Saho, N. et al, 1999).*

	Chlorophyll-a (µg/L)	Marine Bacteria (cells/mL)
Chattonella antiqua		
influent	169	-
effluent	6.3	-
% removal	96	-
Heterocapsa circularisquama		
influent	169	5,670
effluent	6.3	440
% removal	96	92

Treatment of oil-contaminated water

A contaminated sample for a treatment experiment was made by adding oil to tap water and agitating it to emulsify it. As the photomicrograph in Figure 10(a) shows, the diameter of the emulsified particle suspended in water ranges from 1 to 10 µm. Magnetic powder, a flocculant, and a high-molecular-weight polymer are mixed in with the sample. When stirred, the oil particles and powder coagulate and flocs are formed [Figure 10(b)]. Figure 11 plots the results of this experiment. A TOC evaluation shows that the removal rate is 90% or more. The concentration of TOC in the recovered sludge was 23,000 mg/L, which is 960 times thicker than the original contaminant concentration of

24 mg/L. This result suggests that the developed water-treatment system demonstrated in this experiment can be applied to the treatment of oil-contaminated water from offshore oil rigs, and the resulting treated water can be discharged directly into the ocean.

Conclusions

A continuous water-treatment system consisting of superconductor bulk magnets, which generate a high-intensity magnetic field, was developed and experimentally evaluated in tests on purifying several contaminated-water samples. The experiment showed that more than 90% of the particles in the contaminated water can be removed in about five minutes. This result indicates that this system is capable of purifying water continuously and at high speed within a limited space. Moreover, the recovered sludge is highly concentrated, being tractable for easy disposal. It is concluded that the new water-treatment system is potentially very effective for the treatment of ballast and oil-contaminated water.

References

Saho, N. 2000. *German-Japan Workshop on High-Temperature Superconductivity*, SRL ISTEC Tokyo Japan.

Tomita, M. & Murakami, M. 2000. *Improvement of the mechanical properties of Bulk superconductors with resin impregnation*, Supercond. Sci. Technol, No.13 , p. 722.

Saho, N., Isogami, H., Takagi, T., Morita, M., Yamaoka, Y. & Takayama, H. 1999. *Development of Continuous Superconducting-Magnet Filtration System.* The Fourth International Conference on the Mediterranean Coastal Environment. The Fourth International Conference on the Environmental Management of Enclosed Coastal Seas, vol. 3, pp. 1398-1410.

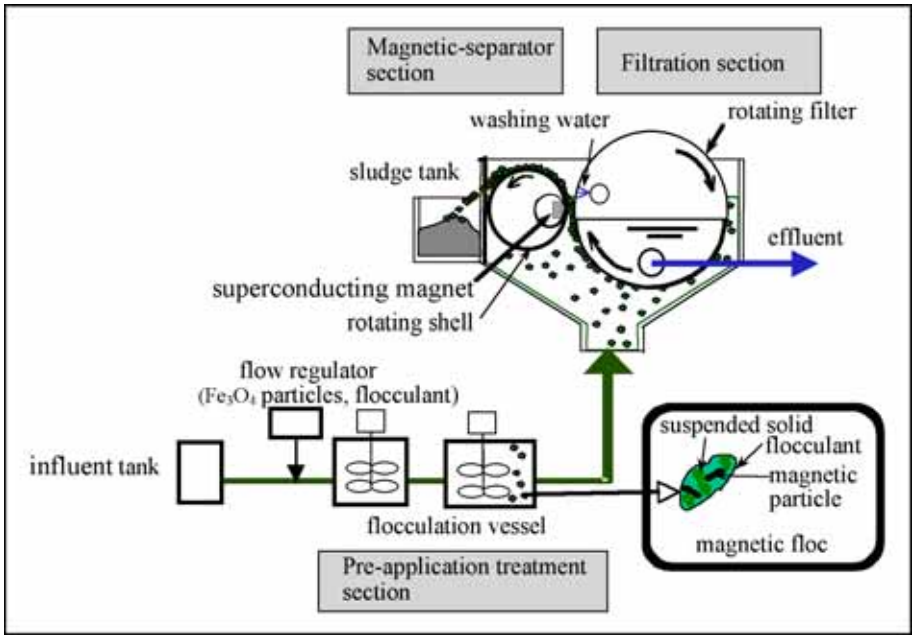


Figure 1. *Structure of water-treatment system using high-temperature bulk superconducting magnet for filtration-magnetic separation to clean ballast water.*

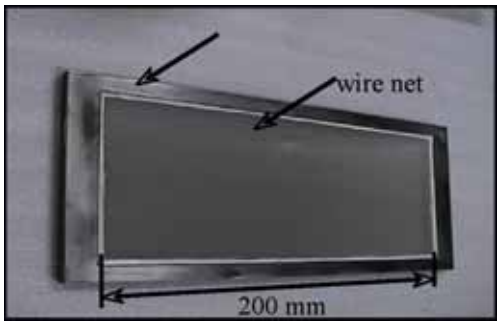


Figure 2. *One filter unit with a frame and a wire net. A stainless steel wire net with a micro-pore diameter of 43 μm is used as the filter, and the width of the aperture inside the stainless steel frame is 200 mm.*

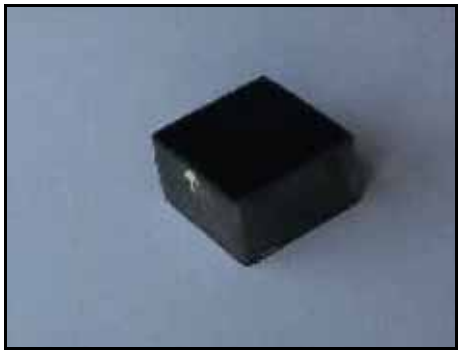


Figure 3. *$YBa_2Cu_3O_7$ bulk superconductor impregnated with epoxy resin (20 mm thick). Eleven such bulk magnets form a 387-mm-long trial HTS bulk magnet.*

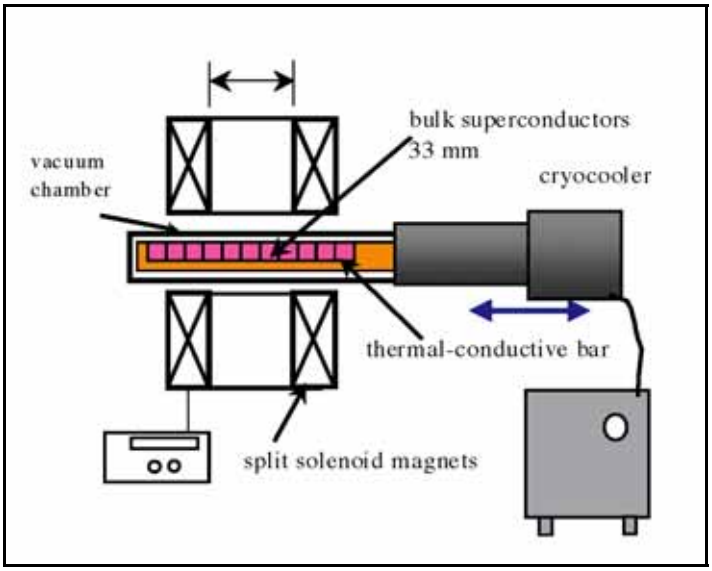


Figure 4. *Magnetization system for bulk superconductors. The magnetic field in the tunnel between the split magnets is 70 mm in diameter and approximately 100 mm long.*

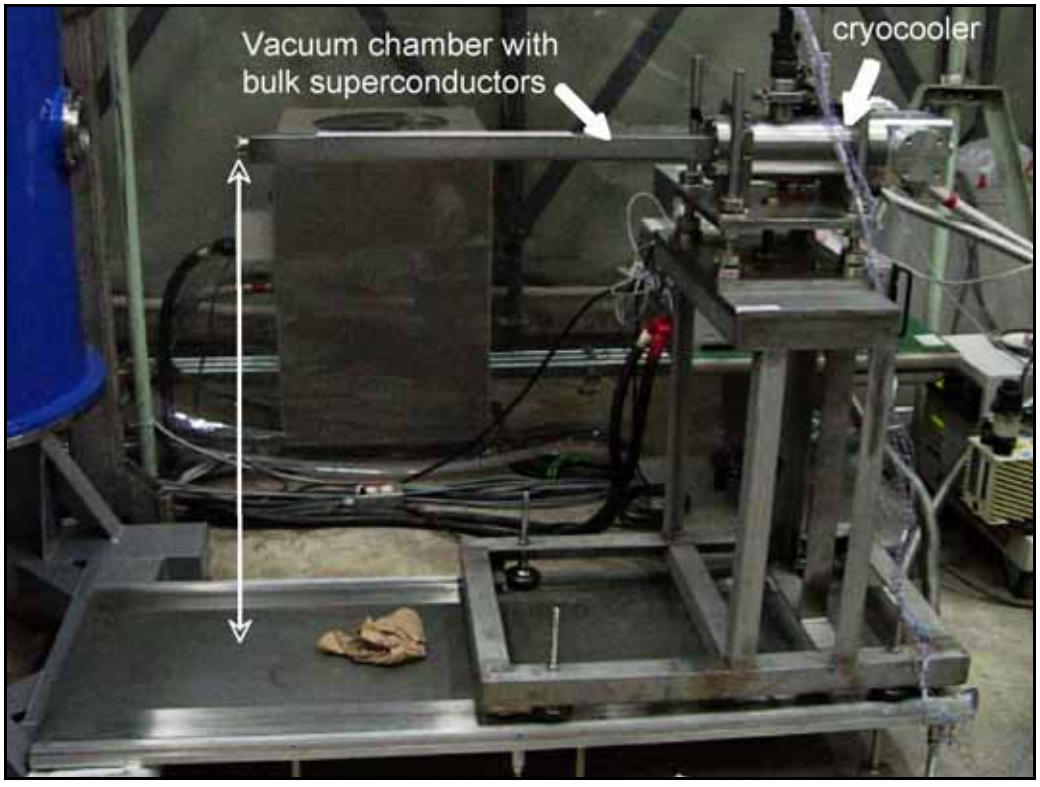


Figure 5. *Superconducting magnet system with bulk superconductors. Under steady-state conditions, the temperature of the bulk magnets is 34 K and all superconductors are uniformly cooled by the GM cryocooler.*

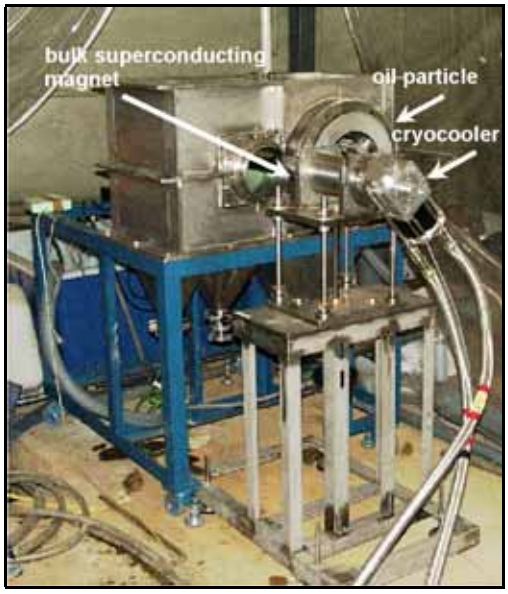


Figure 6. *Photograph of the magnetic separator at a treatment flow rate of 100 m^3/day.*

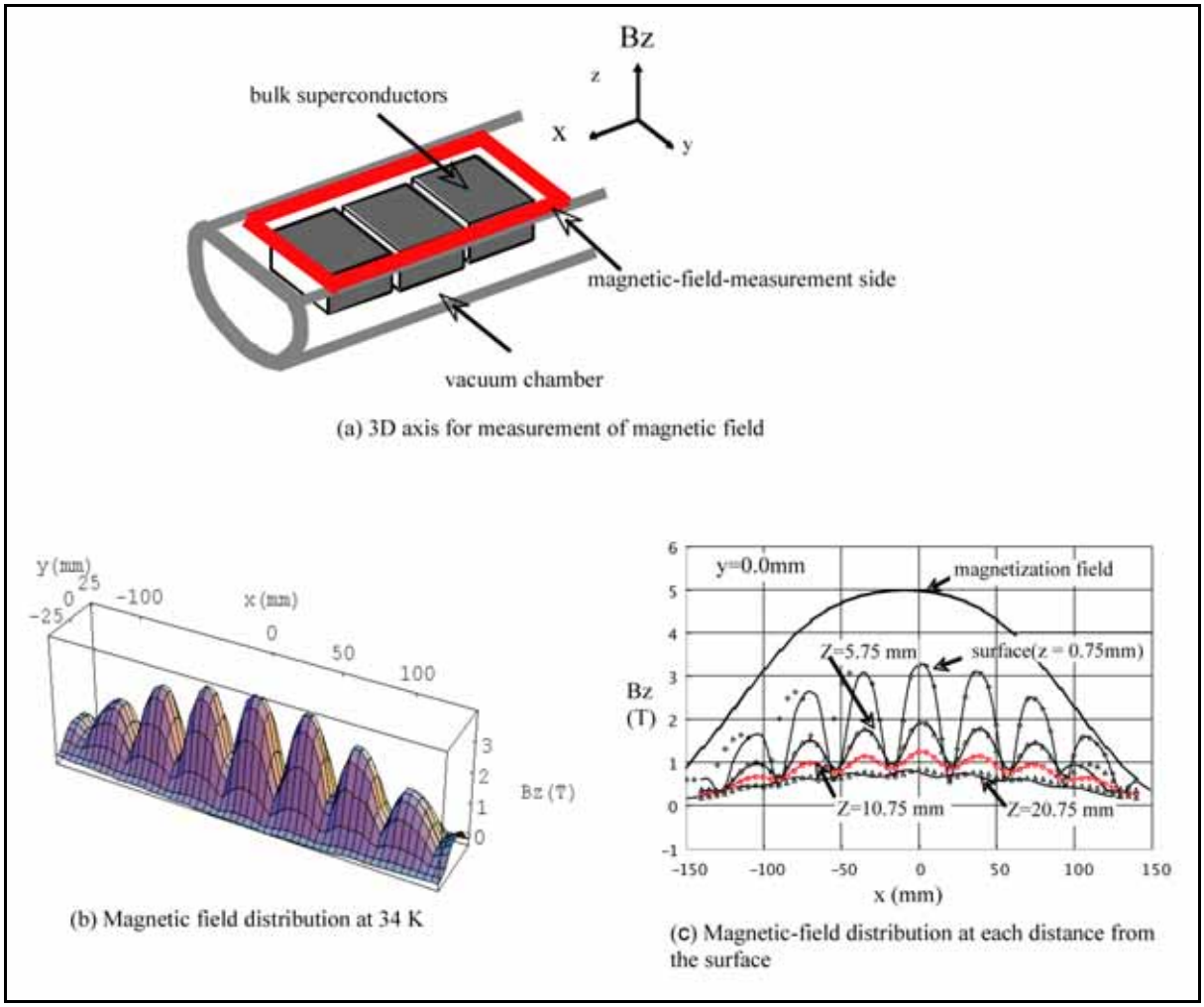


Figure 7. *Measured magnetic field distribution of bulk superconductors on the surface of the vacuum chamber obtained by zero-field cooling.*

Figure 8. *Views of the test influent containing kaolin particles and of the processed effluent*

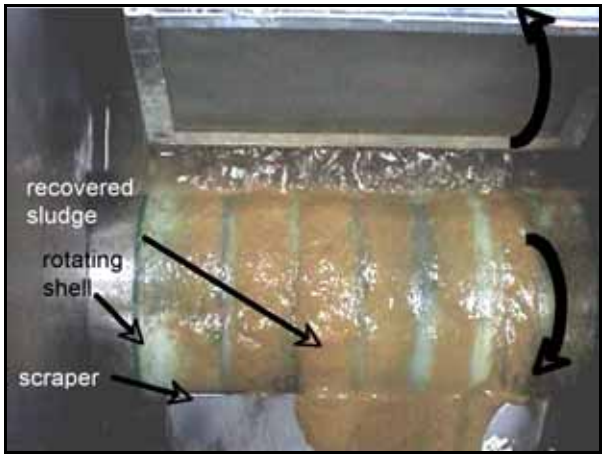


Figure 9. *Recovering sludge by magnetic separation.*

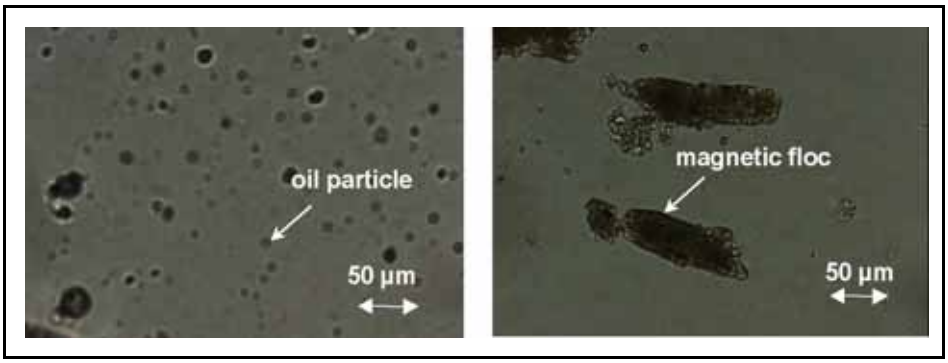


Figure 10. *(a) Photomicrograph of emulsified oil particles in influent and (b) magnetic flocs in pre-application treatment water.*

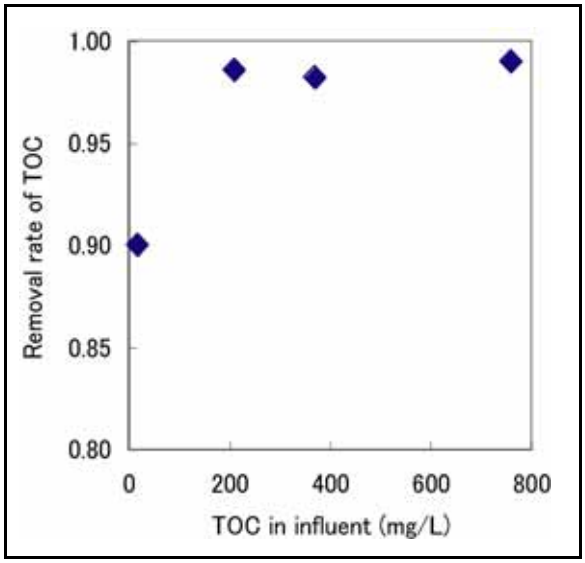


Figure 11. *Efficiency of removing oil from water.*

Session 3: Chemical-based Treatment Systems

Sodium hypochlorite as a ballast water biocide

D.T. Stocks[1], M. O'Reilly[2] & W. McCracken[3]

[1]*BMT Fleet Technology Ltd, Canada*
[2]*ESG Stantec Consulting Inc, Canada*
[3]*Consultant, USA*

Political and regulatory context

Legislation was introduced in the Michigan Senate for the regulation of ballast water in January 2000. This proposed legislation required, among other things, that all ballast water discharged in Michigan be "sterilized", and that such discharges be authorized by permits issued by the Department of Environmental Quality. Shortly thereafter, in March 2000, the Department of Environmental Quality established the Ballast Water Work Group, a group of people with technical knowledge about the shipping industry. This Work Group was asked to help identify practical methods, currently available, to minimize the problem of ballast-borne invasive aquatic species in the Great Lakes. "Practical, currently available methods" were defined as not needing extensive research to establish efficacy, not needing extensive ship retrofitting, and not needing shore-side facilities. In April 2000, the Ballast Water Work Group concluded that the only methods which met these criteria were improved management practices and chemical biocides.

During the summer of 2000, the Ballast Water Work Group set forth lists of improved management practices for oceangoing vessels ("salties") and Great Lakes vessels ("lakers"). In response to a request from the Work Group, the Department of Environmental Quality developed plans for laboratory and shipboard testing of chemical biocides during the fall of 2000. In February 2001, those plans were finalized, focusing on two biocides, sodium hypochlorite and copper ion. These were the plans which were presented at the March 2001 IMO Symposium. In June 2001, Michigan selected BMT Fleet Technology, Ltd., of Kanata, Ontario, as the contractor for the project, and work began.

Meanwhile, much discussion and deliberation took place on the ballast water legislation first introduced in January 2000. In August 2001, Michigan Act 114 was passed and signed into law. It states that a goal of the State of Michigan is "to prevent the introduction of and minimize the spread of aquatic nuisance species within the Great Lakes." However, Act 114 is much different than the original bill. It does not require sterilization or permits for ballast water. Instead, it requires that the Department of Environmental Quality make determinations by certain deadlines as to: a) which ships are complying with the management practices set forth through the Ballast Water Work Group process, b) what treatment methods can be used to minimize invasive aquatic species, and c) which ships are complying with these treatment methods. Listings of these determinations are to be made available to the public. Vessel owners and operators and their customers are not eligible for grants, loans, or awards from the Department of Environmental Quality unless they are on the listings.

A key provision of Act 114 requires that the Department of Environmental Quality makes a determination by March 1, 2002, of "Whether one or more ballast water treatment methods, which protect the safety of the vessel, its crew, and its passengers, could be used by oceangoing vessels to prevent the introduction of aquatic nuisance species into the Great Lakes." Also, the Act requires the Department to determine a time period after which the treatment method could be used by all oceangoing ships on the Great Lakes. If a treatment method is not now available, the Act requires the Department to determine the actions needed and the time period for finding a viable treatment method. Although the legislative deadline has passed, the requirement to make the determinations is still in effect.

During the fall of 2001, the shipboard testing was completed, and the laboratory testing was completed during the winter of 2002. The draft project report was completed in early March 2002.

Then the draft project report was discussed with the Ballast Water Work Group in late March. The Work Group expressed concern about several aspects of the draft project report. As a result, the Department of Environmental Quality requested the Governor to convene a Panel of the Michigan Environmental Science Board to carry out a critical review of the findings of the project. The Governor agreed, and the Panel was assembled and met on May 29, 2002. The Panel included four permanent members of the Michigan Environmental Science Board, and five invited experts in the areas of ballast water and corrosion. One of the invited Panel members was Stephen Raaymakers of the IMO staff.

The Michigan Environmental Science Board published the report of its review of the draft project report in September 2002. The "Major Findings and Conclusions" of the Board are contained in Attachment 5. Key statements included the following:

> **For Copper Ion***:* "In summary, the Study's toxicity data, as a whole, suggest that in sufficiently high concentrations, copper ion could be an effective biocide. However, at the concentrations needed to achieve the desired effectiveness, the level would be far too high to be discharged into the Great Lakes. Given this, and in the absence of any known neutralizing agent that would allow copper to be safely discharged into the Great Lakes, the MESB Panel concludes that copper ion cannot be considered to be a viable ballast water biocide alternative at this time."
>
> **For Sodium Hypochlorite***:* "The Study's conclusions regarding the effectiveness of sodium hypochlorite as a viable ballast water biocide alternative from the shipboard and laboratory toxicity tests are limited and can only be considered preliminary at best. However, despite the problems outlined in this critique regarding the testing protocols used, the MESB Panel suggests that the use of sodium hypochlorite as a ballast water biocide can have a high degree of efficacy when treating the majority of organisms that were tested in the Study, assuming that sufficient active hypochlorite concentration can be attained to account for sediment loads from both suspended and deposited material." The MESB report raised several other questions about the Study which need to be answered relative to use of sodium hypochlorite, including corrosivity in ballast tanks.

The project report was finalized by BMT Fleet Technology, Ltd. in November 2002. Based on that report and on the conclusions of the Michigan Environmental Science Board, the Department of Environmental Quality could not make a determination under Act 114 as to whether one or more ballast water treatment methods could be safely used by oceangoing vessels. The Department decided to fund a second phase of work in order to gather additional information which may allow that determination to be made for sodium hypochlorite. In November 2002, BMT Fleet Technology, Ltd. was selected to carry out a contract for the Phase 2 Study.

Michigan Act 114 is being implemented. The Department of Environmental Quality has developed listings of which ships, both salties and lakers, are complying with the applicable ballast water management practices. These listings are publicly available on the state of Michigan web page, and are updated as new information becomes available. A determination has been made that these management practices are now conditions of passage on the St. Lawrence Seaway. Although the determination as to whether a treatment method is available has been delayed until further information is developed under the Phase 2 Study, the Department of Environmental Quality remains under the mandate of Act 114 to make that determination.

Invasive aquatic species continue to cause great concern in the Great Lakes region. The need for a solution to the problem, or at least a reduction of the risk of these foreign invaders, is urgent, and keenly felt in the state of Michigan. Questions remain about the use of sodium hypochlorite to treat ballast water, including potential corrosion of ballast tanks, and the problems of sediment biocide demand. However, those working on the Phase 2 Study remain hopeful that it can be shown to be a viable ballast water biocide. There are several potential advantages of sodium hypochlorite: it is a widely used, proven biocide; it can be neutralized prior to discharge; and it is readily available. Although concerns about dangerous byproducts have been raised, the amount of sodium hypochlorite

needed to treat ballast water would be very small in comparison to other uses of chlorine. Thus, the increase in relative risk to the environment should be small. This is being further verified as part of the Phase 2 Study. Criticism that it is not effective on 100% of foreign species should not rule out its use, at least on an interim basis, because adequate dosages will destroy most of the foreign organisms in ballast water and greatly reduce the risk of new invasions.

Phase 2 studies

Background

After a review of the MESB findings the MDEQ concluded that follow up efforts were required to address the issues raised. The issues included;

- The practical implementation, on board ship, of a sodium hypochlorite chlorination and de-chlorination system to ensure effective and efficient use (minimization) of chemical additives.
- The effect of typical Great Lakes ballast water temperature ranges on the efficacy of sodium hypochlorite as a biocide.
- The effect of ballast tank sediments on the efficacy of sodium hypochlorite as a biocide.
- The quantification and impact of the formation of chlorinated compounds by typical sodium hypochlorite treatment of ballast tanks in Great Lakes waters.

The first round of work included an examination of the effect that sodium hypochlorite and copper might have on the structural integrity of the ship's ballast tank. This work was included in the evaluation of the biocides in response to ship owners and classification societies concern over accelerated corrosion of the steel. An investigation of these effects along with an assessment of tank coating damage effects was undertaken, however, due to the large number of variables necessarily examined and available time frame for the project only short duration tests were conducted. The MESB review recommendations suggested longer term test be conducted on hypochlorite be conducted to quantify the life cycle effects of exposure to biocides in the ballast tank.

The objective of this study is to provide additional information to support the MDEQ's determination of whether sodium hypochlorite can be recommended for general application as a ballast water biocide.

Issue 1: Appropriate dose control

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

The problem can therefore be stated as one to develop an application of existing technology for TRC monitoring that can be utilized as a monitoring and control system suitable for the ship ballast tank environment.

Approach

To address this, an engineering design is being undertaken by BMT/FTL to determine the appropriate type, placement and operational constraints of a sodium hypochlorite/sodium bisulfite treatment system.

Issue 2: Temperature

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

Great Lakes shipping typically starts during the spring months of March or April and lasts until December, depending on conditions. During a typical shipping season temperatures in the Great Lakes varies from lows of 1 to 3°C in cooler months to 15 to 26°C during summer and fall depending on the lake and water depth. As is the case with many oxidizing chemicals, the temperature of application can impact their biocidal properties. Given the range of temperatures that can be found in the Great Lakes during a typical shipping season, more or less hypochlorite may be required to achieve similar endpoints at different times of the year.

Approach

To address this, a literature review was conducted prior to initiating the study. The literature review discussed studies of a similar nature to determine whether temperature is expected to impact the biocidal efficacy of hypochlorite.

Issue 3: Sediments

The effects of sediment on the efficacy of sodium hypochlorite as a biocide.

The amount of sediment suspended in new ballast water, and in the re-suspension of residual ballast water, will impact the amount of biocide needed to account for the chlorine demand. The impact of the presence sediments on the efficacy of sodium hypochlorite needs to be evaluated.

Approach

To address this, toxicity tests involving *Hyalella azteca* are being conducted at Stantec's (formerly ESG International) Ecotoxicity Laboratory in Guelph, ON. Tests are 48-hour static acute toxicity tests conducted at 15°C. Test endpoints include lethal concentration to 90% mortality (LC90) and lethal time to 90% mortality (LT90). Tests are being conducted in triplicate using a linear dilution of hypochlorite against a logarithmic concentration of sediment. The amount of chlorine required to achieve treatment levels for each sediment level is determined.

Issue 4: Disinfection by-products

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

The mixing of hypochlorite in a ballast tank containing water and sediment is expected to produce some level of disinfection by-products (DBPs). The interaction of hypochlorite with organic matter commonly found in ballast water and sediments can produce trihalomethanes (THMs), haloacetic acids (HAAs), and liberate metals from the sediments into the overlying water. Additionally, dechlorination of treated ballast water using neutralizing agents can reduce the dissolved oxygen content and pH of the discharged ballast water. This portion of the study is designed to determine the amount and types of DBPs that may be produced from the interaction of hypochlorite and a dechlorinating agent with the sediments and water associated with ballast tanks.

Approach

To address this, tests to determine the extent and amount of DBPs produced during the chlorination of ballast water and sediments are being undertaken at Stantec's (formerly ESG International) Ecotoxicity Laboratory in Guelph, ON. Samples of sediments will were collected from the ballast tanks of three ocean going ships. Natural water and increasing levels of sediment were mixed, chlorinated, and dechlorinated (after 48 hours exposure). Samples of overlying solutions were then collected and analyzed for THM's, HAA,s, metals etc.

Issue 5: Structural deterioration

The quantification and impact of exposure of a ships ballast tank structure, including coating systems, to periodic doses of Sodium Hypochlorite.

Aqueous corrosion of steels in natural waters depends entirely on the availability of oxygen. When the source of oxygen is air in an open natural system with pH between 4 and 10, the rate of attack has been observed to average approximately 0.1mm/year (0.004 inches/year or 4mpy) at ambient temperatures and this rate is controlled by the diffusion rate of oxygen from the bulk solution to the steel surface. In short term exposures, the rate tends to be higher on clean bare surfaces but the rate tends to decrease with longer exposures as surface scales build up. In the temperature range encountered in nature, corrosion rates increase with temperature, doubling every 30°C because diffusion rates increase with temperature. Other factors which accelerate bulk diffusion such as agitation in the liquid which reduces the thickness of the boundary layer and wetting and drying cycles which afford atmospheric oxygen better access through the meniscus in the drying stage also accelerate corrosion. These factors account for the enhanced attack observed at the waterline and splash zone in marine environments.

Other oxidizing agents added to oxygenated water may have positive or negative effects on corrosion rates of steels. Some anions, such as chromates or permangenates, are effective inhibitors and result in corrosion rates approaching zero. Hypochlorite ion has no inhibiting effect and, on the contrary, acts as additional oxidizing agents to accelerate the corrosion of steel. The hypochlorite ion has been compared to wet chlorine in its effects on materials. Not many metals show good resistance even at low temperatures and concentrations.

The fundamental requirements of the barrier system, i.e. tank paint coatings are that the coating should be (a) impermeable to damaging ionic species and, if possible, to oxygen and (b) that it should maintain adhesion to the steel under wet corrosion conditions. Sufficient impermeability to water is not possible except in very thick films (>20 dry mils) and ingress of water leads to de-adhesion. Impermeability to ionic solutions and oxygen are entirely more practical objectives and, consequently, these factors are rate determining for corrosion beneath intact barrier films.

Approach

To address this, tests to determine the extent and amount of corrosion in the typical ballast tank exposures including fully submerged and splash zones are being conducted at BMT FTL laboratories in Kanata Ontario. Tests are also being conducted on the permeability of paint systems and the effects of surface damage to paint systems. All tests are being conducted in fresh and salt water with varying exposure levels of hypochlorite.

Issue 6: Life cycle impacts

The practicality and impact of adopting Sodium Hypochlorite as a ballast water biocide for use in the Great Lakes on the shipping industry and the discharges into the basin.

The economic impact on the ship is significant, systems will have to be engineered to ensure correct dosing levels are applied; biocide will have to be carried or generated on board and infrastructure developed to ensure proper training etc. The impacts of discharges need also to be evaluated to assess the relative risk of damage to the environment.

Approach

A life cycle model will be developed based on the results of the toxicity testing which will establish appropriate dosing levels, the traffic level of ships into the Great Lakes which will establish the total exposure and the economics of fitting engineered solutions to the ship.

Selected Phase 1 study results

Project composition

The project is comprised of three parts:

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

Field trials on board 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"): (Bilbao Spain) An ocean port in a saltwater environment. Cargo was off-loaded, and ballast water taken on.

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

Port #3 ("Great Lakes Port #1"): (Burns Harbor Indiana) A Great Lakes, fresh water port. Cargo was off-loaded, and

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

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.

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.

Efficacy – chlorine

Table 1 lists the range of lethal 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).

Within the freshwater species, algae (including *S. capricornutum, S. obliquus,* and *Nanochloris sp.*) exhibited the lowest tolerance to chlorine (IC99s ≤ 0.1 mg/L), followed by *D. magna* (LC99 = 0.2 based on exposure of neonates (< 24-h old)). The most tolerant species, based on exposure of the resting egg or "ephippia", was *D. magna* (IC99 = 76.3 ppm). Lethal effect levels for all other species were in between this range with LC99s below 10 ppm chlorine.

For the marine species, the bacterium, (*V. fischeri*) and the alga (*S. costatum*) exhibited the lowest tolerance to chlorine with LC99's estimated to be 0.15 and 0.20 mg/L, respectively. The most tolerant species was the brine shrimp (*A. salina*), based on exposure of the cyst (LC99 ≈ 486 ppm). All other species were in between this range with estimated LC99s below 10 ppm chlorine.

Table 1. *Lethal concentrations (estimated LC99, IC99) of chlorine for selected biota.*

Lethal Concentration Range (ppm as TRC)	**Freshwater**	**Marine**
< 1	Alga *S. capricornutum*	Bacteria *V. fischeri*
	Alga *Nanochloris sp.*	Alga *S. costatum*
	Alga *S. obliquus*	
	Invertebrate *D. magna* (neonate)	
1 to 10	Bacteria *B. subtilis*	*Amphipod E. estuarius*
	Mollusc *D. polymorpha*	Fish *C. variegatus*
	Benthic invertebrate *L. variegates*	
	Fish *C. carpio*	
10 to 100	Invertebrate *D. magna* – (ephippia)	
100 to 1000		*Invertebrate A.salina* (cyst)

Structural integrity.

Figure 1 shows the test tanks set up with test coupons at the start of an experiment. Test coupons are exposed to varying levels of chlorine (10 ppm and 40 ppm) over a 15 day period in both salt water and fresh water. A control tank is also provided with no chlorine. Coupons are mounted on a rotating wheel to simulate the splash zone, suspended in the solution to provide continuous exposure and suspended in the air space inside the enclosure to simulate the damp conditions of the partially filled tank. In addition a set of coupons were buried in inert sand in the bottom of the solution tank to simulate under sediment low oxygen conditions.

It is common in ship building to coat the steel with zinc rich pre-weld primers under an epoxy paint system. The primer protects the steel during construction but in the presence of damage paint may provide for an anodic reaction with different metal. A series of tests were also conducted with 4 different paint products in typical use in ship building. These test were done in accordance with the standard ASTM "scratch" procedure whereby a prescribed damage is introduced in to the paint surface and the extent of damage increase monitored.

Figure 2 shows the experimental results in terms of annual diminution rates from the accelerated corrosion tests on bare steel coupons in salt and fresh water. 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.

Figure 3 shows a comparative measure of coating loss, in accordance with the ASTM rating score for three coating systems, and reveals the following:

- 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.
- 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.

Table 2. *Economics of ship installation.*

	Copper Ion Generator	**On Board Chlorine Generation**	**Purchase commercial concentration Sodium Hypochlorite**	
Item	0.2 ppm on 50 tonnes	330 kg (725lbs) per day 0.8%	Buy and store onboard	Deliver to the ship as required
Capital cost	$104,696	$ 437,710	$ 207,025	$ 77,318
Element replacement cost	$18,750	$ 50,000	$ 10,000	$10,000
Element replacement (years)	5	5	5	5
Ballast operations per year	12	12	12	12
Raw material costs	$ 0.09	$318	$ 504	$ 756
Vessel charter rate (per day)	$9,000	$9,000	$9,000	$9,000
Return rate	15%	15%	15%	15%
Inflation rate	3%	3%	3%	3%
Amortization period	20	15	15	15
Increase charter to maintain return	$ 48.08	$ 207.73	$104.03	$ 60.54
%increase to cost of shipping	0.53%	2.31%	1.16%	0.67%

Economics of ship installation

Sodium hypochlorite can be purchased as a liquid in concentration of 15% sodium hypochlorite, or it can be 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.

A life cycle economic analysis of various systems was conducted and the increase in ship charter rate (cost to user) necessary to support the ballast water treatment computed.

Figure 1. *The test tanks set up with test coupons at the start of an experiment.*

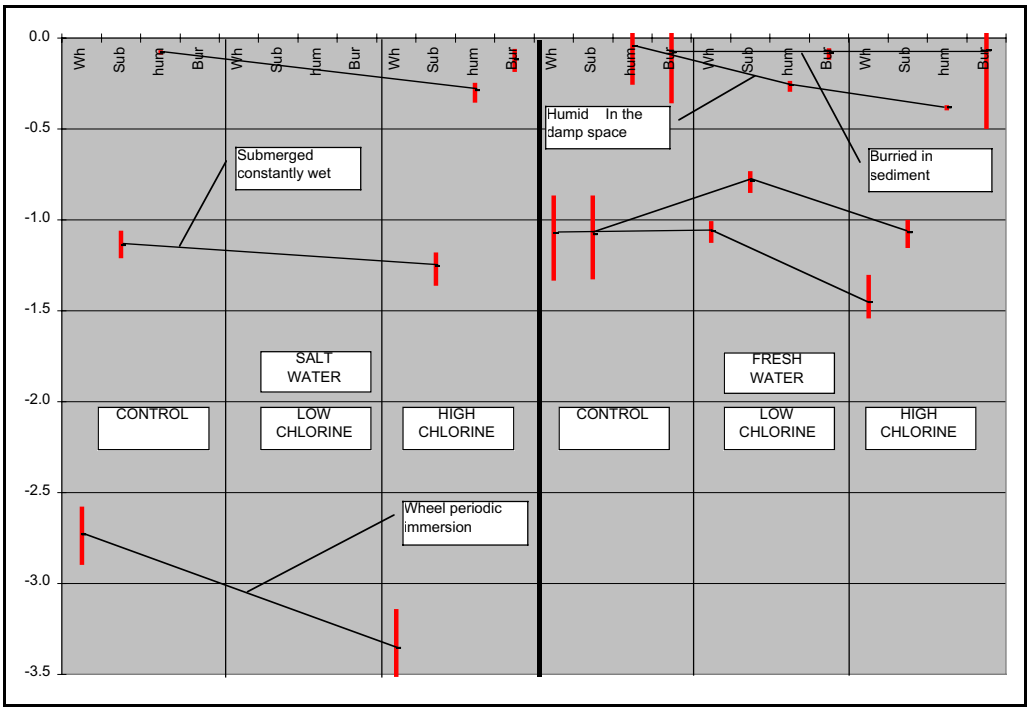


Figure 2. *The experimental results in terms of annual diminution rates from the accelerated corrosion tests on bare steel coupons in salt and fresh water.*

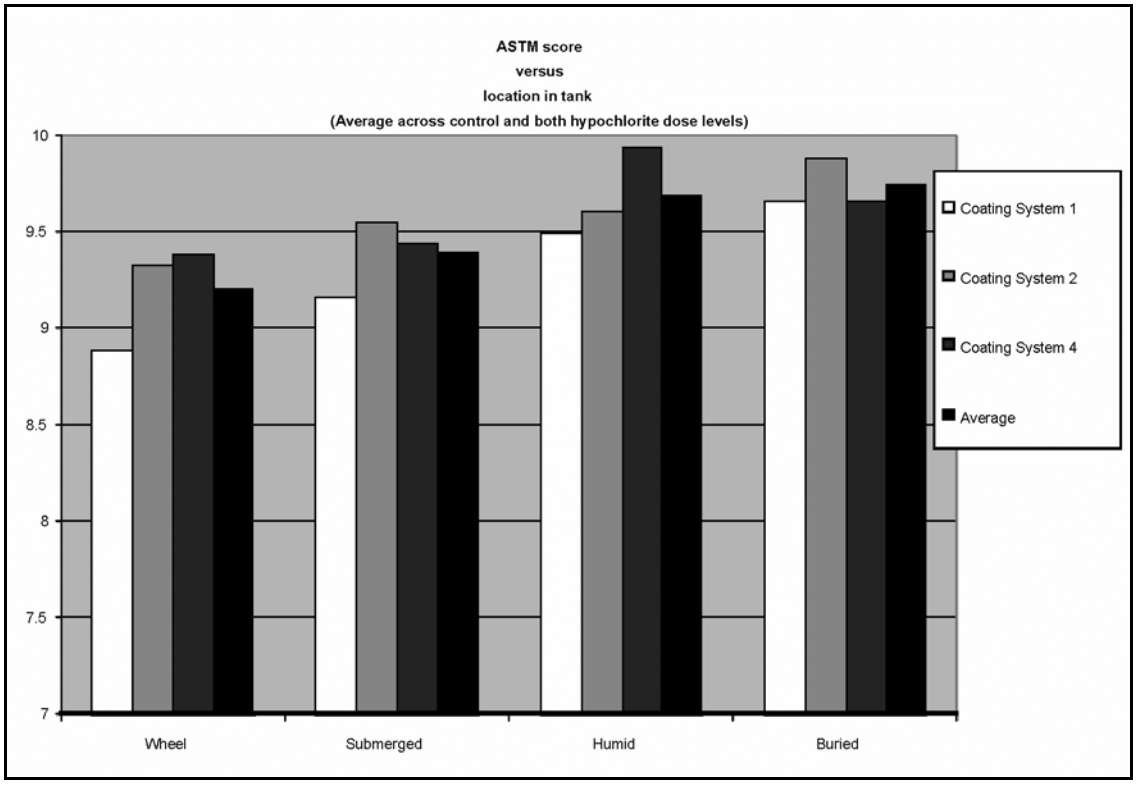


Figure 3. *Comparative measure of coating loss.*

Effects of the chlorination treatment for ballast water

S. Zhang, X. Chen, D. Yang, W. Gong, Q. Wang, J. Xiao, H. Zhang & Q. Wang

Dalian Maritime University,
P.R.China
zhangshuohui@yahoo.com.cn

Treatment options being researched

Chemical

Aims and objectives of the project

This project deals with the effects of the chlorination treatment for ballast water. Chlorination treatment is selected mainly based on three facts.

Firstly, chemical method is widely adopted to kill organisms and bacteria in large-scale water treatment. Secondly, among chemical methods chlorination treatment is earliest and most common. For instances, many countries including China, use chlorination to disinfect and kill bacteria for potable water, water from hospital and water for aquaculture. Since late 80s, State Entry-exit Inspection and Quarantine of China has been using chlorine to treat ballast water containing vibrio bacteria from epidemic area. Thirdly, due to easy operations and low expenses, chlorination is feasible to be used on board without special apparatus to treat ballast water.

Our experiments selected Sodium Hypochlorite as biocide. The results prove that chlorination treatment is effective in killing organisms and bacteria in seawater. They also show that available chlorine with concentration of 20 mg/L is able to kill almost all the bacteria in the seawater. However, the concentrations of available chlorine for phytoplankton, zooplankton and benthic invertebrate's treatment vary depending on the species and the density, ranging from 5 mg/L to 100 mg/L. The exposure duration is not considered in this experiment.

Ame's and luminescent bacteria's tests of treated byproducts in laboratory and onboard field-test have not been done for various reasons, and we will do them before long.

Test design

Bacteria test

The bacteria test is conducted to determine the efficacy of Sodium Hypochlorite on total anaerobic bacteria (Membrane filter method, reported as CFU/10cm^3), Vibrio (Membrane filter method, reported as CFU/10cm^3) and E.Coli. (MPN fermentation method, reported as CFU/10dm^3) in seawater.

Phytoplankton test

We selected four kinds of phytoplankton algae, namely *Nitzschia closterum* (diatoms), *Dicrateria spp*. (chrysophyta), *Platymonas spp.*(green alga) and *Pyramidomonnas sp.*(green alga) with the density of 10^9/L. This is the typical density when "red tide" occurs. The objective was to find out absolute lethal concentrations (LC_{99}) of sodium hypochlorite for every selected phytoplankton algae.

The culture of adaptability: phytoplankton algae in laboratory were cultured with f/2 general culture media for phytoplankton algae (in 22°C, 2200 Lux and 12:12 photoperiod) for 3 days prior to being treated.

Determination of available chlorine: Available chlorine of sodium hypochlorite (NaOCl) bought from market was determined using Chinese National Standard methods (GB10666).

Chlorination: Water samples were treated by sodium hypochlorite with the concentrations of available chlorine (nominal) of 5, 10, 20, 40, 80 and 100 mg/l, respectively.

Regrowth and examination of phytoplankton: After chlorination, water samples were placed in the light/dark (which simulates the condition of ballast tank) for 7 and 15 days. Then they were regrown (at 22°C, 2200 Lux and 12:12 photoperiod) for 20 days and examined.

Natural seawater test

The natural seawater used in the experiments was obtained from the sea nearby Lingshuiqiao and was filtered prior to use. The objective was to find out absolute lethal concentrations (LC_{99}) of sodium hypochlorite for all organisms in natural seawater.

The culture of adaptability: natural seawater was cultured with f/2 general culture media (in 22°C, 2200 Lux and 12:12 photoperiod) for 3 and 20 days prior to being treated.

Determination of available chlorine: Available chlorine of sodium hypochlorite (NaOCl) bought from market was determined using Chinese National Standard methods (GB10666).

Chlorination: Water samples were treated by sodium hypochlorite with the concentrations of available chlorine of 5, 10, 20, 40, 80mg/l, respectively.

Regrowth and examination: After chlorination, water samples were placed in the light/dark (which simulates the condition of ballast tank) for 7 and 15 days. Then they were regrown (in 22°C, 2200 Lux and12:12 photoperiod) for 20 days and examined.

Amphipod test

We selected a kind of amphipod, *Corophium acherusicum* Costa, that belongs to the benthic invertebrate group. The test was conducted using standard toxicity tests. However, the exposure duration was altered to 48h. The objective was to find out the concentration-effect relationship for *Corophium acherusicum* Costa.

Chlorination treatment for *Corophium acherusicum* Costa was mainly using ASTM methods (E1367-92 Standard Guide for Conducting 10-day Static Sediment Toxicity Tests with Marine and Estuarine Amphipods) and Chinese industrial standard (Standard for conducting marine sediment toxicity tests with amphipods: pending authorisation).

Table1. *Summary of test conditions for determining acute lethality to* Corophium acherusicum *Costa.*

Test type:	Static-renewal
Test duration:	48- h
Temperature:	Water bath at 22°C
Lighting:	Ambient laboratory illumination
Feeding regime:	No feeding
Beaker volume:	1000 ml
Test solution volume:	500 ml
Thickness of Sediment	3-4cm
Renewal of test solution:	24-h
Age of test organisms:	7-10 days old
Number of animals/test beaker:	20
Number of replicates	2
Dissolved oxygen	Saturation
Measured end points:	Mortality

*Brine shrimp (*Artemia salina*) test*

The test involved cysts, nauplii and adults of Brine Shrimp (*Artemia salina*), which is a representative of zooplankton. The test was conducted using standard toxicity tests. The objective was to find out the concentration-effect relationship for cysts, nauplii and adults of Brine Shrimp.

Chlorination treatment for *Artemia salina* was carried out as per the Chinese national standard GB18420.1-2001 (Biological toxicity inspection method for pollutant from petroleum exploration and exploitation) and Germany ATS benchmark (The ATS-benchmark for chemical treatment options).

Table 2. *Summary of test conditions for nauplii (GB18420.1-2001)*

Test type	Static-renewal
Test duration	96h
Temperature	24°C
Light intensity	1000 lux
Photoperiod	12 h light, 12 h dark
Feeding regime	No feeding
Test beaker volume	100 ml
Water volume	50 ml
Age of organisms	Hatch 24-36h
Number of animals/test beaker	10
Number of replicates	4
Dissolved oxygen	Saturation prior to treatment
Dilution water	Manmade seawater(35‰, pH7.9)
Measured end points	Median lethal concentration (LC50)
Test Validity	Invalid if mean 96h died in control >10%

Table 3. *Summary of test conditions for cysts, nauplii and adults (Germany benchmark)*

Test type:	Static
Test duration:	72h
Temperature:	24°C
Light intensity:	1000 lux
Photoperiod:	12 h light, 12 h dark
Feeding regime:	No feeding (cysts and nauplii) Feed with phytoplankton (adults)
Test beaker:	100ml (cysts and nauplii) 2000 ml (adults)
Water volume:	50 (cysts and nauplii) 1000 ml (adults)
Age of organisms:	Hatch for 24-36h (nauplii) 14-16 days old (adults)
Number of animals/test beaker	50
Number of replicates:	4
Dissolved oxygen	Saturation prior to treatment
Dilution water:	Manmade seawater(35‰, pH 7.9)
Measured end points:	Hatch rate mean% Mortality mean%

Breakdown test of available chlorine

In theory the concentration of available chlorine added equals to residual chlorine in water. However, in practice, because of illumination, volatilization and substances including living things consuming chlorine in water, some chlorine will be lost, even in distilled water. We designed the experiment in

which the available chlorine, in treated solutions with different biomass and initial concentration, breaks down with time.

We selected *Pyramidomonnas* sp. and nauplii of brine shrimp with different biomass and added sodium hypochlorite to make the concentration of available chlorine to be 5, 10, 20 and 40 mg/l respectively, and then examined total residual chlorine (TRC) in the water samples at 1h, 4h, 24h and 48h.

In this test, we examined residual chlorine with colorimetric method (GB5750-85), with a detection limit of 0.01 mg/l. The sample of phytoplankton chlorination is filtered prior to detection.

Test results

Results of bacteria test

Table 4. *Efficacy of chlorination for the bacteria in natural seawater*

Bacterial type	Before chlorination (24 hours)	After chlorination, available chlorine (mg/l)				
		0	5	10	20	40
Density of anaerobic bacteria (Membrane filter method) CFU/10cm^3	9.9x10^5	3.3x10^6	1.5x10^3	3.3x10	0	0
Density of Vibrio (Membrane filter method) CFU/10cm^3	1.1x10^5	6.0x10^5	0	0	0	0
Density of E.Coli.(MPN fermentation method) CFU/10dm^3	3.3x10^2	7.9x10^2	4.9x10	<2	<2	<2

Table 4 indicates that after 24 hours of chlorination the density of various bacteria decreases dramatically in water. In the group of 5 mg/l available chlorine, anaerobic bacteria and E.coli are 0.15% and 0.05% of the initial concentrations before chlorination, 14.8% and 6.2% in contrast with the control group and no vibrio was detected in 10 cm^3 of water samples. In the groups above 20 mg/l available chlorine, there are no bacteria in 10 cm^3 of water samples.

These results indicate that chlorination of 5 mg/l available chlorine can kill 99.85% of anaerobic bacteria, 100% of vibrio and 85.2% of E.coli. respectively, while above 20mg/l available chlorine can kill almost all bacteria.

Results of phytoplankton test

Table 5. *Absolute Lethal Concentrations (LC_{99}) of sodium hypochlorite for selected phytoplankton algae.*

Density of algae (/ml)	*Platymonas spp*	*Pyramidomonnas sp.*	*Nitzschia clostertum*	*Dicrateria spp.*
10x10^6	100mg/l	20mg/l	15mg/l	20mg/l
7.5x10^6	100mg/l	10mg/l	15mg/l	20mg/l
5.0x10^6	100mg/l	5mg/l	10mg/l	10mg/l
2.5x10^6	60mg/l	5mg/l	5mg/l	5mg/l

These results indicate that absolute Lethal Concentrations (LC_{99}) varies depending on the species and the density of algae, ranging from 5 mg/L to 100 mg/L.

The order of the endurance of algae selected in our test from high to low is as follows:

Platymonas spp .>Pyramidomonnas sp and *Dicrateria spp.> Nitzschia closterum*

We make a comparison between the two conditions, which are in light and in dark. As seen from the LC_{99} for phytoplankton algae, there is no difference between the two conditions. However, with the duration in dark being extended, phytoplankton algae recover more slowly.

Besides killing phytoplankton algae**,** sodium hypochlorite also has a strong discoloration effect.

Results of natural seawater test

Before chlorination, there were many kinds of phytoplankton algae in natural seawater, such as: *Thalassiosira* sp, *Navicula* spp., *Nitzschia* sp, *Leptocylindrus danicus*, A*sterionella japonica* Cleve, *Cyclotella* sp., *Dunaliella* sp., *Gloeothece linearis*, *Oscillatotia* sp., *Synechococcus* sp, *Glenoddinium* sp. etc. There are also some kinds of protozoan, such as: *Euciliata* sp, *Euplotes*, *Difflugia* sp, *Brachionus calyciflorus* and *planula* larva etc.

After 20 days of culture, there were multicellular algae in natural seawater, such as: *Cladophora oligoclada* and *Cladophora rudolphiana* etc. Total biota density is much greater than that in primary natural seawater.

Table 6. *Absolute Lethal Concentrations (LC_{99}) of chlorination for the organisms in natural seawater.*

Regrowing time (day)	concentration of available chlorine (mg/l)					
	0	**5**	**10**	**20**	**40**	**60**
3	+O	+	+	—	—	—
20	+O	+	+	+	+*	—

+ = algae can survive and reproduce;
O = protozoan can survive;
- = neither algae nor protozoan can survive.
* = there are only some benthic diatoms.

These results indicate that 5mg/l available chlorine can kill protozoan while 20 (3 days regrowth) 60mg/l (20 days regrowth) available chlorine can kill both protozoan and algae in natural seawater.

Results of amphipod test

Table 7. *Acute lethality of chlorination for* Corophium acherusicum *Costa*

Concentration of available chlorine	Number of tested organisms	Number of died organisms	Mortalities
160	40	40	100%
40	40	40	100%
10	40	22	55%
5	40	4	10%
2.5	40	2	5%

Results of brine shrimp test

The LC_{50} Sodium hypochlorite for nauplii of Artemia sallina*:*

Table 8. *Toxicity test data of Sodium hypochlorite for nauplii of* Artemia sallina *(GB18420.1-2001).*

Available chlorine (mg/L)	Control	0.83	1.25	1.43	1.67	2
Mortality (%)	7.5	15	40	67.5	92.5	100

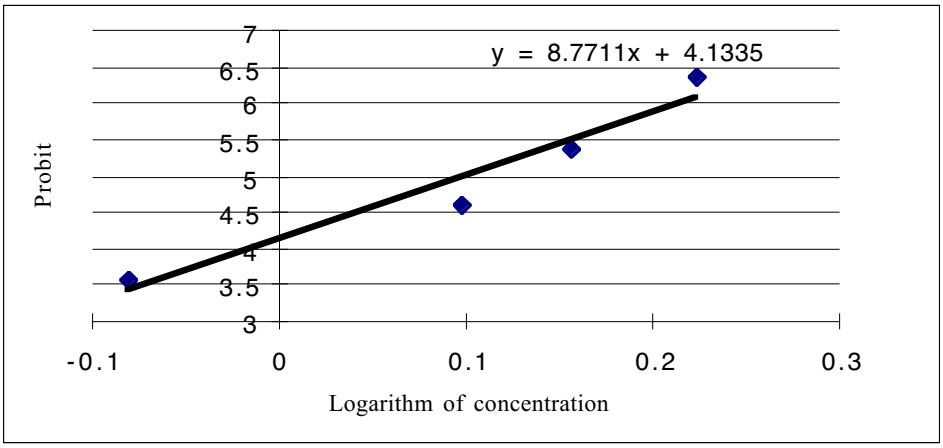


Figure 2. *LC_{50} Calculation for Sodium hypochlorite for nauplii of* Artemia sallina.

Based on probit method, we found out that the LC_{50} of sodium hypochlorite for the nauplius of *Artemia salina* in seawater is 1.26mg/L, and the 95% confidence interval is 1.16~1.36mg/L.

Efficacy of chlorination for Artemia sallina *(Germany ATS benchmark)*

Chlorination effects for hatching of the cysts of Artemia sallina

Firstly, an orthogonal test is designed with three factors (temperature, illumination, salinity) and four levels. From the summation or average of each factor, we find out the key factor that influences the hatching rate is salinity, while temperature is the second and the illumination is the last. Through level selection, the perfect conditions were: temperature 24°C, salinity 35% and illumination 1000 lux. These were also the conditions of our hatching experiment.

Secondly, we conducted concentration-effect test for hatching rate under different concentrations of available chlorine.

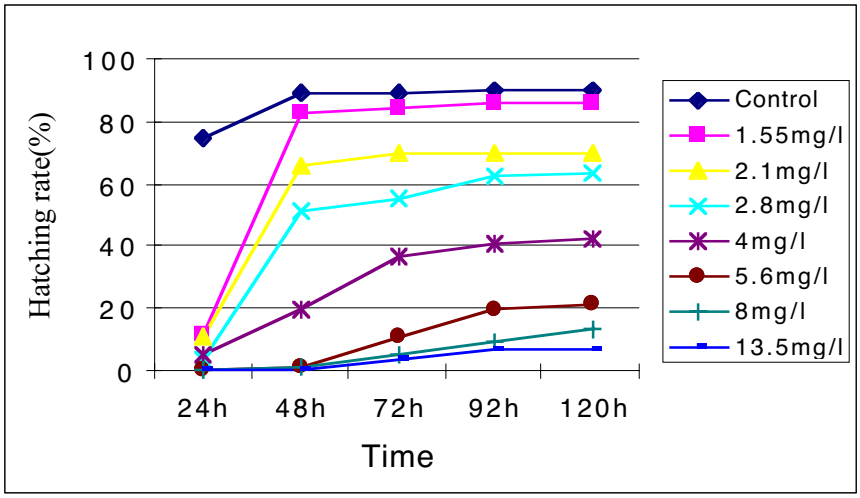


Figure 3. *Hatching rate under different concentrations of available chlorine.*

Figure 3 indicates that sodium hypochlorite has an obvious constraint efficacy on the hatching. With the concentration increasing, the constraint efficacy is more obvious. In addition, there is certain delay effect on the hatching in all treated groups.

Concentration-mortality relationship for the nauplii of Artemia sallina

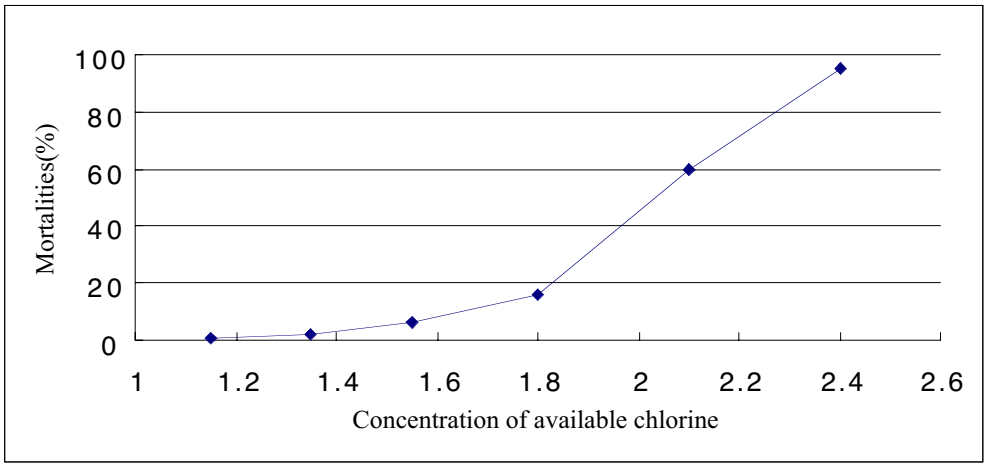


Figure 4. *Mortalities under different concentrations of available chlorine.*

With the concentration increasing, mortalities increase. In the treated group of 2.4 mg/l, there is no survival. In contrast with the adults, nauplii have a higher endurance at low concentrations.

Concentration-mortality relationship for the adults of Artemia sallina

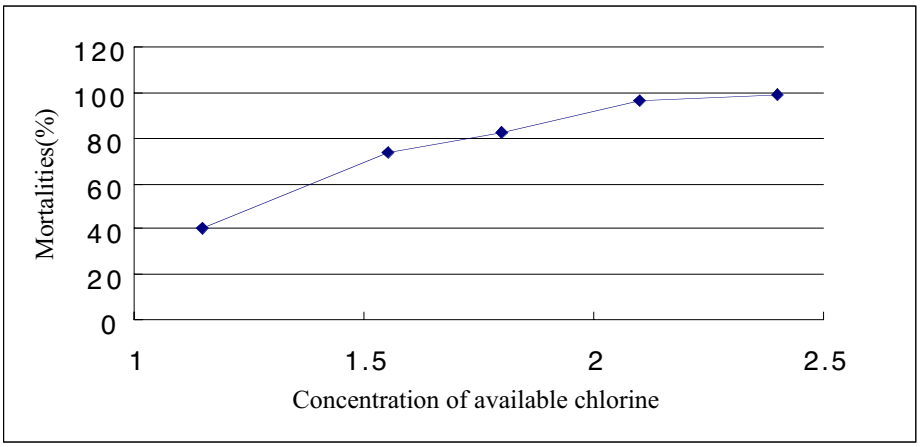


Figure 5. *Mortalities under different concentrations of available chlorine*

With the concentration increasing, mortalities increase. In the treated group of 2.4 mg/l, there is no survival.

Results of available chlorine's breakdown test

Breakdown of available chlorine with different density of nauplii (The concentration of available chlorine added is 5 mg/l).

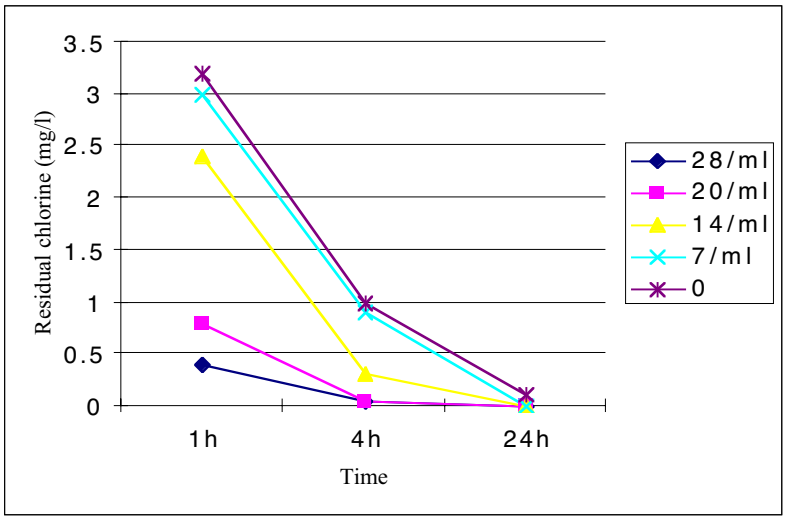


Figure 6. *The breakdown of available chlorine.*

Table 9. *The breakdown of available chlorine.*

Density of nauplii	Residual chlorine (pH value)		
	1h	4h	24h
28/ml	0.4(8.01)	0.05	0.01
20/ml	0.8(8.03)	0.05	0.01
14/ml	2.4(8.04)	0.3	0.01
7/ml	3(8.04)	0.9	0.01
0	3.2(8.09)	1	0.1

Breakdown of available chlorine with different density of nauplii. (The concentration of available chlorine added is 10 mg/l)

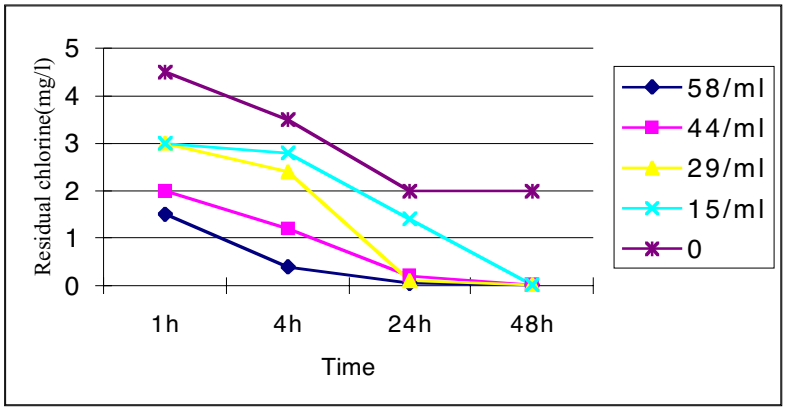


Figure 7. *The breakdown of available chlorine.*

Table 10. *The breakdown of available chlorine.*

Density of nauplii	Residual chlorine (pH value)			
	1h	4h	24h	48h
58/ml	1.5	0.4(7.85)	0.05(7.33)	0.01(7.18)
44/ml	2	1.2(7.94)	0.2(7.40)	0.01(7.22)
29/ml	3	2.4(8.08)	0.1(7.54)	0.01(7.33)
15/ml	3	2.8(8.20)	1.4(7.96)	0.01(7.81)
0	4.5	3.5(8.28)	2(8.16)	2(8.05)

Breakdown of available chlorine with different density of nauplii. (The concentration of available chlorine added is 20 mg/l)

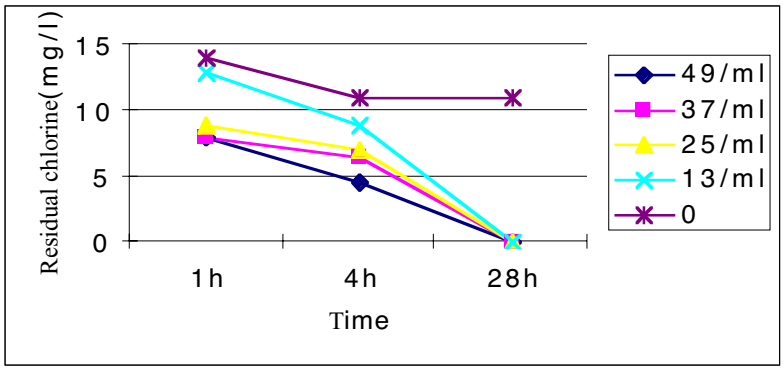


Figure 8. *The breakdown of available chlorine.*

Table 11. *The breakdown of available chlorine.*

Density of nauplii	Residual chlorine (pH value)		
	1h	4h	28h
49/ml	8	4.5(8.29)	0.01(7.44)
37/ml	8	6.5(8.37)	0.01(7.53)
25/ml	9	7(8.42)	0.01(7.81)
13/ml	13	9(8.46)	0.01(8.00)
0	14	11(8.52)	11(8.20)

Breakdown of available chlorine with different density of nauplii. (The concentration of available chlorine added is 40 mg/l)

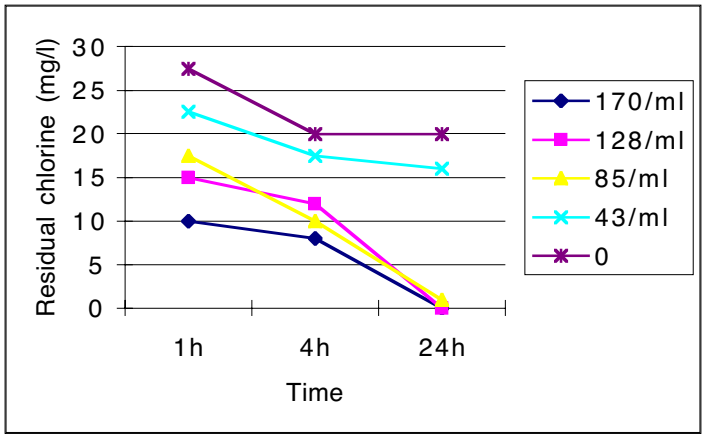


Figure 9. *The breakdown of available chlorine.*

Table 12. *The breakdown of available chlorine.*

Density of nauplii	Residual chlorine (pH value)		
	1h	4h	24h
170/ml	10(8.77)	8	0.01(7.92)
128/ml	15(8.80)	12	0.01(7.98)
85/ml	17.5(8.83)	10	0.9(8.03)
43/ml	22.5(8.83)	17.5	16(8.29)
0	27.5(8.88)	20	20(8.44)

The results indicate that if other parameters are the same, the higher the density of organisms is, the higher the amount of available chlorine demand. The consumption of available chlorine becomes faster with the density of brine shrimp increasing. After a period of time, in the treated group with no brine shrimp, the concentration of available chlorine no longer decrease or decrease slowly. In the treated groups with the density of nauplii below 30/ml under 40 mg/l available chlorine, there are no survival after 24h.

Conclusions and recommendations

(1) The chlorination treatment can kill harmful organisms in ballast water, but the concentration of available chlorine demand varies with different target organisms.

(2) Because chlorinated compounds belong to oxidizing disinfectants, the concentration of available chlorine demand increases with the biomass of organisms. The maximum concentration of available chlorine demand for ballast water and natural seawater is 20-60 mg/l.

(3) Because of high pH value, the chlorination treatment using a high concentration of available chlorine will corrode the ballast tank.

(4) The available chlorine breaks down quickly and it is hard to mix in tank. In addition, chlorination should be carried out before the cysts and spores with high resistance to biocide are produced. So the pipe and installation for biocide addition should be installed near to the entrance of ballast water.

(5) Further tests on harmful effects of the by-products of chlorination treatment should be done.

Acknowledgements

As part of the Global Ballast Water Management Program in China, this project is funded by GEF/UNDP/IMO. We would like to thank these international organizations.

We also wish to acknowledge the assistance provided by Maritime Safety Administration of China.

Use of chlorine for ballast water treatment

J. S. Vianna da Silva & F. da Costa Fernandes

IEAPM
Admiral Paulo Moreira Marine Research Institute
Brazil
julieta@mar.com.br
flaviocofe@yahoo.com

Treatment options being researched

This study explored the potencial of using chlorine as a biocide to treat ballast water and the formation of toxic subproducts like trihalomethane (THM).

Timeframe of the project

The project was carried out from March 1999 to September 2001. The experiments were done during 8 days on board and 3 days in laboratory, between June and July of 2000.

Aims and objectives of the project

The objective of this study was to assess the efficacy of chlorine as a biocide, to determine its minimum concentration to eliminate organisms in ballast water and to observe the formation of trihalomethane, on board. This study also is concerned about the evaluation of survival of microalgae and trihalomethane formation in laboratory in different concentrations of chlorine and cells.

Research methods, test protocols and experimental design

On board of the bulk carrier Frotargetina.

The Experiments were carried out on board during a trip from Port of Forno in Arraial do Cabo, Rio de Janeiro State, to Areia Branca Terminal in Areia Branca, Rio Grande do Norte State, Brazil. Four superior lateral tanks, on the port side, were kept as control and other four, on the starboard side, were treated, with different concentrations of chlorine: 1, 3, 5 and 10 ppm. During 4 days before the departure of the ship, according to the unload of cargo, 2 tanks (control and test) were ballasted at Forno Port. Every day, during 6 to 8 days, samples of water from all tanks were collected to analyze salinity, pH, temperature, dissolved oxygen, ammonia, nitrite, nitrate, phosphate and chlorine. The analyses of salinity, pH, temperature and chlorine were done on board. The dissolved oxygen was also analyzed immediately after the sampling, according to the Winkler technique described by Strickland & Parsons (1972). For qualitative and quantitative analysis of zooplankton, 100 liters of water were pumped, filtered with a sieve with a mesh of 75µm and analyzed in lab with a Leitz stereomicroscope. For the qualitative and quantitative analysis of phytoplankton, 500 mL of water were collected. After sedimentation in 50 mL tubes, the cells were counted in an Olympus inverted microscope by the Utermöhl method. The samples of zooplankton and phytoplankton were done daily, in all tanks, with three replicates and fixed in formalin at 4%. In the last day of the experiment, 500 mL of water were pumped from the test tanks for trihalomethane analysis, using the gas chromatography method.

In the laboratory

For the analysis of the THM formation, 24 liters of seawater were collected, filtered, through Millipore HA filter of 47 mm with pore of 0.45µm and kept in erlenmeyers of 1 liter. The experiment, done in duplicate, was kept for 72 hours in the darkness with temperature and salinity similar to those

found in the ballast tanks (25°C and 35 ppp),. Four concentrations of chlorine were tested: 1, 3, 5 and 10 ppm in three different concentrations of organic matter: $10x10^6$, $5x10^6$ and $1x10^6$ cells/liter, using the microalgae *Tretaselmis chui.*

Results

Chlorine is the most used biocide in chemical industry and in sewage treatment. For several decades it has been chosen as a disinfectant in water treatment. However, the efficiency of the chlorine is related to the neutral pH. In general, the water is usually neutralized before using chlorine. Seawater has an alkaline pH, around 8, and possibly this is one of the disadvantages of using chlorine in ballast tanks. The other disadvantage is the combination of chlorine with organic matter that form trihalomethane, a carcinogenic substance.

Physical and chemical characteristics of the water in the ballast tanks

The physical and chemical variables were relatively stable during all the experiment. The salinity, around 35, remained constant. The temperature had a slight increase, especially in the tanks on the left side, due to the solar incidence, varying from 2l.5°C to 25.5°C. The changes of temperature inside of the ballast tanks are related to the environment temperature to which the ship is submitted (Carlton *et al*., 1993).

The dissolved oxygen presented a variation from 4.06 to 5.50ml/L. This variation is related to the initial concentration, density of organisms, size of the tank and to the quantity of air that remains in the tank after the ballast (Committee on Ships Ballast Operations, 1996).

The water pH was constant, around 8, in all tanks, except in tank 1, treated with a higher concentration of chlorine (10 ppm), where the pH was around 5, during the whole experiment. Nutrients also were very constant during all the experiment. The values were kept about the same of the beginning of the experiment.

Zooplankton: characterization, mortality and survival

The zooplankton abundance on the first day of the experiment varied from 2.010 to 10.281 individuals.m^{-3}. There was a gradual decrease of the individuals during the experiment in all the tanks, varying, on the last day, from 40 to 276 individuals.m^{-3} in the control tanks, and from 5 to 130 individuals.m^{-3} in the chlorinated tanks. The mortality of the organisms, in the last day, in the eight studied tanks varied from 96.26% to 99.01%.

On the second day, however, 24 hours after the application of the sodium hypochlorite, an important decrease in the zooplankton mortality was observed in all tanks, varying from 67.32% to 90.88%. Despite of the difference in the number of individuals in each tank, the organism composition was the same in all tanks. Among the organisms collected in the control tanks, 33.24% were copepod; 32.23%, nauplii; 32.02%, barnacle larvae; 1.43%, mollusk larvae; 0.74%, polychaete larvae and 0.33%, other groups with low density (foraminiferans, tintininas, cladocerans, appendicularians and isopodes).

In the chlorinated tanks, the copepods were the most abundant with 52.26%, followed by barnacle larvae with 26.39%, nauplii with 17.76%, mollusks larvae with 2.06%, polychaete larvae with 0.71% and others with 0.82%.

Phytoplankton: characterization, mortality and survival

The phytoplankton abundance, on the first day of the experiment, varied from 1.187×10^3 to 2.640×10^3 cells.m^{-3}. The gradual decrease observed in the zooplankton organisms, during the experiment, also occurred with the phytoplankton cells, in all tanks, varying, on the last day, from 173×10^3 to

640×10^3 cells.m^{-3} in the control tanks, and from 0 to 387×10^3 cells.m^{-3} in the chlorinated tanks. The mortality of the organisms on the last day, varied from 75.75% to 100% in all tanks. As occurred with zooplankton, twenty-four hours after the application of the sodium hypochlorite, the phytoplankton had an important density reduction in all tanks, varying from 24.50% to 76.47%. The phytoplankton was gathered into three big groups: diatoms, dinoflagellates and coccoliths. Those groups kept the same proportions in the control tanks and chlorinated ones, being 93% diatoms, 6% dinoflagellates, and 1% coccoliths.

Efficiency of the chlorine

To confirm the chlorine concentrations in the tanks, it was measured ten minutes after its application. On the next day, it was measured again and no chlorine was detected in the tanks with concentrations of 1, 3 and 5 ppm. In the tank with concentration of 10 ppm, we still observed the presence of chlorine after 24 hours, what did not happen after 48 hours. So, although the tanks were analyzed for until eight days, the action of the chlorine in the organism mortality was only effective on the first two days (Figure 1). From the fourth day on, we could notice that the quantity of individuals was similar in the control tanks and in the chlorinated ones. We obtained, on the first 24 hours after the application of the sodium hypochlorite, in all chlorinated tanks, a mortality of the organisms (zooplankton and phytoplankton) from 24.85% to 76.46% . The statistic analysis comparing the tanks with different chlorine concentrations using the Test "t de Student", did not show significative differences ($p>0.05$) among the treatments.

Trihalomethane formation

The trihalomethane are products formed from the combination of chlorine and organic matter and are classified as possible carcinogens. The levels of the trihalomethane tend to increase with the pH, temperature, time and quantity of organic matter. Once it is released, this product persists in the environment, spreading through the trophic chain, accumulating in the adipose tissue, destroying and blocking the hormonal system (Jenner *et al*., 1997).

The Environmental Protection Agency, USA, was the first to recommend, in 1979, that the maximum limit for the concentrations of THM should be of 100 µg/l in potable water. In Brazil, according to the Decree n° 36 from 19/1/1990, from the Ministry of Health, the maximum quantity of THM in potable water was also fixed in 100 µg/l.

In the analysis done in the four chlorinated tanks, it was verified the formation of trihalomethane in all of them, though only in tank 1, where we used chlorine at 10 ppm, the concentration was above the one permitted by law, 430 µg/L (Figure 2). The low formation of THM, in the tank with 5 ppm, a relatively high concentration of chlorine, is probably due to the small quantity of organic matter existing in the water collected in do Forno Port. The region is little impacted, mainly if compared to the big Brazilian ports.

In laboratory we tried to simulate places with low cellular density, as do Forno Port, Arraial do Cabo, RJ ($<1 \times 10^6$cells.l^{-1}), and eutrophic places like the Guanabara Bay, Rio de Janeiro, RJ (10×10^6cells.l^{-1}).

The results of the tests carried out in labs can be observed in Table 1.

Table 1. *THM concentration in different concentrations of organic matter and chlorine.*

Concentration of chlorine (ppm)	Volume (cells/liter)	Concentration of THM (µg/l)
1	$1x10^6$	10
1	$5x10^6$	10
1	$10x10^6$	30
3	$1x10^6$	20
3	$5x10^6$	25
3	$10x10^6$	1105*
5	$1x10^6$	755*
5	$5x10^6$	485*
5	10x106	1170*
10	1x106	685*
10	5x106	480*
10	10x106	1600*

* Values above the ones permitted by law.

As we observe in Table I, only the water treated with 1ppm of chlorine kept the THM levels within the standards permitted by law, varying from 10 to 30 µg/L, in the three concentrations of organic matter. In the water treated with 3 ppm of chlorine, in the experiments with a lower cellular density, the formation of THM was between 20 and 25 µg/L, however it reached 1,105 µg/L, in the highest cellular concentration. In the other concentrations of chlorine and cellular density, the formation of THM varied from 480 to 1600 µg/L, making impossible to use 5 and 10 ppm in ballast water treatments, even with low concentrations of organic matter. All cells of the microalgae *Tretaselmis chui* were dead, in all concentrations of chlorine and organic matter, in 24 hours after the beginning of the experiment.

Conclusions

- The physical and chemical variables (S°/₀₀, T°, pH and nutrients) remained relatively stable in all tanks, control and chlorinated.
- The copepods and nauplii were the predominant organisms of the zooplankton and the diatoms predominated in the phytoplankton, in all tanks, control and chlorinated. In the control tanks we could observe higher richness of species, without alteration of the predominant groups, that were similar in all tanks.
- The samples had a gradual decrease of organisms during the experiment in all tanks and there were significative differences ($p<0,05$) among the control tanks and the chlorinated ones in all treatments. Although there were not 100% efficiency in any treatment, the chlorine increased the mortality inside the tanks.
- The lowest tested concentration, 1ppm, showed a good performance. It presented low concentrations of trihalomethanes, far bellow the one permitted by law, ant its efficiency was the same as the other treatments.
- It seems reasonable the use of low concentrations of chlorine to eliminate the organisms in ballast tanks. It would be interesting to do complementary studies, with daily applications or in a continuous flux, with the aim of maximize the chlorine efficiency. It must also be emphasized that the chlorine is an inexpensive product and easy to handle.
- Chlorine concentrations above 3 ppm should not be used, especially in eutrophic environment, due to the formation of high concentrations of trihalomethane.
- The chlorine dioxide seems to be more suitable to the treatment of ballast water as an alternative to chlorine, because it does not form THM, and it is efficient in low concentrations and in any pH. We suggest experiments with ClO_2 to verify its efficiency to eliminate organisms in ballast tanks, cost and handling on board.

Acknowledgments

This project was supported by Brazilian Petroleum S/A – Petrobras

References

Carlton, J. T.; Reid, D. M. & Van Leeuwen, H. 1993. The role of shipping in the introduction of nonindigenous aquatic organisms to the coastal water of the U.S. and an analysis of control operations. *The National Biological Invasion Shipping Study (NABISS),* 390 pp.

Committee on Ships Ballast Operations. 1996. *Stemming the Tide***.** Ed. Nat. Acad. of Sci.

Jenner, H. A.; Taylor, C. J. L.; Van Donk, M. & Khalanski, M. 1997. Chlorination by-products in chlorinated cooling water of some European coastal power stations. *Marine Environmental Research.* 43:279 - 293.

Strikland, J. D. & Parsons, T.R. 1972. A practical handbook of seawater analysis. *Bull. Fish. Res. Can.* 167:1-310.

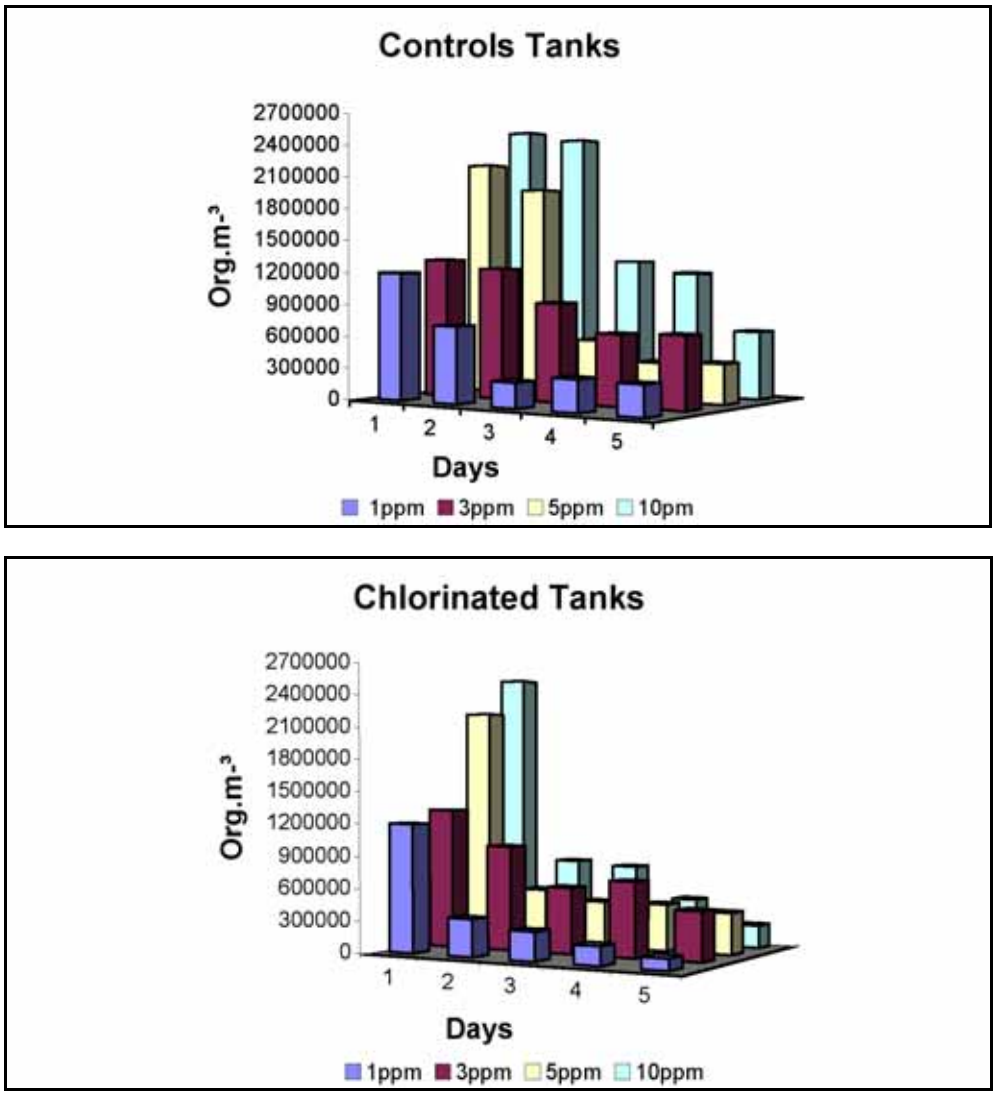


Figure 1. *Total density of the organism (zoo and phytoplankton) in the chlorinated and control tanks.*

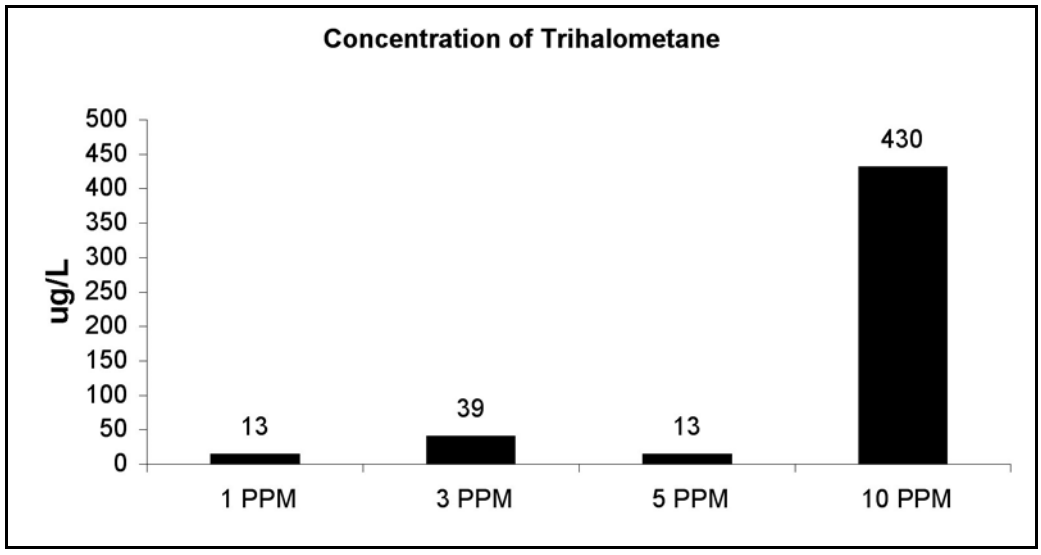


Figure 2. *Concentration of trihalomethane in chlorinated tanks.*

SeaKleen®, a potential product for controlling aquatic pests in ships' ballast water

S. J. Cutler[1], H. G. Cutler[1], J. Glinski[2], D. Wright[3], R. Dawson[3] & D. Lauren[4]

[1] *Garnett, Inc., USA*
cutlers1@bellsouth.net

[2]*Planta Analytica, USA*

[3]*University of Maryland*
Center for Environmental Science
Chesapeake Biological Laboratory
USA

[4]*HortResearch, Ruakura Research Centre*
New Zealand

Abstract

While investigating the use of various natural products as molluskocidal agents, it was observed that several agents belonging to the chemical class of naphthoquinones were found to be highly effective. Further investigation in the structure-activity-relationship led to the biologically active agent menadione, which is being developed under the trademark SeaKleen®. This product has been shown to possess significant efficacy against a wide variety of estuarine and fresh water organisms including Cyprinodon variegatus, Eurytemora affinis, Isochrysis sp., Neochloris sp., and Glenodinium foliacium cysts. In addition, current studies have shown SeaKleen® is very effective against free swimming Glenodinium foliacium, Cyclopoidea sp (Cyclops). In order to gain a better understating of its effects, studies were designed to evaluate SeaKleen® against the edible oyster, Mytilus galloprovincialis . Based on the broad spectrum activity of SeaKleen® against marine organisms and its high potential as a commercial product, it was of interest to determine the degradation of the active component, menadione, when subjected to normal applications. Using an HPLC assay, SeaKleen® was subjected to sterilized and unsterilized sea and fresh water over a period of 72 hours, and samples taken at 24 hour intervals, to determine longevity and breakdown. Results, to date, indicate that SeaKleen® is an environmentally friendly and cost effective ballast water treatment to control invasive species.

Treatment options being researched

Chemical (Biocide)

Timeframe of the project

July 2001-June 2003

Aims and objectives of the project

This project includes the evaluation of SeaKleen® against a variety of aquatic nuisance species residing in ballast tanks of ships. This project fills the gap on tests that have been performed since the last IMO meeting in 2001. Furthermore, this study includes the degradation of the active principle in fresh and salt water studies using High Performance Liquid Chromatography (HPLC).

Research methods, test protocols, and experimental design

In mid 1988, Eurasian zebra mussels, *Dreissena polymorpha*, were found in the Great Lakes, North America, and their entry was determined to have been in the ballast water carried by ships. Within a short time, their effect on commercial and recreational water supplies became readily apparent. By January 2000, twelve years after the initial discovery, zebra mussels had spread from the Great Lakes to Louisiana and west into Texas. Water intake pipes, for example in power plants, have been clogged resulting in a 50% reduced water flow rate. And, the mussels apparently secrete metabolites that etch away ferrous pipes. This occurs whether they are living, or dead. In drinking water, they produce an off-flavor even after water purification. This effect is associated with the production of polyamines, especially cadaverine, the latter being a distinctive odor in decaying corpses, animals and certain plants and fungi. Its main purpose is to attract insects, especially flies, which lay their eggs, then hatch to produce larvae that feed upon the decaying matter, thus ensuring survival of the next generation. In the case of plants, the flies act as pollinators, an example being the Deadhorse Aurum, and, presumably, in fungi they spread propagules to other sites

While attending the 1st World Congress on Allelopathy, 16-20 September, 1996 in Cadiz, Spain, Dr. Horace Cutler listened to the effects of various natural products, as described by CB Rogers of the University of Durban – Westville, South Africa (Rogers 1996). In his presentation, he informed his audience that *Combretum* tree species had no plants growing within its canopy, or dripline and, therefore, he proposed that certain natural herbicides were produced and exuded by the leaves. As an afterthought, Rogers added that the sodium salts of bioactive metabolites, which included mollic acid and imberic acid, were also active against snails, for example *Biomphalaria glabrata*. Recognizing the relationship of snails to zebra mussels (*Dreissena polymorpha*), which are present in the many areas including the Great Lakes of the United States, it was decided to evaluate these compounds as potential biocides in controlling this aquatic nuisance species.

Upon evaluation, it was noted that other natural products had similar structural features and, possibly, similar effects on snails. Furthermore, it was recognized that juglone, a quinone produced by walnuts shells (*Juglans nigra* and other species), had been evaluated by the United States Department of Agriculture as a potential natural herbicide. From this, we began to investigate the usefulness of various quinones against snails and slugs, particularly those that are recognized as aquatic nuisance species.

Other ballast pests

The US Fish and Wildlife Service presently calculates that the cost of introducing non-indigenous pests to North America amounts to more than $100 billion, annually. Other pests, beside zebra mussel, including the spiny water flea, *Bythotrephes cedarstroemi*; the Eurasian ruffe, *Gymnocephalus cernuus*, a non-game fish; and the round goby *Proterorhinus marmoratus*, have been introduced to the US. Other pests, among them the dinoflagellates *Prorocentrum, Gymodinium, Alexandrium* and *Gonyaulax* also hitch rides and become unwelcome visitors. These are well known for their ability to cause blooms that kill fish and destroy commercial shellfish industries. The best known of these is the "red tide", which turns water blood red. It has been speculated that the first plague sent by God to convince Rameses II that he should release the Israelites from captivity, was a "red tide". As the Bible states this caused the Nile (the only river in Egypt) to turn to blood and, *"The fish in the river will die, and the river will smell so foul that the Egyptians will not want to drink the water of it* (**Exodus 7:18**). It should be noted that there followed an interesting development, *"But the magicians of Egypt used their witchcraft to do the same, so that Pharaoh's heart was stubborn....."* (**Exodus 7:22**). The latter actions lends credence, but not proof, to the dinoflagellate theory since a period of time obviously followed the first red flush in the Nile, and may have occurred later in its tributaries.

Another effect caused by dinoflagellates is that they can colonize Caribbean waters, especially where reef fish, such as grouper, feed. The net result is that upon ingestion certain toxins accumulate in the flesh and travelers who consume the fish may become stricken with Ciguatera poisoning, which may

be fatal. This is manifested by characteristic symptoms where the subject may feel tingling, or numbness at the extremity of the fingers, and will feel cold on hot days to the point of wanting to wear an overcoat when it is 30°C. Cold liquids, especially those containing ice, will feel scalding hot to the mouth, and conversely, hot liquids feel ice cold. Recovery may take several months, and death is not uncommon. The medical costs have not been included in the economic equation for this class of marine pests.

An algal bloom toxin reported to have killed over fifty sea lions in Monterey Bay, in 1999, may also be affecting blue and humpback whales, both endangered species. A bloom that appeared in the summer of 2000 had entered the food chain on which the whales fed (Atlanta Journal, 2001).

Yet another ballast water import is the cholera bacterium, *Vibrio cholera*. Although some public concern was voiced over the discovery of this bacterium in ships entering the Chesapeake Bay, it should be noted that *Vibrio* bacteria are common in Chesapeake Bay waters while conditions do not support the development of the disease. In the Southern United States, the conditions do favor the development of cholera. The vector appears to be planktonic copepods (crustaceans), which emigrate from South America to the US Gulf coast ports, their initial route being from Europe to South America. It is, in fact, this tortuous passage *via* ballast water that points to the seriousness of the migratory pest problem. So much so, that legislation has been enacted in the USA.

In 1990, the United States Congress passed Public Law 101-646. The legislation, "The Nonindigenous Aquatic Nuisance Prevention and Control Act", an article of which was the, "National Ballast Water Control Program." Therein, are mandated studies to control the introduction of aquatic pests into the United States. Among the propositions posed are ultraviolet irradiation, filtration of all types including voraxial separators, ultrasonic perturbation, ozonation, thermal and electrical treatments, reduction in available oxygen, and chemical treatment.

If chemical treatment is to be successfully employed it must be effective, environmentally benign and, therefore, biodegradable. It must also have high specific activity and be target specific. To reiterate, such characteristics are typical of organic natural products. Consequently, upon examination of the three natural products discussed earlier, menadione, 1,2- and 1,4-naphthalenedione, were the most likely candidates to control aquatic phytoplankton by growth inhibition, or phytocidal activity, was menadione. Any other effects would be gratuitous, for example, controlling the growth of zebra mussels, or dinoflagellates, or cholera, and other pests.

Initial experiments (*vide infra*) showed that many of the quinones evaluated had toxicity towards aquatic nuisances species. Of these, three naphthalenediones had specific activity against target pests. It became apparent that if we were to proceed toward the ultimate goal of a practical aquatic pest control product, price would be an overriding factor, coupled to the availability and generally known toxicity. Of the three, menadione (vitamin K_3) became the selected candidate. On a cost basis, menadione is 50 cents/gram; 1,2-naphthalenedione is $14.30/gram; 1,4-naphthalenedione is $1.20/gram (all costs are calculated as price/gram even though, for example, the minimum purchase for menadione is 5 grams. Aldrich Catalog 2002-2003). However, it is imperative to realize out that fine laboratory chemicals are extraordinarily expensive relative to the source material.

Menadione

Vitamins belonging to the K group are polyisoprenoid substituted naphthalenediones with vitamin K_3 serving as the parent template. Although initially believed to be simply a synthetic derivative of vitamin K_1 and K_2, after therapeutic administration, menadione is readily converted, in the liver, to vitamin K_2 (Marcus and Coulston, 2001). As a group, these are ubiquitous, natural compounds that are found in microorganisms, plants, and animals. Vitamin K_1 and K_2 are essential substances that are required by all mammals, including humans, for the regulation of normal blood clotting factors. Found in leafy dark vegetables, which may serve as a dietary source, the major requirements of the body are met by gut microorganisms that feature the ability to synthesize vitamin K_1 (Bently and Meganathan, 1982).

The vitamin is absorbed from the gastrointestinal tract where it circulates in the blood, playing a critical role in the biosynthesis of prothrombin, a protein responsible for blood clotting. Posttranscriptional modification of prothrombin, as well as factors I, VII, IX, and X, results in the formation of blood clotting proteins which may be found in the plasma. This posttranscriptional process is totally determined by vitamin K in which it converts the glutamate residues of the precursor proteins to gamma-carboxyglutamate residues of the functional coagulation factors. These specific products are the sites of the Ca^{+2} binding, and are essential to their role in the clotting cascade.

Menadione is used in chicken feed to control a hemorrhagic syndrome brought on by feeding synthetic rations, hence the term vitamin K [for Koagulans vitamin, a term coined by Henrik Dam] (Dam & Schonheyder, 1935). Dam *et al.,* isolated vitamin K from alfalfa and fishmeal, in the K_1 and K_2 forms. In addition, menadione is used in feeds for turkeys, swine, cattle, and catfish, with the latter serving as an aquatic application of menadione at use rates of 4.4 ppm. (Robinson et al, 2001). Although primarily produced by synthetically, menadione is found to exist naturally (Mikhlin, 1942; Mikhlin, 1943). Although there has been skepticism to these publications, the United States Department of Agriculture Agricultural Research Service (USDA-ARS) has isolated menadione from various walnuts (Binder et al, 1989; Thomson, 1997) The world's primary source of menadione, which can be synthesized from β-methylnaphthalene by oxidation with chromic oxide under mild conditions, is used clinically as a prothrombogenic [a blood clotting agent]. One of the most significant uses today involves hypothrombinemia of newborn infants. In this condition, the neonate is incapable of producing enough vitamin K, but this can be remedied by administering the deficient vitamin, as menadione (Committee on Nutrition, 1961). In veterinary medicine it is used in hypoprothrombinemia and bishydroxycoumarin poisoning, and sweet clover poisoning (Merck Index, 1996). On a molar basis menadione is identically active to vitamin K_1 and may be used orally, intramuscularly, and intravenously. C^{14} studies indicate that it is converted *in vivo* to vitamin K_2, the side chain genesis being through mevalonic acid. While it has limited solubility in water, 1 gram dissolves in ~ 60 mL ethanol. It is stable in air, but is rapidly degraded by sunlight and ultraviolet. However, its most utilitarian form is as menadione sodium bisulfite [1,2,3,4-tetrahydro-2-methyl-1, 4-dioxo-2-naphthalenesulfonic acid] and it is this form that is used pharmaceutically: one gram will dissolve in ~ 2 mL of water.

Initial aquatic experiments with naphthalenediones

As presented at the first International Maritime Organization meeting in London (Wright, 2001), replicated experiments were conducted with menadione and menadione sodium bisulfite against the following organisms: the marine alga, *Isochrysis galbana*; the freshwater green alga, *Neochloris* sp.; zebra mussel larvae, *Dreissena polymorpha*; an estuarine copepod, *Eurytemora affinis*; a bacterium congeneric with *V. cholerae, Vibrio fischeri*; the toxic marine dinoflagellate, *Proprocentrum minimum*; dinoflagellate cysts, *Glenodinium* sp.; the benthic amphipod crustacean, *Leptocheirus plumulous*; Sheepshead minnow, eggs and larvae, *Cyprinodon variegatus*; and oyster larvae, *Crassostrea virginica* (Table 1).

1,2-naphthalenedione was tested against *I. galbana*; *E. affinis ; and V. fischeri*, while 1,4-naphthalenedione was tested in all these, plus *Neochloris*, in replicated experiments (Table 2).

Table 1. *A Summary of the Effects of Menadione (Vitamin K3) Against Assorted Ballast Water Pests[1].*

Organism	***Toxicity Levels***
T. Isochrysis galbana Marine Algae	Toxic at 1.0 ppm and above
Neochloris sp. Freshwater algae	Toxic at 500 ppb and above
Dreissena polymorpha Zebra mussel larvae	Toxic at 500 ppb and above
Eurytemora affinis Estuarine copepod	Toxic at 1.5 ppm and above in less than 20 hours
Vibrio fisheri Congeneric with *V. cholerae*	Toxic at 1.0 ppm and above
Proprocentrum minimum Marine dinoflagellate cysts	Toxic at 500 ppb and above
Glenodinium sp. Dinoflagellate cysts	Toxic at 2.0 ppm after 2 hours
Leptocheirus plumulous Benthic amphipod crustacean	Toxic at 2.0 ppm and above
Cyprinodon variegatus Sheepshead minnow	Eggs: toxic at 1.0 ppm. Kills and/or prevents hatch Larvae: toxic at 1.0 ppm and above
Crassostrea virginica Oyster larvae	Toxic at 500 ppb and above

[1]Results obtained from replicated experiments; toxicity represents 100% kill

Table 2. *A Summary of the Effects of 1,2- and/or 1,4-Napthalenedione (NLD) Against Assorted Ballast Water Pests[1].*

Organism	***Compound***	***Toxicity Levels***
T. Isochrysis galbana Marine Algae	1,2-NLD 1,4-NLD	Toxic at 375 ppb after 1 minute Toxic and bleaches at 1 ppm
T. Isochrysis galbana Marine Algae	1,2-NLD 1,4-NLD	Toxic at 750 ppb after 1 minute Toxic at 750 ppb
Vibrio fisheri Congeneric with *V. cholerae*	1,2-NLD 1,4-NLD	Toxic at 500 ppb Toxic at 500 ppb
Neochloris sp. Freshwater algae	1,4-NLD	Toxic at 1 ppm after 24 hours

[1]Results obtained from replicated experiments; toxicity represents 100% kill.

Based on these findings, it was of interest to determine the concentration-response that menadione has against *Isochrysis galbana* and *Glenodinium foliaceum*. This report describes the experiments used to determine these effects. Furthermore, since menadione is being considered for use in ship trials on the west coast of the United States, it was important to gain understanding of the toxic profile it possess against the indigenous aquaculture that is present. Studies were performed on *Mytilus galloprovincialis* in order to determine the effects menadione on this edible mussel. Also, the degradation of menadione was evaluated in fresh and salt water using high-performance-liquid-chromatography (HPLC) so that the half-life could be calculated.

Research methods

The media and test organisms *Isochrysis galbana* and *Glenodinium foliaceum* were obtained from the culture facility of Carolina Biological (Burlington, North Carolina USA) and maintained under 16h:8h light/dark regime at 22°C. Exposure of *Glenodinium foliaceum* cysts to SeaKleen® were conducted at the Kalmar Marine Institute, Kalmar, Sweden (Professor E. Graneli) where they were examined by

epifluorescence microscopy. The assays involving *Mytilus galloprovincialis* were performed by a contract laboratory, Northwest Aquatic Labs (New Port, Oregon USA).

All cell counts were preformed using an Improved Neubauer, 1/400 square mm Hemacytometer (Hausser Scientific, Horsham, PA USA). All counts were completed in duplicated and an average of these counts was used.

Isochrysis and Glenodinium

The alga *Isochrysis galbana* was cultured in Soil Water Medium as a 1 liter stock culture. The initial average cell density count was determined to be 816 x 10^6 cells per liter. From the stock culture 10 ml was placed into 12 sterile micro Petri dishes (Fisher Scientific, Norcross, Georgia USA). These were divided into four groups one of which was a control group and the others three concentrations of testing for SeaKleen®. The concentrations of formulated menadione included 0.0 ppm (control), 0.250 ppm, 0.750 ppm, and 1.5 ppm and were run in triplicate. Formulated menadione was dissolved in sterile water as a stock solution. Aliquots were taken from the stock menadione solution and added to each of the 12 sterile Petri dishes. For the control group, only sterile water was added at the same volume used in the test concentrations. Cell counts were performed at 2, 4, 6, 24, 48, 72, and 96 hours after the test solution was added. The cultures were maintained under 16h:8h light/dark regime at 22°C during this 96 hour period.

The dinoflagellate *Glenodinium foliaceum* was cultured in Alga Gro® Medium as a 1 liter stock culture. The initial average cell density count was determined to be 147 × 10^6 cells per liter. From the stock culture 10 ml was placed into 12 sterile micro Petri dishes (Fisher Scientific, Norcross, Georgia USA). These were divided into four groups one of which served as a control group and the others as three concentrations of testing for SeaKleen®. The concentrations of formulated menadione included 0.0 ppm (control), 0.250 ppm, 0.750 ppm, and 1.5 ppm and were run in triplicate. Formulated menadione was dissolved in sterile water as a stock solution. Aliquots were taken from the stock menadione solution and added to each of the 12 sterile Petri dishes. For the control group, only sterile water was added at the same volume used in the test concentrations. Cell counts were performed at 2, 4, 6, 24, 48, 72, and 96 hours after the test solution was added. The cultures were maintained under 16h:8h light/dark regime at 22°C during this 96 hour period.

The dinoflagellate cysts were collected from marine sediments cleaned of debris using mild ultrasonic cleansing and exposed to 2.0 ppm of formulated menadione. Light microscopy and epifluorescence microscopy were employed to examine the cysts for oxidative damage and chloroplast disruption following treatment at 2.0 ppm level.

Mytilus

Formulated menadione was tested in order to estimate the chronic toxicity of water discharge from a source such as a ballast tank. This was performed by assaying bivalve larval development in a 48-hour static test. This protocol complies with the U.S. EPA West Coast chronic toxicity annual (EPA/600/R-95/136), ASTM bivalve toxicity method (E 724-89), and the WDOE (Washington State Department of Ecology) toxicity guidance manual (WQ-R-95-80).

Adult mussels (*Mytilus gallaprovincialis*) were collected from Yaquina Bay, Oregon and immediately used in testing. The source of the gametes were from 1 female and 1 male (gametes of male physically stripped from gonads). Eggs from the female were filtered (200-300 µm) to remove feces and pseudofeces and adjusted in concentration to about 2500-6000/ml. Eggs were then fertilized by addition of sperm from the male. Ten minutes after adding the sperm, the egg and sperm mixture was poured through a 25 µm screen to remove excess sperm; then the eggs were rinsed and resuspended in water. The embryo density was adjusted to between 1500 and 3000/ml. Embryos were kept suspended by frequent gentle agitation with a perforated plunger and the temperature was maintained at

approximately 16°C. The quality of the embryos was verified before testing by microscopic examination. Embryos were used 2.7 hours post-fertilization.

Three formulations of SeaKleen® were used in this study;100:0, 80:0, and 0:100, menadione sodium bisulfite:menadione, respectively. Five concentrations of the three formulations were prepared 2 days prior to the bioassay test and on the day of the test. Vials containing 8 mg of each formulation were mixed in 4 liters of filtered seawater to make up the highest concentration (2 ppm) and were subsequently diluted to make up the remaining concentrations of 1.0, 0.5, 0.2, and 0.1 ppm. A control group (0 ppm) was used for comparison. The 2 day solutions were then either stored under dark or light conditions at 15°C prior to the bioassay testing.

Larvae were placed in 30 ml glass vials containing 10 ml of test solutions. The average number of embryo in the 10 ml solution was 247. The temperature was maintained at 20°C with a photo period of 16:8 hours (light:dark) for 48 hours to permit development into prodissoconch I larvae. Larvae were subsequently counted to determine the total number of abnormal and normal surviving larvae. Each sample was performed in quadruplet.

Where data permitted, the EC50s and LC50 were calculated using either the Maximum-Likelihood Probit or the Trimmed Spearman-Karber methods. NOEC and LOEC values for survival and normality were computed using either Dunnett's test, T-test with Bonferroni's adjustment, Steel's Many-one Rank Test, or Wilcoxon Rank Sum Test with Bonferroni Adjustment. The statistical software employed for these calculations was Toxcalc, v.5.0.23N (Tidepool Scientific Software).

HPLC Studies

The tests were performed using a bulk sample of seawater collected from either Flax Mill Bay or Raglan, or river water collected from the Waikato River in the Hamilton City area of New Zealand. For tests involving exposure to aquatic organisms, pond water was collected from catfish ponds in either Indianola, Mississippi or at the National Warmwater Aquaculture Center, Stoneville, Mississippi. The water samples were stored at 6°C prior to testing. Samples of SeaKleen® were used at either a 2.0 ppm or 1.0 ppm concentration of active material. These concentrations were prepared using the collected water samples and all samples were analyzed at 4, 24, 36, 48, 72, and 96 hours. For the river and sea water, samples were stored at 6°C in darkness or under full exposure to daylight. For the pond water assay, SeaKleen® was only evaluated under normal photoperiods of day and night during the summer of 2002.

Analysis of the samples was accomplished using High-Performance-Liquid-Chromatography (HPLC) (Hewlett-Packard model 1090) with simultaneous fluorescence and UV detection or with a Diode Array Detector. The HPLC column used was a YMC C18 ProPack (100 mm x 3 mm, 3 µm particle size (YMC Co. Kyoto, Japan). The mobile phase consisted of acetonitrile and 0.1% trifluoroacetic acid. The column oven temperature was set at 450C with a flow rate of 0.6 ml/min. The detection wavelength as set at 230 nm (to monitor menadione sodium bisulfite) and 263 nm (to monitor menadione). The injected sample volume was 4 µl. Calibrations of the HPLC response for menadione sodium bisulfite and menadione was performed using a series of dilution of standards obtained from the United States Pharmacopeia (USP). The detection limit for menadione was determined to be 0.56 µg/l (0.56 ppb).

Results

Isochrysis and Glenodinium

The effects of SeaKleen® on *Isochrysis galbana* and *Glenodinium foliaceum* were found to be within the range of 0.25 ppm and 1.5 ppm of active ingredient. After the organisms were allowed to equilibrate, SeaKleen® was added at four concentrations in order to determine the concentration-response curve. These results are listed in Figure 1 and Figure 2 for *Isochrysis galbana* and

Glenodinium foliaceum, respectively. SeaKleen® produced a significant inhibition in the growth of both these organisms at 0.750 and 1.5 ppm. In addition, it produced a significant inhibition of Glenodinium at the 0.250 ppm.

Using light microscopy and epifluorescence microscopy, Figure 3 shows the effect of SeaKleen® at 2.0 ppm against cysts of *Glenodinium foliaceum*. It is clear from this figure that the cysts suffered oxidative damage and chloroplast disruption following treatment.

Mytilus

The edible mussel, *Mytilus gallaprovincialis*, was used in a bioassay to gain an understanding of the effects of SeaKleen® released from ballast tanks into United States harbors. Therefore, studies were conducted to evaluate the effects of SeaKleen® on aquatic organisms present in Puget Sound, USA. As shown in Tables 3 and 4, SeaKleen® exhibited similar effects whether stored under light or dark conditions. In the 80:20 (menadione sodium bisulfite:menadione) formulation, there was a sharp drop off in toxicity from 0.5 ppm to the 0.2 ppm concentrations, while with the 0:100 (menadione sodium bisulfite:menadione) formulation, this drop off was seen at a lower concentration (0.2 ppm to 0.15 ppm). This is to be expected as the weight of active ingredient is greater for menadione than for menadione sodium bisulfite since the sodium bisulfite (inactive material) constitutes 37.7% of the weight for that particular salt. Therefore, the actual active ingredient, menadione, in the salt is 62.3%. Using this correction, the studies involving the 80:20 formulation yield similar cut-off values to those obtained in the 0:100 formulation.

Table3. *Effects of SeaKleen® towards* Mytilus gallaprovincialis *(80:20 Formulation).*

	Dark Storage - 48 Hrs Bioassay - Dark Conditions	***Dark Storage - 48 Hrs Bioassay - Dark Conditions***	***Light Storage - 48 Hrs Bioassay - Light Conditions***
Concentration ppm	*% Mortality*	*% Mortality*	*% Mortality*
0.5	100*	100*	100*
0.2	0	7.3	4.3
0.1	0	1.6	0
0.05	0	0	0
Control	0	0	0

*$p \leq 0.05$

Table 4. *Effects of SeaKleen® towards* Mytilus gallaprovincialis *(0:100 Formulation).*

	Dark Storage - 48 Hrs Bioassay - Dark Conditions	***Dark Storage - 48 Hrs Bioassay - Dark Conditions***	***Light Storage - 48 Hrs Bioassay - Light Conditions***
Concentration ppm	*% Mortality*	*% Mortality*	*% Mortality*
0.5	100*	100*	100*
0.2	25.3*	3.7	8.0*
0.1	1.7	0	0
0.05	0	0	0
Control	0	0	0

*$p \leq 0.05$

HPLC Studies

Since SeaKleen® is being developed for use in treating ballast water it is necessary to calculate the degradation of the active material under normal use conditions. Studies employing HPLC were executed in order to monitor the degradation of SeaKleen® under dark conditions, which is typical of

ballast tanks, and light conditions, which is expected after the release of water from a tank into the environment. In addition, since the mechanism of action for menadione involves interaction with aquatic organisms, it is expected that interrelationships might facilitate the degradation of SeaKleen®. As such, it was importance to evaluate the fate of menadione under conditions where aquatic nuisance species were present in the water.

HPLC studies under dark conditions and in the absence of high levels of aquatic nuisance species show that menadione is relatively stable in sea water with a drop of 8.5% in menadione concentration after 72 hours. After 28 days, only 21% of the original starting concentration of active ingredient was present. Studies under light conditions were differed to the dark studies in that the rate of degradation was faster. After 72 hours, only 47% of the original starting concentration was present.

In river water, the HPLC studies show that the degradation is slightly different than seen under sea water conditions. In the absence of high levels of aquatic nuisance species, under dark conditions, the degradation was almost identical to the dark sea water results. After 72 hours, there was 80.5% of the original concentration, but after 28 days, the concentration was only 22%. However, under light conditions, only 8% of the original concentration of SeaKleen® remained after 72 hours. This was attributed to a higher microbial load present in the river water used in this assay. It is believed that this phenomenon caused SeaKleen® to be more actively consumed, because for each organism at least one mole of SeaKleen® is expended. Based on this, it was decided to perform HPLC studies in the presence of aquatic nuisance species.

When SeaKleen® was used at 0.8 ppm active ingredient, in the presence of the aquatic nuisance species *Oscillatoria perornata*, degradation was very rapid. At 48 hours, SeaKleen® was approaching the lower levels of detection limits (0.56 ppb) and after 72 hours, it was no longer detectable. This suggests that the degradation of SeaKleen® is dependent on many factors, especially the presence of aquatic nuisance species. It is believed that there is a direct relationship between the number of moles of menadione in a given treatment and the number of organisms. Simply, Avogadro's number most likely plays a definite role in aquatic nuisance species death and in the degradation of SeaKleen®.

During the HPLC studies, non toxic by-products were detected. This was accomplished by following the degradation of SeaKleen® by HPLC as well as the concomitant use of Liquid-Chromatography-Mass spectrometry (LC-MS).

Conclusions and recommendations

Initial studies suggested that SeaKleen® has potential as an agent to control aquatic pests in both fresh and salt water at 1 ppm, or less. Studies, to-date, show that there is a correlation between concentration and toxicity. For most aquatic organisms, the toxicity is found to be between 0.50 ppm and 1.5 ppm active ingredient. Further, there is a sharp, acute drop-off in toxicity suggesting that when released from ballast tanks, the dilution of any residual material should result in below toxic levels to indigenous organisms.

Additionally, HPLC studies suggest that under typical ballast conditions (i.e., dark environment) SeaKleen® is present for a sufficient period of time to ensure complete removal of all aquatic nuisance species. However, it is important to realize that the presence of organisms will facilitate the degradation of SeaKleen® to non-toxic levels within the normal travel time of most cargo ships. Furthermore, the HPLC studies, in conjunction demonstrate that the SeaKleen® degrades to harmless metabolites suggesting that it is an environmentally friendly natural product.

The low use rates and highly acute but transient toxicity implies that the material can be administered in low amounts, thereby making it cost effective. It is calculated that 1 gram of SeaKleen® will treat 1 metric ton of ballast water. Thus, a ship with a 10,000 metric ton ballast tank should cost approximately less than US $2,000. Over the ship's lifetime, this cost should represent significant savings to the owners. In addition, due to the cost of repairs and replacement parts, the savings are

even more pertinent. One final, but high practical point, is the ease with which SeaKleen® can be administered.

References

Atlanta Constitution, 14 January, pA8, 2001.

Bently, R., Meganathan, R. 1982. Biosynthesis of vitamin K (menaquinone) in bacteria. *Microbiol Rev* 46: pp. 241-280.

Binder, R.G., Benson, M.E. & Flath, R.A. 1989. *Phytochemistry* 28(10): pp. 2799-2801.

Committee on nutrition, American Academy of Pediatrics (1961) Vitamin K compounds and the water-soluble analogues; use in therapy and prophylaxis in pediatrics. *Pediatrics* 28: pp. 501-506.

Dam, H., Schonheyder, F. 1935. The antihaemorrhaig vitamin of the chick. *Nature* 135: pp. 652-653.

Marcus, R. & Coulston, A.M. 2001. Fat soluble vitamins. In: Hardman, J.G. & Limbird, L.E. (eds): *Goodman & Gilman's The Pharmaceutical Basis of Therapeutics. 10th ed.* pp. 1783-1786.

Merck Index 12th Edition 1996. page 994.

Mikhlin, D.M. 1942. Vitamin K3, an antihaemorrhage: Corn source for Vitamin K. *Comptes Rendus (Doklady) de l'Acadaemie des Sciences de l'URSS* 37(5-6): pp. 191-192.

Mikhlin, C.R. 1943. The peculiarities of the antihemorrhagic factor of the maize stigmata (Vitamin K_3) *Biokhimiya* 8(4): pp. 158-167.

Robinson, E.H., Menghe, H.L. & Manning, B.B. 2001. *A practical guide to nutrition, feeds, and feeding of catfish.* Mississippi Agricultural and Forestry Experiment Station, Office of Agricultural Communication, Division of Agriculture, Forestry, and Veterinary Medicine, Mississippi State University. Oxford, Mississippi.

Roger, C.B. 1996. *The allelopathic action of Combretum leaf secretions*. 20 September 1996. Symposium 8. 1st World Congress on Allelopathy. Cadiz, Spain.

Thomson, R.H. in *Naturally Occurring Quinones IV Recent Advances*, Blackie Academic & Professional, London, 1997, p 112.

Wright, D.A. & Dawson, R. 2001. "SeaKleen® - A potential natural biocide for ballast water treatment. *1st International Ballast Water Treatment R&D Symposium. International Maritime Organization, London 26-27 March 2001: Proceedings*. GloBallast Monograph Series No. 5, IMO London. Pp. 73-75.

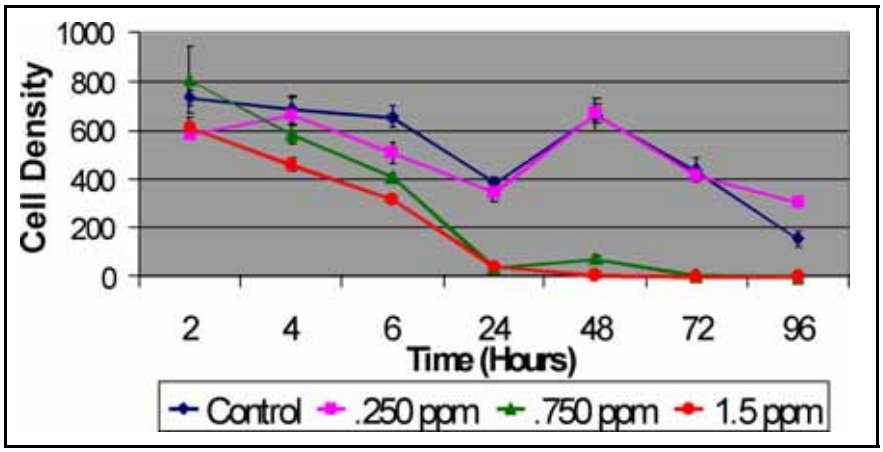


Figure 1. *The effects of SeaKleen® on Isochrysis galbana.*

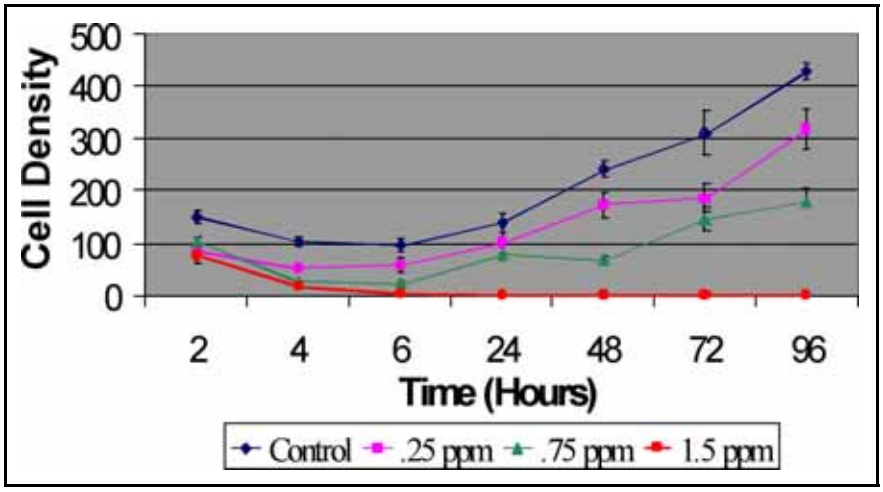


Figure 2. *The effects of SeaKleen® on Glenodinium foliaceum.*

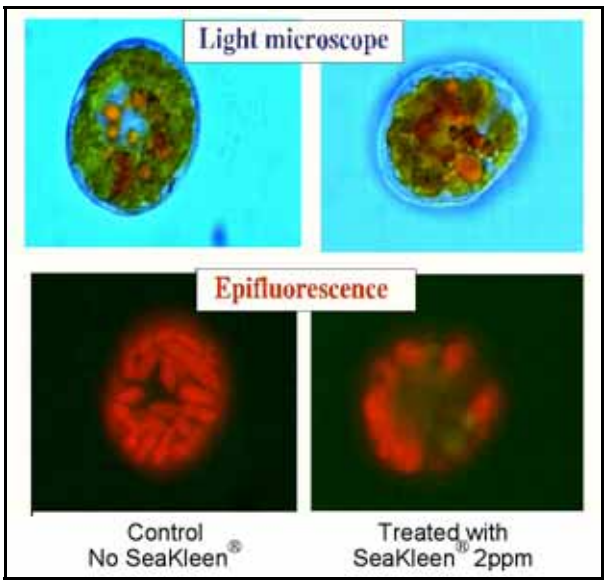


Figure 3. *Glenodinium foliaceum cysts 2 hours after exposure to SeaKleen®.*

Peraclean® Ocean – A potentially environmentally friendly and effective treatment option for ballast water

R. Fuchs & I. de Wilde

Degussa AG, Germany
rainer-g.fuchs@degussa.com

Introduction

The transfer of human pathogens and the introduction of non-indigenous species through the ballast water of ships has been recognized as a significant problem. The introduction can result in tremendous costs and may impose a threat on local ecosystems. Globally, approximately 3 billion tons of ballast water are transported per year. Various treatment options for ballast water have been suggested (Gollasch, 1997).

Chemical and environmentally friendly treatment with Peraclean® Ocean is one method to effectively remove unwanted organisms and pathogens in ballast water. This paper summarizes the laboratory results of a partially funded and already finished research project and covers experimental results of a shipboard test. It provides details on the efficacy and toxicological properties of Peraclean® Ocean.

Name of project

Testing of Peraclean® Ocean as a chemical ballast water treatment option has been part of a research project in Germany (1998 – 2001), that was funded by the industry (Degussa AG) and the German Federal Ministery of Education and Research (BMBF) with the title 'Process for the removal of organisms from different waters[1].

Properties of Peraclean® Ocean

Peraclean® Ocean is a liquid biocide formulation based on peroxygen chemistry. One active component in the formulation Peraclean® Ocean is peracetic acid (PAA). PAA- containing formulations are widely used in the food and beverage industry as well as in sewage treatment plants and other water treatment processes. They are widely used in the treatment of cooling water and as a pre-treatment of biologically contaminated waters prior to discharge into the environment. PAA is accepted in the USA as a secondary and indirect food additive at concentrations up to 100 mg/l.

Peraclean® Ocean is a fast-acting oxidizing biocide effective against a broad spectrum of micro-organisms: bacteria, spores, yeasts and moulds, protozoa, algae and viruses (Block, 1991; Schliesser, & Wiest, 1979; Baldry, 1983). Peroxyacetic acid products are effective over a wide range of conditions. Peraclean® Ocean is most active at pH values of 5-7 but also displays good activity even under mildly alkaline conditions up to pH 9. Peraclean® Ocean remains effective even at temperatures of 4°C and below. The microbial activity of peroxyacetic acid based products is relatively unaffected by organic matter, compared to other oxidising biocides (Block, 1991).

The shelf-life of Peraclean® Ocean is more than 1 year, and: more than 90% of the original activity is still present after one year`s storage at room temperature. Peraclean® Ocean is commercially available

[1] This publication is based on the results of a research project funded and supported by the Ministry for Research and Technology of Germany under registration number 02/WA9912. The authors are solely responsible for the content of this publication.

in 220-kg drums, 1 m^3-IBC or in 20-m^3 bulk containers. Peraclean® Ocean is readily biodegradable according to OECD Screening Test 301 E guidelines.

Peraclean® Ocean does not persist in the environment and breaks down into innocuous degradation products, being acetic acid, water and oxygen:

$$CH_3CO_3H + H_2O \rightarrow CH_3CO_2H + H_2O_2$$
$$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O$$

The hydrolysis products of Peraclean® Ocean are also readily biodegradable.

The half-life of Peraclean® Ocean amounts to minutes to hours in seawater, depending on pH value, salinity and temperature. In fresh water, the half-life of Peraclean® Ocean is 2-24 hours. Enhanced decomposition of Peraclean® Ocean may occur in contact with sediments.

Efficacy tests – laboratory tests

Several studies showed that many organisms from different trophic levels can be found in ballast water tanks. For that reason the efficacy testing of a chemical treatment should include organisms from more than one trophic level (Voigt, 1999).

For a first evaluation of the performance of Peraclean® Ocean, the *Artemia* Testing Standard (ATS) was applied. This benchmark test uses the brine shrimp, *Artemia salina,* as indicator organism. The ATS involves 4 different development stages of the brine shrimp: adults, larvae, nauplius-stages, pre-incubated eggs and cysts. The results of the benchmark tests are summarized in Table 1.

Table 1. *Results of Peraclean® Ocean on different development stages of the brine shrimp,* Artemia salina*; Values in brackets represent the highest mortality reached at the end of the experiment.*

Testorganism Brine shrimp, *Artemia salina*	Parameter observed	Concentration of Peraclean® Ocean (ppm)	Max. Hatching Rate after 72 hrs	Time (hrs.) needed to reach 100% mortality
Cycts[1]	Hatching rate	350	3%	
	Survival of	700	0%	
	hatched Nauplii	1 400	0%	
Pre-incubated Eggs[2]	Hatching rate	350	9%	
	Survival of	700	0%	
	hatched Nauplii	1 400	0%	
Nauplii	Mortality	350		(97%; 72 h)
		700		36
		1 400		8
Adults	Mortality	350		(38%; 72 h)
		700		12
		1 400		8

1 = untreated control group: 52 +/- 8,4%
2 = untreated control group: 47,4 +/- 2,2%.

The ATS data showed that the addition of Peraclean® Ocean at levels of above 350 ppm resulted in 100% mortality of all *Artemia* live stages. The pH of the treated seawater is slightly reduced from pH 8.2 to 6.1, due to the acidic properties of Peraclean® Ocean.

After the initial tests, further experiments were carried out with a number of indicator organisms. The experimental designs applied included different salinities and temperatures. In each case, the experimental conditions represented optimum environmental conditions for the test species.

Experiments with nauplii of the brine shrimp, *Artemia salina*, indicated, that only 400 ppm Peraclean® Ocean is required to reach 100% mortality under varying environmental conditions (Tab. 2).

Table 2. *Experiments with Peraclean® Ocean in different water qualities. Test organism: nauplii of brine shrimp (*Artemia salina*). Values represent average of 3 parallel experiments. Note: Observations were made after 1, 2, 4, 8, 12, 24, 36, 48 and 72 hours.*

Testorganism Brine shrimp, *Artemia salina*	**Water Quality**	**Parameter observed**	**Concentration of Peraclean® Ocean (ppm)**	**Time (hrs.) needed to reach 100% mortality**
(Nauplii)	Salinity 13.5ppt Temp. 24°C	Mortality	400 800 1 200	16 8 4
(Nauplii)	Salinity 13.5ppt Temp. 32°C	Mortality	400 800 1 200	11 4 4
(Nauplii)	Salinity 31ppt Temp. 24°C	Mortality	400 800 1 200	36 19 5
(Nauplii)	Salinity 31ppt Temp. 32°C	Mortality	400 800 1 200	24 7 4

ppt= parts per thousand

Experiments with fertilized eggs of Atlantic herring (*Clupea harengus*) followed. The eggs were pre-incubated in clean water for one week to assure an undisturbed start of the larval development. In this case too, 400 ppm were sufficient to reach 100% mortality of the embryos. Concentrations as low as 200 ppm also resulted in high mortalities above 98%, with the lowest killing rate (98.3%) being observed under marine conditions (salinity = 31 ppt) and temperatures of 12°C (Tab. 3).

Table 3. *Experiments with Peraclean® Ocean in different water qualities. Testorganism: pre-incubated eggs of Atlantic Herring (*Clupea harengus*). Values represent average of 3 parallel experiments. Note: Observations were made after 1, 2, 4, 8, 12, 24, 36, 48 and 72 hours. Values in brackets represent the highest mortality reached at the end of the experiment.*

Test organism Fertilised eggs of Atlantic Herring *Clupea harengus*	**Water Quality**	**Parameter observed**	**Concentration of Peraclean® Ocean (ppm)**	**Time (hrs.) needed to reach 100% Mortality**
Pre-incubated eggs	Salinity 13.5ppt Temp. 5°C	Mortality of embryo	200 400 800	16 8 2
Pre-incubated eggs	Salinity 13.5ppt Temp. 12°C	Mortality of embryo	200 400 800	15 3 1
Pre-incubated eggs	Salinity 31ppt Temp. 5°C	Mortality of embryo	200 400 800	12 4 1
Pre-incubated eggs	Salinity 31ppt Temp. 12°C	Mortality of embryo	200 400 800	(98.3%; 72 h) 1 1

Organisms of the zooplankton showed even higher sensitivities. The dosing of only 400 ppm Peraclean® Ocean resulted nearly instantly in 100% mortality of the test organisms. After a maximum of 2 hours exposure time, all of the organisms were dead (see Tab. 4).

Table 4. *Experiments with Peraclean® Ocean with plankton organisms. Testorganisms: crustaceans from freshwater and brackish water communities. Values represent average of 3 parallel experiments.*

Testorganism	Water Quality	Parameter observed	Concentration of Peraclean® Ocean (ppm)	Time (hrs.) needed to reach 100% mortality
Freshwater Plankton (Cultures)	Freshwater, room temperature	Mortality	200	2
Cyclops sp. (Copepod)			400	1
			800	1
Bosmina sp. (Cladocera)	Freshwater, room	Mortality	200	1
	Temperature		400	1
			800	1
Daphnia sp. (Cladocera)	Freshwater, room	Mortality	200	-
	Temperature		400	2
			800	2
In situ Plankton Baltic Sea (wild catch)	Brackish water, about 13 ppt Sal.	Mortality		
Copepods (30% of taxa)	room temperature		400	< 1
			800	< 1
Nauplii (66% of taxa)		Mortality	400	< 1
			800	< 1
Cladocera (4% of taxa)		Mortality	400	1
			800	< 1

Experiments with phytoplankton cultures (indicator organism: *Chlorella* sp.) showed similar results: even 200 ppm Peraclean® Ocean killed the algae within 48 hours (See Table 5). However, higher concentrations of Peraclean® Ocean (concentration range from 400 ppm to 1600 ppm) did not result in significantly faster eradication of the algae.

Table 5. *Experiments with algae. Testorganism: Chlorella sp.. Parameter: photometric measurement of extinction at 3 different wave lengths: 750 nm, 663 nm and 645 nm. The following results represent the average of three parallel experiments each.*

Testorganism	Water quality	Parameter observed	Concentration of Peraclean® Ocean (ppm)	Time needed to reach 100% mortality
Chlorella sp.	Salinity: 31 ppt room temperature	Chlorophyll a and b	200	48
			400	48
			800	48
			1 200	48
			1 600	48

Efficacy tests – ship board trial

A ship board trial was organized from Maritime Solutions Inc. at the harbour of Baltimore, USA. On the vessel "CAPE MAY", a ship with roughly 30,000 dwt and 10,000 tons ballast water capacity. A field trial was done during summer 2001.

50 – 400 ppm of Peraclean® Ocean without any pre-separation of organisms or solids was dosed into ballast water (water out of the harbour of Baltimore) that went into the ship`s ballast tanks and into plastic containers. See Table 6.

Peraclean® Ocean effectively killed:

- Copepod Adults, Copepod Nauplii and Nematodes at 50 ppm Peraclean® Ocean concentration
- Polychaetes, Bivalves, Rotifiers and Nematodes at 100 ppm Peraclean® Ocean concentration
- Ostracods and Protozoans at 200 ppm Peraclean® Ocean concentration.

Table 6. *Ship board trials: treatment with Peraclean® Ocean, without any pre-separation of species or solids*

Testorganism	Mortality of untreated control group[a)] [%]	Mortality [%] of treated groups in different tanks		Applied Concentration of Peraclean® Ocean [ppm]	Exposure Time [hours]	100 % kill.
		Plastic tank (Mesocosm tank)	Ship`s Ballast Tank			
Copepod Adults	3-42	**100**	98	**50**	24	
	6-40	**100**	**100**	**50**	48	**X**
Copepod Nauplii	3-68	**100**	**100**	**50**	24	**X**
Polychaetes	0-3	**100**	20	**50**	24	
	0-3	**100**	25	**50**	48	
		100	**100**	**100**	24	**X**
Bivalves	7-42	**100**	0-100	**50**	24	
	15-26	**100**	50	**50**	48	
		100	**100**	**100**	24	**X**
Rotifiers	0-100	**100**	**100**	**50**	24	
	18-71	**100**	89	**50**	48	
		100	**100**	**100**	24	**X**
Nematodes	0-NF [a)]	NF [a)]	**0**	**50**	24	
	0-NF	NF	NF [a)]	**50**	48	
		NF	**100**	**100**	24	**X**
		NF	NF	**100**	48	
Ostracods	0-12	NF	**0**	**50**	24	
		NF	0-50	**50**	48	
	0-11	0		**100**	24	
		NF		**100**	48	
		100	90	**200**	24	
		NF	**100**	**200**	48	**X**
		100	**100**	**400**	24	**X**
Protozoans	40-84	**100**	**100**	**50**	24	
	70-95	**100**	40	**50**	48	
		100	99	**100**	24	
		100	94	**100**	48	
		NF	**100**	**200**	24	**X**
		NF	**100**	**200**	48	**X**

(a) Values of different control groups; highest and lowest numbers are given.
(b) NF = not found.

Conclusions

The results of all the experiments indicate that Peraclean® Ocean is potentially an effective biocide for the treatment of ship`s ballast water. 100% mortality of different test organisms from different trophic levels were found at Peraclean® Ocean concentrations between 50 ppm and 400 ppm.

The short half-life of Peraclean® Ocean in seawater indicates that even the discharge of great quantities of ballast water in sheltered areas with limited water exchange (e.g. harbours and bays) may not have a negative impact on the environment. Furthermore, the physical properties of Peraclean® Ocean (easy storage and long shelf-life) favour both, on board and land based ballast water treatments as a stand-alone method, or in combination with filtration and/or gravity separation.

A lower dosage of Peraclean® Ocean could be sufficient if a separation of solids and bigger organisms takes place before Peraclean® Ocean is applied.

References

Baldry, M.G.C. 1983. The bactericidal, fungicidal and sporicidal properties of hydrogen peroxide and peracetic acid. *J. Appl. Bact*. 54, pp. 417-423.

Block, S.S. 1991. *Disinfection, sterilization, and preservation*. 4th ed., Chapter 9, peroxygen compounds. Lea & Felbinger, Philadelphia PA, pp. 167-181.

Gollasch, S. 1997. *Removal of barriers to the effective implementation of ballast water control and management measures in developing countries.* Desk study carried out for GEF/IMO/UNDP, 187 pp.

See also:

Grenman, D., Mullen, K., Parmar, S. & Friese C. 1997. *Ballast water treatment systems: A feasibility study*. 61 pp.

From the internet: http:/www.ansc.purdue.edu/signis/publicat/papers/.

Schliesser, T.H. & Wiest, J.M. 1979. Catalase-mediated redox reactions. In: Doyer PB (ed) *The Enzymes vol XIII Oxydation-Reduction Part C* 3rd ed. Academic press, New York NY, pp. 389-395.

Voigt, M. 1999. *Treatment Methods for Ballast Water*. 2nd Annual Conference "Managing environmental risks in the maritime industry", London, 30 Sept-1 Oct 1999.

Acrolein as a potential treatment alternative for control of microorganisms in ballast tanks: five day sea trial

J. E. Penkala, M. Law & J. Cowan

Baker Petrolite Corporation
USA
Joseph.Penkala@BakerPetrolite.com

Abstract

Ballast water discharge by marine vessels at destination ports poses serious health, economical and ecological repercussions due to the introduction of non-indigenous nuisance organisms into new environments. Current attempts to mitigate this problem via ballast water exchange programs have been marginally effective (75% removal of organisms at best) and restricted by ship safety limits. An alternative chemical strategy being investigated is acrolein, a broad spectrum biocide with proven efficacy against bacteria, algae, and other microorganisms. Extensive toxicity testing has demonstrated its effectiveness against macroorganisms as well, including molluscs, crustaceans, fish, and aquatic plants. Recent laboratory studies demonstrated that 1-3 ppm of acrolein can effectively control various marine microorganisms.

Based on these findings, a sea trial was conducted on board an 8000 MT DWT container vessel during a 5 day voyage from Venezuela to Florida. Dedicated ballast tanks were treated with 1, 3, 9, or 15 ppm of acrolein during ballast intake in Venezuela. Monitoring of viable bacteria and acrolein residuals was conducted prior to treating, daily during the voyage, and during discharge. When applied at treatment concentrations of 9 ppm, acrolein maintained 99.99% efficacy for 2 days. At 15 ppm, acrolein was shown to be 99.9999% effective for 3 days as compared to untreated ballast tanks. En route monitoring confirmed that regrowth of microorganisms was minimized when the acrolein residual was maintained at $\geq$2 ppm. At the time of discharge, the acrolein residuals were zero ppm, a consequence of its reaction with water, thus allowing its safe discharge overboard. These findings indicate that the use of acrolein can be an effective treatment strategy which can be managed safely, can be safely discharged into the marine environment, and can be economical in the control of organisms in ballast water.

Introduction

Biopollution via ballast water uptake and discharge

The introduction of invasive marine species into non-native environments via ballast water discharge by marine vessels poses a serious threat in the form of biopollution (Shipley, et al., 1995; Fuller et al., 1999). Shipping transfers approximately 3 to 5 billion tons of ballast water internationally each year and possibly a similar volume domestically within countries and regions (NRC, 1996). Ballast water provides an essential function in the transport of cargo by ships in maintaining stability and efficiency. At the same time it serves as a vector for the transfer of non-indigenous organisms, resulting in a potential threat to the ecology, economics, and even health of a particular region.

It is estimated that globally at least 7,000 different species are being ferried in the ballast tanks NRC, 1996). However, the majority of these species do not survive during transit due to the trauma of ballasting and deballasting, the incompatibility with the ballast tank environment, and inability to adapt to the new environment upon discharge. Occasionally, however, a species is able to survive these conditions and establish a reproductive population in the host environment. In that case, the consequences can be devastating.

There are several key examples of the impact of aquatic invasive species on the host environment. In the USA, the European Zebra Mussel *Dreissena polymorpha* has infested over 40% of the internal waterways (Nalepa and Schloesser, 1993). It is estimated that between 1989 and 2000 approximately $750 million to $1 billion was spent on control measures. In southern Australia, the Asian kelp *Undaria pinnatifida* is invading new areas rapidly, displacing the native seabed communities (Pughuic, 2002). In the Black Sea, the filter-feeding North American jellyfish *Mnemiopsis leidyi* has proliferated and in some cases reached densities of 1kg of biomass/m^2 (Gollasch, 1998)) It has decimated native plankton stocks thereby seriously impacting the Black Sea commercial fisheries. In several countries, the 'red tide' algae (toxic dinoflagellates) have been introduced. This type of algae is responsible for fish kills and when absorbed by filter-feeding shellfish can cause paralysis and even death in humans who consume the shellfish.

In Texas, it is widely suspected that the brown mussel, *Perna perna*, which invaded rocky intertidal surfaces in South Texas, originated from ballast water discharge in the Port Aransas area (McGrath et al., 1998; Hicks et al., 2000, 2001). Two mussels were found in 1990 at Port Aransas. Within 3 years they had spread nearly 100 miles south and 50 miles north of Port Aransas. It is estimated that the Galveston Bay System currently has at least 10 introduced species of fish, most of which originated in subtropical or tropical environs (Fuller et al., 1999). More recently, an invasive species of encrusting tunicate, identified as *Didemnum perlucidum*, has been found covering active petroleum production platforms as well as decommissioned platforms being used as artificial reefs offshore Galveston (Harper, 2002, personal communication). Because the epicenter of the tunicate invasion appears to be very near shipping lanes, it is suspected that ballast water is the source of this tunicate.

Recently, the pathogen responsible for cholera (*Vibrio cholerae*) has been detected in various ports, including Chesapeake Bay, off the coast of Mobile, Alabama and the Galveston, Texas (EPA, 2000; DePaulo et al. 1992; McCarthy et al., 1992). Certain strains have been tracked to Latin American port waters. It has been determined that one third of the ballast discharge in these Gulf Coast regions contain *V. cholerae*.

The examples of nuisance invasive species are numerous and these present serious problems to the health, economy, and/or ecology of a locale. It is imminent that effective control measures be implemented to mitigate this threat of biopollution.

Treatment options

The only method currently available to reduce the risk of transfer of harmful aquatic organisms is ballast water exchange at sea. This method is being recommended by the International Maritime Organization (IMO) in their pending guidelines on ballast water management (Pughuic, 2002; Gollasch, 1998). But the protocol is subject to serious ship safety limits and even when fully implemented, this technique is at most 75% effective. Some reports suggest that reballasting at sea may itself contribute to the wider dispersal of harmful species, and that island states located 'down-stream' of mid-ocean reballasting areas may be at particular risk from this practice.

It is therefore important that alternative, effective ballast water management and/or treatment methods are developed as soon as possible, to replace reballasting at sea.

Options being considered include: 1) mechanical treatment methods such as filtration and separation, 2) physical treatment methods such as sterilization by ozone, ultra-violet light, deoxygenation, electric currents and heat treatment, and 3) chemical treatment methods such as adding biocides to ballast water to kill organisms.

Although research efforts are being focused on developing such methods, there are certain difficulties being encountered in 1) accommodating the dynamics of the ballasting schedules, 2) customizing to the ships' ballast system and operations, 3) effectively treating ballast tanks which have a great deal of internal structures and contain sediment that harbors and protects the resident organisms, and 4) expanding the treatment program from lab scale to a magnitude that can deal with the large quantities of ballast water carried by ships such as tankers. Ultimately, a successful treatment must be

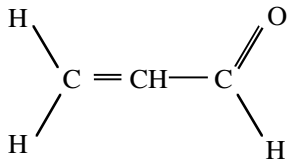
biologically effective, economically feasible, safe to ship personnel, environmentally acceptable, and simple to implement.

Acrolein technology

We have been investigating the use of acrolein, an organic biocide, as a treatment option for ballast water. Marketed by Baker Petrolite Corporation as MAGNACIDE® B Microbiocide, acrolein is used extensively in the oilfield as a biocide to mitigate bacteria in produced fluids. It is a wide spectrum biocide that is extremely effective against aerobic microorganisms as well as sulfate reducing bacteria. In addition this chemical is also marketed as MAGNACIDE® H Herbicide, which is widely used in irrigation canals throughout the world as an aquatic herbicide to control submerged plants and algae that can impede water flow.

Acrolein is a small 3-carbon molecule that is highly reactive chemically. The molecule is

a vinyl aldehyde and the reactivity is due to its carbon-carbon double bond conjugated with the double bond of an aldehyde carbonyl.



Acrolein
2-Propenal

The biocidal efficacy of acrolein at low dosages appears to stem from its ability to inhibit several enzyme systems within the living cell and the denaturing of proteins. This high degree of activity at low concentrations makes it a very good candidate for the ballast water treatment program.

As a ballast tank treatment alternative, acrolein exhibits several key advantages. It is an extremely potent biocide against not only bacteria, but algae, mollusks, crustaceans, fish, and aquatic plants. Laboratory studies have shown an effective concentration of 1-3 ppm when tested against marine microorganisms (results reported in this paper). At the same time, acrolein has a relatively short half life, 8-24 hours, in water due to a hydration reaction. The reaction products rapidly break down into carbon dioxide (CO_2) and water. Acrolein can be easily neutralized by reaction with ammonium bisulfite or soda ash. In addition, acrolein can be safely applied by injecting directly into the ballast line during ballast tank filling. The application involves no major capital expenditure for equipment or installation. Furthermore, this product is non-corrosive and compatible with the common epoxy-based linings used in ballast tanks (Mills, 2002, personal communication). These features render acrolein as a highly effective and economic treatment option that can be safely applied, is relatively inexpensive, and due to rapid degradation poses no threat to the marine environment during discharge.

Aim of study

In the current study, the authors undertook to investigate the efficacy of acrolein as a potential ballast water treatment alternative. To accomplish this, a compilation was made of toxicity data evaluating the impact of acrolein on a range of freshwater and marine aquatic macroorganisms. The results indicated the biocidal efficacy of acrolein is achieved at a low (<1 ppm) concentration. The second phase of the study involved laboratory experiments examining the biocidal efficacy of acrolein against marine microorganisms under conditions mimicking exposure time in ballast tanks during a voyage. It was determined that a concentration of 3 ppm would effectively control all species tested. In the third and final phase of this study, a sea trial was conducted using acrolein for ballast treatment on board an 8000 MT DWT container vessel. Nine ballast tanks were tested with acrolein concentrations ranging from 0 to 15 ppm. The ballast water was treated inline during ballast uptake by injecting the chemical at the suction side of the ballast pumps. Comprehensive monitoring of chemical residual and viable

microorganisms was conducted on the water during uptake and discharge and daily during the voyage. The results are described in the following report.

Laboratory studies

Efficacy of acrolein against aquatic organisms

As an initial step in evaluating the efficacy of acrolein for control of aquatic organisms in ballast tanks, a review was made of the existing toxicity and environmental tests conducted to date on this product over a range of various aquatic species. These aquatic toxicity tests were standard flow-through tests determining the LC_{50} or EC_{50} for organisms that included molluscs, crustaceans, fish, and aquatic plants. Both marine and freshwater organisms had been tested. The compiled data are presented in Table 1. The greatest sensitivity to acrolein was observed with freshwater fish and daphnia: 0.022-0.024 ppm. The aquatic plants, including diatoms, green and blue green algae ranged from 0.034 ppm for the marine diatom (*Skeletonema costatum*) to 0.072 ppm for duckweed (*Lemna gibba*). The highest tolerance was detected in the marine invertebrates and fish, ranging from 0.180 ppm for the eastern oyster to 0.570 ppm for the sheepshead minnow.

Table 1. *Toxicity of acrolein to various aquatic organisms*

Organism Tested	Test	Acrolein Concentration (ppm)
Marine Mollusk: Eastern Oyster (*Crassostrea virginica*)	96-hr EC50	0.180
Marine Crustacean: Mysid Shrimp (*Mysidopsis bahia*)	96-hr EC50	0.500
Marine Fish: Sheepshead Minnow (*Cyprinodon variegates*)	96-hr EC50	0.570
Freshwater Fish: Rainbow Trout (*Oncorhynchus mykiss*)	96-hr EC50	0.024
Freshwater: Bluegill Sunfish (*Lepomis macrochirus*)	96-hr EC50	0.024
Freshwater Crustacean: Water flea (*Daphnia magna*)	48-hr LC50	0.022
Duckweed (*Lemna gibba*)	14-day EC50	0.072
Green Algae (*Selenastrum capriconutum*)	5-day EC50	0.050
Freshwater Diatom (*Navicula pellicosa*)	5-day EC50	0.068
Bluegreen Algae (*Anabaena flos-aquae*)	5-day EC50	0.042
Marine Diatom (*Skeletonema costatum*)	5-day EC50	0.034

These data indicated that acrolein has the potential as an effective treatment for ballast water organisms in low effective concentrations such that the treatment would be economical and the chemical could be neutralized by the end of the voyage via its hydration reaction with water, rendering it safe for discharge.

Efficacy of acrolein against marine microorganisms

Next a series of experiments were conducted to evaluate the efficacy of acrolein against common marine microorganisms. The first experiment tested the response of four common marine bacterial strains to acrolein: 1) *Pseudomonas fluorescens*, a Gram negative, non-sporulating bacterium, 2) *Bacillus cereus* a Gram positive, spore-forming bacteria, 3) *Bacillus subtilis*, a Gram positive, spore-forming bacteria, and 4) *Staphylococcus epidermidis*, a Gram positive, non-sporulating bacterium. Each isolate was streaked and revived on nutrient agar, then transferred to nutrient broth and maintained until the time of the efficacy test. The culture conditions were 3.5% total dissolved solids (TDS) and 30°C incubation temperature. Acrolein was tested at 0, 1, 3, and 10 ppm for contact times of 24 and 72 hours to mimic conditions of a short voyage. Following the contact time, a serial dilution was made into nutrient both to enumerate the number of surviving bacteria. The results (Figure 1) indicate that significant reductions in bacterial number occurred at all acrolein concentrations tested. The control organisms (0 ppm) exhibited at least 10^6 bacteria per ml for all strains tested. At 10 ppm acrolein no greater than 10^1 bacterial per ml were observed for any strain at either 24 or 72 hours

contact (>99.999% reduction). At 3 ppm acrolein, no greater than 10^2 bacteria per ml were detected (>99.99% reduction).

In a second experiment, heterogeneous cultures of general aerobic and facultative anaerobic bacteria (GAB) and sulfate reducing bacteria (SRB) obtained from seawater in the Gulf of Mexico at Galveston, Texas were tested to model populations that might be encountered in port water used for ballast. Cultures were maintained in modified formulations of phenol red dextrose (for GAB) and Postgate's broth (for SRB) at ambient temperatures (17-23°C) at 3.5% TDS. The test conditions were identical to those in the first experiment: 0, 1, 3, and 10 ppm of acrolein and 24 and 72 hour contact times. Enumeration was performed by serial dilution into the appropriate culture media. The results (Figure 1) show no detectable growth of GAB or SRB at 10 ppm of acrolein, an 11 order of magnitude reduction. At 3 ppm acrolein limited SRB growth to 10^2/ml at 24 hour contact and to below detection with 72 hour contact compared to 10^{11}/ml in the controls. At 3 ppm, GAB growth was limited to 10^3/ml after 24 hours contact and 10^1/ml after 72 hours contact compared to 10^{11}/ml in the controls. These results show that acrolein is effective at 3 and 10 ppm for control of microorganisms in Galveston Port water.

A third experiment was conducted using the marine dinoflagellate, *Gymnodinium sanguineum*, the red tide former associated with fish and jellyfish mortality. The dinoflagellate was cultured in L1 medium at ambient temperature (17-23°C) under a 12L/12D photoperiod. For the efficacy test, the cells were transferred to filter-sterilized Galveston seawater and appropriate concentrations of acrolein (0, 1, 3, and 10 ppm) were added for 24 and 72 hours contact. Surviving dinoflagellates were enumerated by serial dilution into L1 media. In addition, light microscopy observations were made on the diluted organisms to verify motility and viability. These results are presented in Table 2 and Figure 2.

Table 2. *Efficacy of acrolein against the marine dinoflagellate Gymnodinium sanguineum*

Acrolein Concentration (ppm)	24 hour Contact Time			72 Hour Contact Time		
	Mean No. Organism/mL	% Reduction from Control	Structurally Inact Motile Cells?	Mean No. Organism/mL	% Reduction from Control	Structurally Inact Motile Cells?
0	10^5	-	Yes	10^4	-	Yes
1	BD	≥99.999	No	BD	≥99.999	No
2	BD	≥99.999	No	BD	≥99.999	No
10	BD	≥99.999	No	BD	≥99.999	No

The results indicate that all concentrations of acrolein were able to reduce the concentration of viable dinoflagellates to below the detectable limit of the assay. No viable or motile dinoflagellates were observed in any of the acrolein-treated samples. The integrity of the dinoflagellate cell was completely destroyed by the treatment with acrolein as seen in Figure 2.

On-board ballast trial

Overview of sea trial

Based on toxicity data and laboratory studies presented in the previous sections, it was concluded that acrolein would be a good candidate for chemical control of ballast water. The information was presented to shipping companies and an opportunity for a test voyage was obtained. The sea trial was undertaken aboard an 8000 MT DWT container vessel sailing from Guanta, Venezuela to Panama City, Florida. The trial took place from November 4-10, 2002. Ballast uptake, pre-treatment sampling and chemical treatment were conducted the evening of November 4. The ship set sail the morning of November 5. Ballast discharge and post-treatment sampling took place on the evening of November 9 at 100 miles offshore Panama City, Florida. This discharge procedure was conducted in accordance with the US Coast Guard. The ship arrived at the destination port on November 10.

Ballast system, chemical application, and sampling protocol

Ten ballast tanks were selected (5 pairs) so that discharge and some of the tank filling could be done on parallel tanks. The ballast system and treatment design are illustrated in Figure 3. The ballast water enters the ship via a single line and then passes through a 5 mm mesh filter. It then separates into two parallel lines each feeding a charge pump. The normal operating rate of each pump is 250 m^3/hour. The line pressure was approximately 15 psi. The two lines then converge downstream of the pumps to a common line that transports ballast water to the parallel ballast tanks.

The application and sampling points were set up on each of the parallel lines feeding the charge pumps. Acrolein was injected into the line on the suction side of one pump and water samples were obtained on the parallel line on the discharge side of the second pump. In that way, acrolein treatment and sampling could be carried out simultaneously. Both the acrolein cylinder and the sample drum were placed on the weather deck, and chemical/sample lines were run down to the ballast room via an escape hatch. This facilitated operations and optimized both safety (the acrolein could be stored topside, secluded from all personnel) and convenience (once the sample water was filtered for collection of the target organisms, it could be dumped over the side of the ship). The acrolein was delivered from a 58 lb (net weight) cylinder via a standardized BPC manifold using nitrogen pressure. Chemical volumes were metered using a Sponsler digital flowmeter at a rate to achieve maximum chemical injection time during ballast tank filling. Injection rates varied between 114 ml/min and 280 ml/min. The minimum metering rate for the flowmeter was reported to be 40 ml/min although only 80-90 ml/min at best was achievable during the test. Each ballast tank was filled to capacity with tank volumes ranging from 125 to 340 m^3. The tanks were confirmed to be at full capacity by detecting the level at the sounding tubes. Ballast water injection rates averaged 200 m^3/hr. For accurate monitoring of sample volume, sample collection was conducted using an industrial hose fitted with a Great Plains Industry (GPI) flowmeter (maximum flow rate of 20 gal/min).

Untreated control tanks were filled first in order to ensure that the ballasting operation, flow rates and sampling were proceeding properly. The first treated tank (Wing Tank #1 - Port) received 3 ppm (v/v) of acrolein. The parallel starboard tank (Wing Tank #1 – Starboard) received 1 ppm of acrolein. After measuring residuals in these tanks using differential pulse polarography (DPP; see Appendix for description of this method) it was determined that the acrolein in these two tanks had been immediately consumed as no residual was detectable. Therefore adjustments were made and subsequent tanks were treated with 15 ppm acrolein (Double Bottom #2 Port and Double Bottom #2 Starboard) and 9 ppm of acrolein (Double Bottom #1 Port and Double Bottom #1 Starboard).

On the evening of November 9, ballast discharge and then reballasting were conducted. At the time of discharge, the chemical residuals in the treated tanks were below the 10 ppb detection limit of the DPP. Sampling was conducted for acrolein residuals and microbiological specimens during discharge. However, additional planned tests were aborted due to the presence of a severe tropical storm.

It should be noted that this study was originally designed to also obtain data on a) ballast sediment, b) ballast tank residual water before filling, and c) macroorganisms, including ichthyoplankton, zooplankton, and phytoplankton. However, due to logistical complications with the ship's schedule and inclement weather during discharge, these studies could not be completed during this sea trial. Therefore, the partial data on macroorganisms will not be included. Preparations are being made for a more comprehensive analysis on a second voyage which is currently being planned.

Analysis of microorganisms and acrolein residuals

Water samples were collected by delivery topside via a $^1/_2$ inch industrial hose. Three 100 ml samples were obtained in triplicate during the filling operation of the ballast tanks approximately 15 minutes apart. These samples were immediately diluted into culture bottles and parallel samples were fixed for microscopy. This procedure was used during ballast uptake as well as discharge. The discharge operation was a reverse of the ballast tank filling, using the same sample port and line. One tank was omitted during this procedure (Double Bottom #3 Starboard). This was one of the four untreated tanks

and was not sampled in order to save time, since the ship had to remain stationary (engines off) during this procedure.

During the voyage, each of the test ballast tanks were sampled daily via the sounding tubes, using a siphon tube with hand-operated pump. The siphon tube was attached to a plumb line to deliver it near the bottom of the ballast tank. Each tank was sampled in triplicate and tested for acrolein residuals and bacterial cultures.

A detailed description of the bacterial enumeration methods and measurement of chemical residuals is included in the Appendix at the end of this report.

Results of sea trial

Physical data on Port Guanta Water used for ballast uptake

At the time of ballast uptake, the water in port was calm, the sky was 100% overcast with a wind at 5 kph and an air temperature of 28.3°C. The port water exhibited a dark green color. Vertical visibility through the water column was estimated at 1.3 m whereas total water depth was 11.1m

Hydrographic data are shown in Table 3. There was a 2.5°C decrease from surface to bottom and a 1.3 ppm decrease in dissolved oxygen from surface to bottom.

Table 3. *Hydrographic characteristics of water column in Port Guanta, Venezuela prior to ballast uptake*

	Depth in Water Column		
Parameter	**1.0m**	**5.5m**	**10.9m**
Temperature (°C)	27.73	25.59	25.21
Conductivity	48.70	49.20	49.30
Salinity (ppt)	31.90	32.20	32.30
Dissolved Oxygen (ppm)	5.15	3.56	3.81

Results of bacterial monitoring

General aerobic and facultative anaerobic bacteria (GAB) were monitored by serial dilution into the appropriate culture medium. As seen in Table 4, The GAB concentrations in the ballast uptake samples ranged from 4-5 $\log_{10}$ GAB/ml for each of the 10 tanks. The average concentration for all samples collected was 4.3 x 10^4 GAB/ml. These concentrations are within the range of what is typically encountered in seawater samples (unpublished observations).

Table 4. *Average Log_{10} Number of GAB/ml in Ballast Water*

Ballast Tank	Applied Concentration of Acrolein (ppm)	4-5 Nov	6-Nov	7-Nov	8-Nov	9-Nov	10-Nov
		Uptake					Discharge
DB#3 Port	Control	5.00	8.00	8.00	12.00	12.00	12.00
DB#3 Star	Control	5.00	8.00	8.00	12.00	12.00	12.00
DB#4 Port	Control	4.00	8.00	8.00	12.00	12.00	12.00
DB#4 Star	Control	4.00	8.00	8.00	12.00	12.00	12.00
DB#5 Star	1 ppm	5.00	8.00	8.00	12.00	12.00	12.00
DB#5 Port	3 ppm	4.00	8.00	8.00	12.00	12.00	12.00
DB#1 Port	9 ppm	4.00	6.33	7.00	12.00	12.00	12.00
DB#1 Star	9 ppm	4.00	6.00	7.67	12.00	12.00	12.00
DB#2 Port	15 ppm	4.00	1.00	2.67	11.33	11.67	12.00
DB#2 Star	15 ppm	4.00	1.67	2.33	11.67	12.00	11.67

In the four control tanks, the GAB numbers increased dramatically from 10^4 to 10^8 GAB/ml within 24 hours to 36 hours (November 6th) after filling the tanks (Table 4). On November 7th, 48 hours after filling the tanks, the same concentration was encountered in all control samples. It is important to note that on November 6th and 7th, only an 8 $\log_{10}$ serial dilution was used, not anticipating growth beyond this limit. However, the maximum number of bottles had turned positive, so that the concentration measured was at least 10^8 GAB/ml, possibly more. For subsequent sampling on November 8th -10th (72 hours to 120 hours) a 12-bottle serial dilution was used. For each of the subsequent time points, samples collected from the control tanks showed positive cultures in all 12 bottles, indicating that the GAB concentrations tanks were greater than or equal to 10^{12}/mL.

In Wing Tanks #5 Port and Starboard, treatments of 3 ppm and 1 ppm of acrolein were used, respectively. The GAB concentrations were the same as reported for the untreated tanks described above (Table 4). On November 6th and 7th, the GAB concentrations were greater than or equal to 10^8 GAB/ml. On November 8th-10th, the GAB concentrations were greater than or equal to 10^{12} GAB/ml. Therefore, it can be concluded that the acrolein treatment applied had no impact on the concentration of GAB in these tanks. This finding is not surprising, since chemical monitoring revealed no residual acrolein in the tanks immediately after treatment (See Results of Acrolein Residual Monitoring and Figure 6).

The Double Bottom Tanks #1 Port and Starboard were both treated with 9 ppm acrolein. On November 6th, a reduction in GAB concentration to approximately 10^6 GAB/ml was achieved as compared to the control tanks (Table 4 and Figure 4). However, this still represented a 2 $\log_{10}$ increase over the intake water. Since approximately 10% of the tank volume remained following discharge and prior to uptake and chemical treatment, it is presumed that bacteria in this residual ballast water contributed to the rapid increase in GAB seen the day after filling. On November 7th, the GAB concentration had increased to approximately 10^7 GAB/ml. This was still less than the controls but steadily increasing as the acrolein residuals decreased to less than 1 ppm.

The Double Bottom Tanks #2 Port and Starboard were each treated with 15 ppm acrolein. On November 6th, the GAB had decreased to well below the concentration in the uptake water: less than 10^2 GAB/ml (Table 4 and Figure 5). This represents an approximate 99.9% reduction of the bacteria in the uptake water. Furthermore, this represents greater than 99.9999% decrease in GAB compared to the untreated tanks. On the November 7th, the GAB concentration was slightly greater than 10^4 GAB/ml, approximately the same concentration as seen in the uptake water. However, this represents a greater than 99.99% GAB reduction as compared to the untreated tanks.

Sulfate reducing bacteria (SRB) were enumerated in the water samples by serial dilution into appropriate culture medium. No SRB were observed in the port water during uptake to fill the ballast tanks.

On November 6th (24 – 36 hours) only Double Bottom Tank #3 Starboard (control) showed positive cultures of SRB (Table 5). Until November 8th (72 hours), no SRB were detected in any of the treated tanks. At this time point, three tanks, one control, one at 1 ppm, and one at 15 ppm were positive for SRB. The maximum number of SRB detected (10^2/mL) was observed in Double Bottom Tank #3 Starboard. At the time of ballast discharge (November 10th), seven of the nine tanks discharged for the test contained SRB. Concentrations ranged up to 10^3 SRB/ml in Double Bottom Tank #2 Starboard (15 ppm).

The contamination by SRB may be due to residual populations that have become established in the tanks over time.

Table 5. *Average Log_{10} Number of SRB/ml in Ballast Water*

Ballast Tank	Applied Concentration of Acrolein (ppm)	4-5 Nov	6-Nov	7-Nov	8-Nov	9-Nov	10-Nov
		Uptake					Discharge
DB#3 Port	Control	NT	0.00	0.00	0.00	0.00	1.00
DB#3 Star	Control	NT	1.67	0.00	2.00	0.00	X
DB#4 Port	Control	NT	0.00	0.00	0.00	0.00	0.67
DB#4 Star	Control	NT	0.00	0.00	0.00	0.00	1.67
DB#5 Star	1	NT	0.00	0.00	0.33	2.00	2.00
DB#5 Port	3	NT	0.00	0.00	0.00	0.00	0.00
DB#1 Port	9	NT	0.00	0.00	0.00	0.00	2.00
DB#1 Star	9	NT	0.00	0.00	0.00	0.00	0.00
DB#2 Port	15	NT	0.00	0.00	0.00	0.33	0.67
DB#2 Star	15	NT	0.00	0.00	1.33	1.67	3.00

Results of acrolein residual monitoring

Immediately after filling the tanks, residuals were measured in the sounding tubes for two of the ballast tanks, those targeted for 1 ppm, 3 ppm acrolein. No residual was detected in either the 1 ppm or 3 ppm tanks (Figure 6). Accurate sampling of the port and starboard tanks targeted for 9 and 15 ppm acrolein was not possible due to ballasting operations, deck activity, and the schedule of getting underway.

On November 6th (24 hours) the Double Bottom Tanks #1 Port and Starboard (9 ppm) exhibited a residual of 0.5 ppm and 2.5 ppm, respectively. By November 7th (48 hours), the residuals in both tanks were less than 1 ppm and analysis on November 8th showed residuals less than 0.3 ppm. No residuals were detected in either tank on November 9th (96 hours).

Double Bottom Tanks #2 Port and Starboard (15 ppm) exhibited acrolein concentrations of 4 ppm at the 24 hour time point (November 6th), 2 ppm to 3 ppm on November 7th and less than 0.5 ppm on November 8th. On November 9th (96 hours) no residual was detected in these tanks.

Discussion

Persistence of acrolein residuals in ballast tanks during sea trial

The design for treatment of the water in the ballast tanks of the ship was for 1 ppm and 3 ppm treatments. These treatment concentrations were chosen based on a series of laboratory efficacy studies conducted on bacteria cultured from Galveston seawater and bacteria and dinoflagellates obtained from various culture suppliers as well as historical toxicity testing conducted against mollusks and other aquatic organisms. In addition, the proposed treatment concentrations would limit the need for neutralization of acrolein prior to discharge due to the hydration of acrolein during a 4-5 day voyage.

During treatment of the tanks, it was discovered that immediately following treatment at 1 ppm and 3 ppm, no residual was detected. This was confirmed with samples taken approximately 30 hours later. Furthermore, tanks treated with 9 ppm had substantially decreased concentrations (less than or equal to 2.5 ppm) within 24 hours. Finally, the tanks treated with 15 ppm of acrolein also had decreased within 24 hours to only 4 ppm. This degradation rate of acrolein is quite rapid. Typically in oilfield produced waters and canal irrigation waters we have observed half-life ranges from 8-24 hours depending on the water being treated. In laboratory studies comparing artificial brine to Galveston Port water we observed half-lives ranging from 20-25 hours for concentrations of 1, 5, and 10 ppm acrolein. A test of water collected from another Venezuelan port (Puerto Cabello) showed an average half-life of half-life of 52 hours for acrolein concentrations ranging from 1-10 ppm. Thus in this study

the rate of degradation was much steeper, indicating components in the ballast water and tanks contributed to this.

Bacterial control appeared to be immediately diminished in all tanks once the acrolein concentration decreased below 0.5 ppm. Unfortunately, all tanks were below this concentration threshold by November 8th, 48 hours before termination of the project and discharge of the ballast tanks. Based on these findings, a higher concentration of acrolein, possibly 25 ppm or 50 ppm should be considered in future tests.

In future studies it would be best to pre-test the water for acrolein demand and check various parameters such as sulfides and pH in the residual water left in the ballast tanks as well as the uptake water prior to initiating treatment. Although the current study had been designed to examine these parameters, logistical considerations and shipboard operations interrupted this part of the study.

Several factors have been identified as potentially imposing an unexpected demand on acrolein in the treated tanks. Although SRB were not detected in the uptake water, they were cultured from the tanks while en route to Florida. Sulfate reducing bacteria produce soluble sulfide as a result of their respiration process. Acrolein is highly reactive with sulfides and is consumed at a 2:1 molar ratio (3.7 ppm acrolein: 1 ppm sulfide). It is presumed that the SRB recovered were established in the 10% residual water left in each tank prior to treatment. If any soluble sulfide was in this residual water, it would have quickly reacted with acrolein resulting in decreased residuals. Another source of demand on the acrolein may have been organics, solids and other bacteria resident in the residual water and sediment in the tank bottoms. Unfortunately, we did not have the option to examine the tanks for sediments, bacteria or sulfides before treatment. This information might have given a more complete picture of those factors contributing to acrolein demand.

The ideal treatment concentration cannot be predicted from this study. It is a balance between having a sufficiently high concentration of acrolein to maintain adequate control of marine organisms and ensure an adequate residual throughout the voyage while having the concentration low enough so that the application is economical and neutralization/ discharge issues are minimized. Based on this study, a suggested concentration range for acrolein treatment during a 5 day voyage might be 15 to 50 ppm.

Efficacy of acrolein treatment in control of bacteria in ballast tanks

Bacterial control is believed to be the most rigorous test of efficacy of biocide treatment in the ballast tanks. They are the most adaptive organisms, with highly evolved protective mechanisms. Their very short life cycle, as little as 20 minutes in some cases, allows for rapid proliferation. Their sessile communities in tank sediments and biofilms represent a difficult challenge for any biocide. In essence, they are the toughest organisms to control.

Although the GAB levels in the port water during ballast filling were 10^4 to 10^5 GAB/ml, within 24-36 hrs the concentrations in the controls, 1 ppm and 3 ppm-treated tanks were greater than or equal to 10^8/mL using a 8 bottle dilution series. This may have been due to rapid growth within the tank environment or it might have been due to a high initial concentration of GAB in the residual water residing in the tanks prior to filling. Given that the estimated residual water in each tank was 1/10 of the total volume, had it contained 10^9 bacteria/ml, then a 10-fold dilution with incoming ballast water would only reduce this population to 10^8/mL. The concentrations of bacteria in the residual water of the tanks are fairly important and should be accounted for prior to treatment. Not only that, but any sediment or sludge in the tanks which most likely contain sessile bacterial populations could also significantly impact the initial concentration in the tanks once they are filled. In the future, it is important to obtain data on the final concentration of bacteria in the tanks immediately after filling.

Acrolein at 15 ppm had a significant impact on the bacterial load in the tanks as compared to the controls. This comparison is the more critical one when determining efficacy of biocide, not the comparison with intake water. If one uses this comparison, then 24 hours after treatment with 15 ppm acrolein the bacterial levels were reduced by at least 6 $\log_{10}$ units or greater than 99.9999%. The

residual at that time was approximately 4.0 ppm. On the following day (48 hours), when the residual had decreased to approximately 2 ppm, there was still at least a 6 $\log_{10}$ reduction in the number of bacteria in the tank.

Acrolein applied at 9 ppm had a lesser impact on the bacterial load in the tanks as compared to the controls. However, it is important to review what the actual biocide residual is at the time the readings are being made. After 24 hours, the residual was 0.5 ppm in the Port tank and 3 ppm in the Starboard tank. The bacterial load at this time point had been reduced by at least 2 $\log_{10}$ units as compared to the control, or 99% reduction. However, since the dilution limit had been exceeded in the control tanks, the maximum reduction at this time point could not be obtained. Not having data on the initial load in the tanks limits our conclusions. Bacterial control in the 9 ppm-treated tanks becomes further reduced as the residual decreases. In all cases, the tanks no longer exhibited substantial bacterial control after the third day, assuming the untreated tanks had concentrations no more than 10^{12} GAB/ml (the maximum detection limit for this test).

The other class of bacteria examined was sulfate reducing bacteria (SRB). These organisms reduce sulfate to sulfide during respiration. They are also notorious for their involvement in microbiologically influenced corrosion (MIC), which is a concern in ballast tanks. Although none of these organisms were detected in the port water used to fill the tanks, their growth was detected in the tanks, presumably due to SRB resident in the residual water and sediments in the tanks. By the end of the voyage, 7 out of 9 tanks had established planktonic populations of SRB, up to 1000 SRB/ml. These planktonic populations only became established as the acrolein residuals had become negligible and bacterial control was lost.

One advantage to acrolein technology is that it works well against sessile bacteria and SRB. If SRB are becoming established in the tanks of a ship, then the tank integrity is under threat from MIC. Acrolein is non-corrosive and compatible with common ballast tank coatings (Mills, 2002). Therefore, it is well suited for mitigation of MIC.

Proposed strategy for future sea trial

At this time a second sea trial is being secured. The objectives of the follow-up sea trial will include:

- To test acrolein at treatment concentrations of 15-50 ppm. This will insure a minimal $\geq$ 2 ppm residual during the voyage and minimize the potential for bacterial regrowth before the destination port is reached. Measures will be taken to determine the acrolein demand prior to application and the residual in all the tanks will be measured immediately after filling
- To premonitor tanks before filling. This should include bacterial analysis of the residual water in the tanks and an analysis of tank sediments. This should also include measurement of sulfide levels, pH, and dissolved oxygen.
- To conduct a comprehensive analysis of macro-organisms as well as microorganisms. This will include studies on zooplankton, phytoplankton, and ichthyoplankton. It will also include analysis of certain indicator microorganisms such as *Pseudomonas fluorescens*, *Vibrio cholera*, etc.
- To conduct a side by side comparison of the acrolein treatment with ballast water exchange on the same voyage.

Conclusions

- Acrolein at a concentration of 15 ppm was required to have a significant impact on bacteria present in the ballast tanks after filling the tanks. A concentration of 9 ppm, exhibited a lesser degree of effectiveness. Whereas, 1 and 3 ppm acrolein was ineffective.

- Bacteria populations in the control tanks and those tanks treated with <9 ppm increased from 4-5 $\log_{10}$ to greater than or equal to 8 $\log_{10}$ within 24 hours. This extended to greater than or equal to 12 $\log_{10}$ after 72 hours.
- At 15 ppm, acrolein controlled the bacteria for at least 48 hours, but regrowth occurred by 72 hours as the acrolein residual had diminished below 0.5 ppm. It is estimated that a minimum residual of ≥ 2 ppm would be required to maintain control. It is suggested that future studies test a concentration range of 15-50 ppm acrolein for a voyage of comparable duration in order to maintain this minimal residual and prevent the possibility for regrowth.
- The demand for acrolein in the ballast tanks is high, much higher than what was predicted from laboratory testing. Applied concentrations of 1 and 3 ppm were immediately undetectable by the time the tanks had been filled.
- SRB were present in 7 of the 9 ballast tanks tested at the end of the voyage (1-3 $\log_{10}$/mL), although none were present in the seawater that was used to fill the tanks. These organisms are key players in MIC of ballast tanks and ballast lines and also produce the hazardous and explosive gas hydrogen sulfide.
- Overall, the results were encouraging. A very high level of control was maintained by 15 ppm of acrolein, especially given the high concentrations of bacteria observed in the untreated tanks. This study supports the feasibility of acrolein as an alternative ballast water treatment method by showing its potential for high efficacy, safe and simple installation and application, economic viability, and potential for safe discharge.

References

DePaulo, A, Capers, G.M., Motes, M.L., Olsvik, O., Fields, P.I., Wells, J. et al. 1992. Isolation of Latin American epidemic strain of *Vibrio cholera* O1 from US Gulf Coast. *Lancet* 339: p. 624.

Fuller, P.L., Nico, L.G., & Williams, J.D. 1999. *Nonindigenous fishes introduced into inland waters of the United States*. American Fisheries Society, Special Publication 27, Bethesda, Maryland.

Gollasch, S. 1998. *Removal of Barriers to the Effective Implementation of Ballast Water Control and Management Measures in Developing Countries*. Report prepared for the IMO MEPC Ballast Water Working Group. 32 pp. IMO MEPC 41, April 1998.

Hicks, D.W., Hawkins, D.L., & McMahon, R.F. 2000. Salinity tolerance of brown mussel *Perna perna* (L.) from the Gulf of Mexico: an extension of life table analysis to estimate median survival time in the presence of regressor variables. *Journal of Shellfish Research* 19(1): pp. 203-212.

Hicks, D.W., Tunnell, J.W, Jr., & McMahon, R.F. 2001. Population dynamics of the nonindigenous brown mussel, *Perna perna* (L.), in the Gulf of Mexico compared to other world-wide populations. *Marine Ecology-Progress Series* 211: pp. 181-192.

Harper, D. 2002. Texas A&M University Galveston, Personal Communication.

Invasive Species Focus Team, Gulf of Mexico Program. 2000. *An Initial Survey of Aquatic Invasive Species Issues in the Gulf of Mexico*.

McCarthy SA, McPhearson RM, Guarino AM & Gaines JL 1992. Toxigenic *Vibrio cholera* O1 and cargo ships entering Gulf of Mexico. *Lancet* 339: pp. 624-625.

McGrath, M., Hyde, L., & Tunnell, J.W., Jr. 1998. *Occurrence and Distribution of the Invasive Brown Mussel, Perna perna in Texas Coastal Waters*, Center for Coastal Studies. Texas A&M University-Corpus Christi, March 1998. GBNEP-49.

Mills, G. 2002. George Mills & Associates International, Inc., Personal Communication.

Nalepa, T.F. & Schloesser (eds). 1993. Ze*bra Mussels: Biology, Impacts and Control. Boca Raton, Florida*. Lewis Publishers, Inc.

National Research Council. 1996. *Stemming the Tide: Controlling Introductions of Nonindigenous Species by Ships' Ballast Water*. National Academy Press, Washington D.C.

Pughuic, D. 2003. *Ballast Water Management and Control: An Overview. 2001*. International Maritime Organization Publication.

Shipley, F.S., Keilsing, R., Prince, K.A., Bentson, M. A., Lane, W.G., Belk, J.O., & Eemisse, J. 1995. *The Galveston Bay Plan*. The Galveston Bay National Estuary Program.

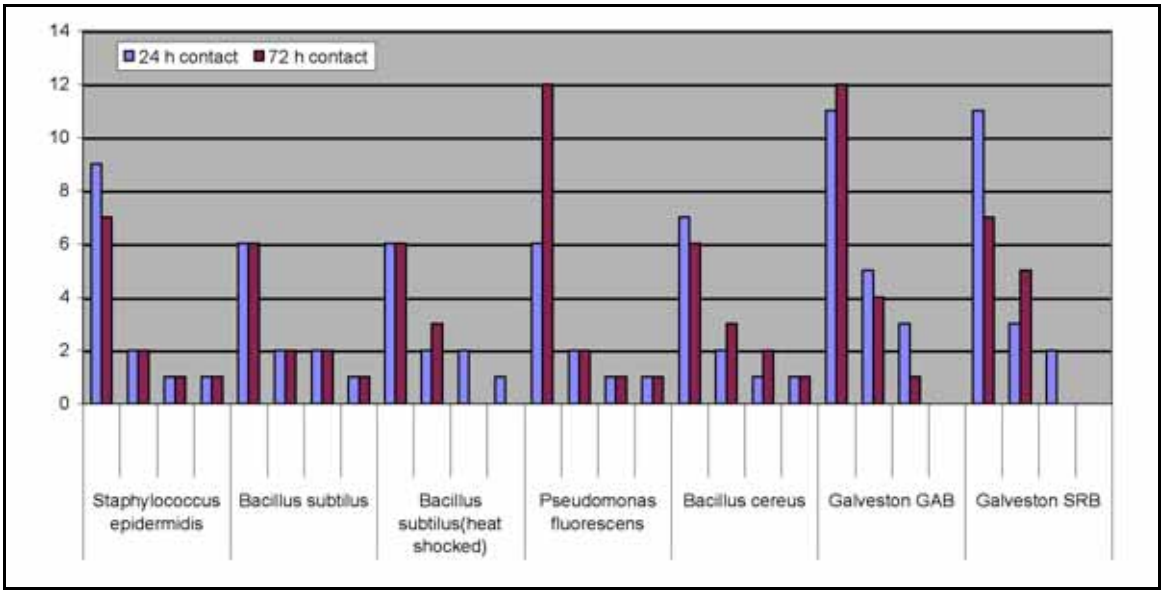


Figure 1. *Laboratory studies: acrolein efficacy vs. marine microorganisms.*

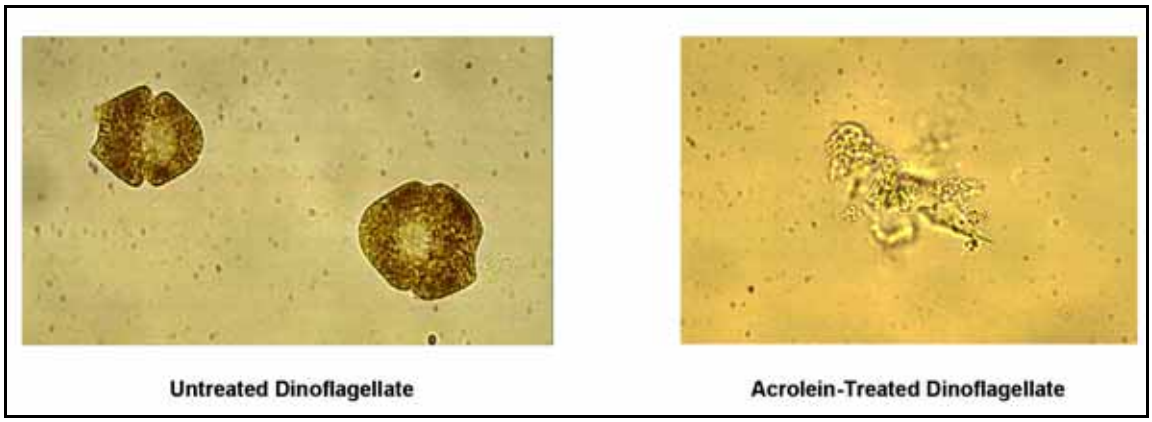


Figure 2. *Effect of acrolein treatment on physical integrity of marine dinoflagellate. Bright field microscopy: 400 X magnification.*

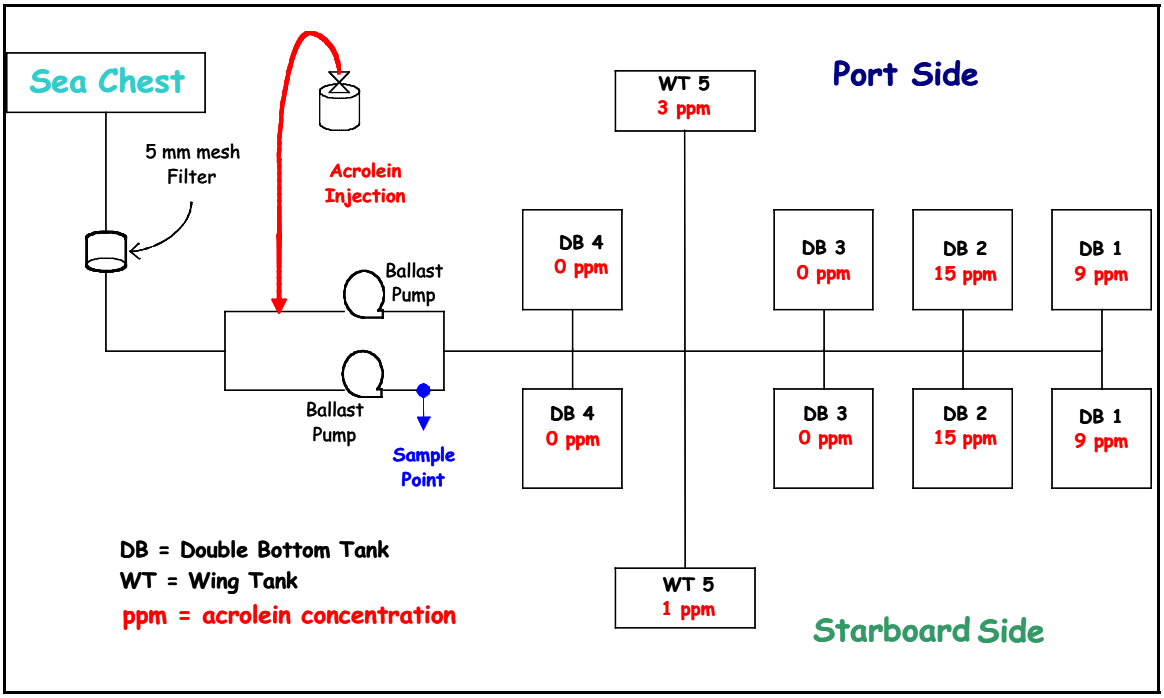


Figure 3. *Intermarine Industrial Century: ballast line schematic.*

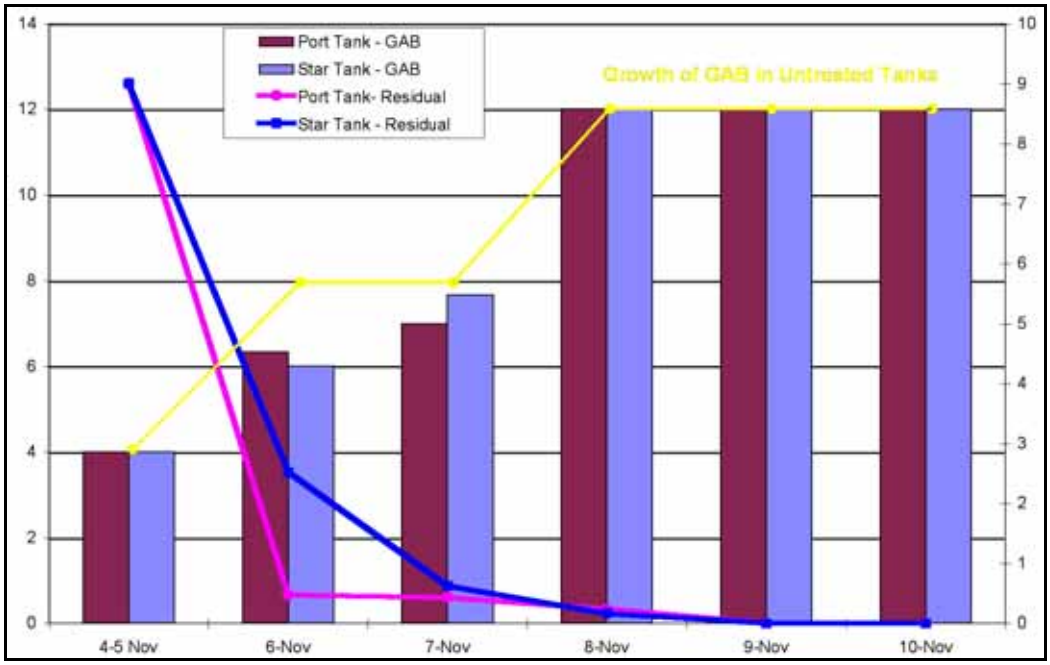


Figure 4. *Acrolein residual versus GAB concentration in tanks treated at 9 ppm.*

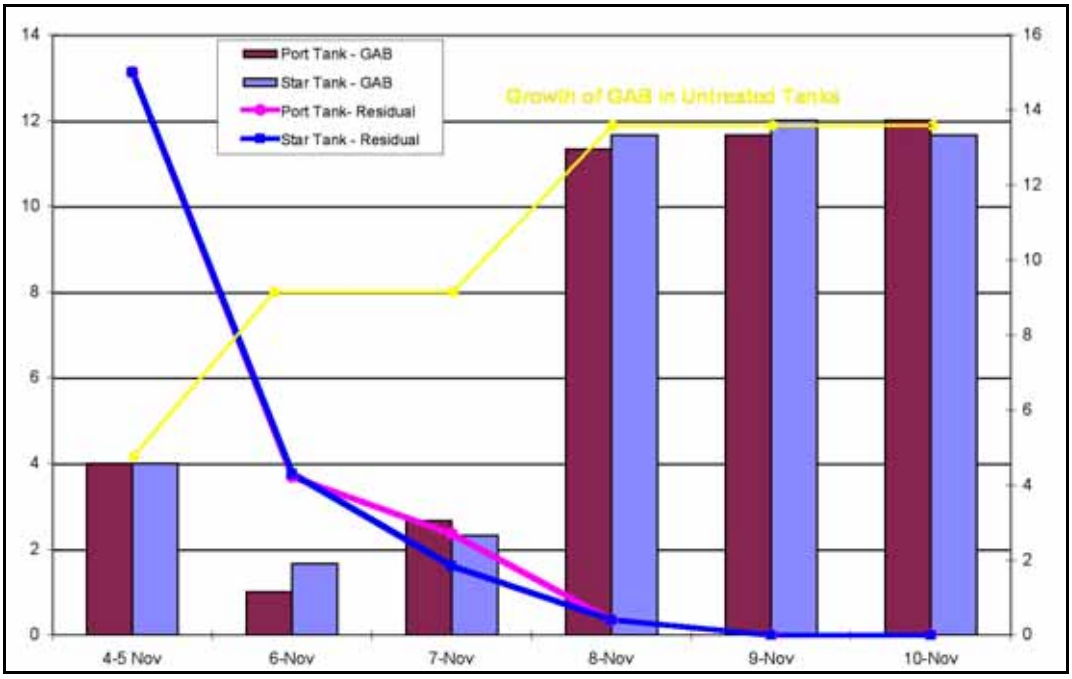


Figure 5. *Acrolein residual versus GAB concentration in tanks treated at 15 ppm.*

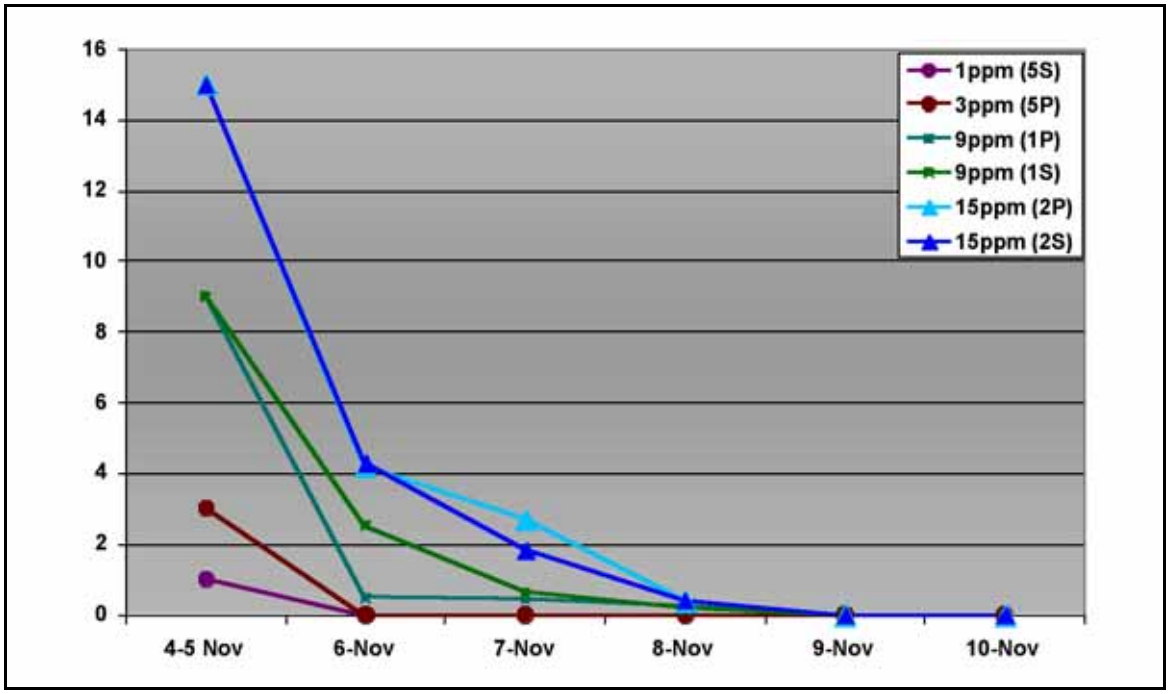


Figure 6. *Intermarine – Industrial Century BW test: acrolein residual profile.*

Appendix

Methods

Serial dilution cultures for bacterial enumeration

Immediately following collection, the water samples were prepared for semi-quantitative enumeration of viable SRB and viable GAB using the serial dilution technique. Samples were diluted into 3.5% TDS modified Postgate's SRB media and 3.5% TDS modified aerobic phenol red dextrose media for GAB growth (C&S Laboratories, Inc. Broken Arrow, OK). Serial dilutions were performed according to the NACE Standard Test Method 0194-94 *Field Monitoring of Bacterial Growth in Oilfield Systems*. The serially diluted culture vials were then incubated at 28°C for 28 days at which time the $\log_{10}$ number of bacterial growth for each sample was recorded.

Measurement of acrolein residuals

The most sensitive and accurate field method to date for determining acrolein residuals is differential pulse polarography (DPP). This method employs an EG&G PARC Model 394 electrochemical trace analyzer connected to an EG&G PARC Model 303A static mercury drop electrode (SMDE).

DPP analysis allows for the determination of a trace chemical, in this case acrolein, which can be electrochemically oxidized or reduced (in this case, reduced) in a sample. A potential is applied to a sample via a conductive electrode. The potential, which serves as the driving force in the experiment, is scanned over a region of interest. When measuring acrolein residuals, all samples are scanned from an initial potential of -0.9 V to a final potential of -1.5 V. At a potential of approximately -1.2 V the acrolein in solution is reduced, producing a current at the working mercury electrode. The magnitude of current produced is proportional to the concentration of acrolein in the solution.

Prior to monitoring acrolein residuals, a standard curve was generated using acrolein standards of 1.0, 5.0, 10.0, and 25.0 ppm. Analysis of each standard was initiated by energizing the solenoid of the SMDE. The solenoid allows for the flow of mercury through the capillary of the Model 303A electrode forming a mercury drop that acts as an electrode with a renewable surface. Measurements of current are performed on these drops. Uninterrupted flow of mercury is established prior to running the samples to ensure the removal of air bubbles from the capillary. The current is sampled twice over the life of each drop; the first sample is taken just before the modulation pulse is applied, the second just before the pulse ends. The modulation pulse is a staircase ramp that is applied to the sample cell with a fixed height modulation pulse superimposed on the ramp just before each drop is dislodged. Each step of the drop lasts one second, and each has a magnitude of 2 mV. The two current measurements are compared, and the change in current becomes the processed signal. The signal is plotted as the inverse of the current ($1/\mu A$) versus the electron potential over voltage (E/V) resulting in a peak with amplitude proportional to the concentration of acrolein in solution. The peak heights obtained for these samples were used to generate a standard curve and had a correlation coefficient (R^2) of 0.993 using the least squares method.

Session 4:
Multiple Technologies and Combined Systems

Solution to ballast water pollution: ship shape and the ports escape?

E. Donkers

Port of Rotterdam
The Netherlands
e.donkers@portofrotterdam.com

Introduction

With this paper and accompanying presentation, the Port of Rotterdam explains its view on on-board treatment and management versus on-shore treatment of ballast water. Next to that, this paper aims to further outline the possible role of the Port of Rotterdam and other ports view to tackle this problem.

Helicopter-view Port of Rotterdam

With 30,000 ships calling every year and a cargo throughput of some 320 million tonnes, the Port of Rotterdam is one of the biggest ports in the world. Rotterdam is Europe's most important port for oil & chemicals, containers, iron ore, coal, food and metals. The port and industrial area covers 10,500 hectares (26,000 acres), stretching out over an area of 40 kilometers, from the center of the city to the North Sea (see figure 1).

Consequently, significant volumes of ballast water are transported in and out of the port area. It has been calculated that around 6 million and 60 million tonnes are respectively imported to and exported from this Port (Aquasense, 1998). This vast amount of exported ballast water can be explained by the high number of oil tankers that arrive with cargo, and leave free of cargo, “in ballast”.

Regional context

Within the port water basin, with “De Nieuwe Waterweg” as its main waterway, powerful tidal currents take place. Regardless of the distance to the sea, in the entire port there is a strong influence of fresh water as well as sea water movements.

In Dutch coastal and port waters, only around 15 species can be regarded as non-indigenous, and this number for the Dutch North Sea is estimated to be 44 (Aquasense, 1998). On the entire North Sea Area, the estimated number of introduced alien species is 108 (North Sea Foundation, 2001). From these total numbers, there are various “vectors” of introduction, besides ships’ ballast water also bio-fouling on ships’ hulls and aquaculture.

From the studies that are currently available, it can be concluded that no significant negative ecological or economic effects have taken place yet in the Dutch coastal waters and the Dutch part of the North Sea, because of introduction of alien species by shipping. The question is whether this is because this water area is relatively less vulnerable for alien introductions, either we are dealing with an “ecological time bomb”. Another question is if “the open character” of the Rotterdam Port Basin decreases the opportunities for non-native species to be introduced in the port area or upstream. A more enclosed port area like San Francisco is known for its massive number of introductions (once every 14 weeks between 1961 and 1995, Pew Oceans Commission 2001), contrary to the estimated low numbers in Rotterdam.

The forthcoming IMO Convention

Most likely, an IMO convention for the control of harmful introductions of aquatic organisms by ships' ballast water discharges will enter into force within a few years. The Port of Rotterdam, and many other ports, are of the opinion that the solution to prevent alien invasions from ballast water must be found on board of ships. "Ship Shape" should be the starting point, to tackle this problem at the source. Swift technical development and upgrading must ensure that effective on-board ballast water treatment techniques (BWTTs) are developed, without causing unacceptable adverse environmental effects or safety hazards.

Given the fact that the development and broad use of BWTTs will take quite some years, ballast water exchange (BWE) will be an allowed interim-option in years to come. In the currently circulating text of the IMO Convention, the possibility for land-based treatment is left open, primarily for "Certain" or "Special Areas". The Port of Rotterdam has serious concerns about a strong focus on land-based treatment. First of all, it is important to highlight the developments on the ship side.

Ship side developments

During its involvement in the EU funded assessment-project "SEAM"[1], the Port of Rotterdam has monitored the development on various on board ballast water management techniques. Primarily techniques that combine hydrocyclone with a secondary treatment such as UV radiation seem to be promising and get broad stakeholder support. Also, heat and filtering prove to be viable options. These signals are reflected in the recent placement of an installation based on hydrocyclone with UV after-treatment on two vessels of Dutch ship-owner "Wagenborg", as well as the cruise vessel "Regal Princess". For broader application, bottleneck appears to be the flow rate of the incoming ballast water of the hydrocyclone. Because of this, application of this technique is currently restricted to relatively small vessels. Pilot-scale testing and upgrading to bigger flow rates is crucial to make such techniques suitable for larger vessels such as oil tankers. Technical research and pilot-testing aimed to increase flow rates is taking place continuously, primarily in the United States.

Besides physical and UV treatment, there is also a possibility to use chemicals. Chemical treatment, often used in combination with hydrocyclone pre-treatment, may cause serious chemical pollution of port or sea water. Pollution of port water with ballast water cleaning effluents could have significant negative environmental impacts. If chemicals such as acids are discharged into port waters, it could by lowering the pH, increase the amount of "free" heavy metals in the environment. Consequently, the sludge that is dredged from the port area might become more polluted, in Rotterdam possibly leading to more sludge that has to be discharged in "De Slufter", a big basin for polluted dredged material. Also, soluble metals are known to accumulate in the ecosystem and food chain. Some chemically treated ballast water might also contain chlorine and bromine, which also have potential negative effects on water and dredged material quality.

It is, however, too premature to exclude chemicals from the "tool-box" of on-board ballast water management techniques. Additional research needs to be done to decide whether the use of chemicals could be allowed in certain cases. Besides determining hazard profiles, it is crucial to know the freights (amounts) and frequency of ballast water discharges, to determine the environmental impact. Besides this, the principle question is whether the risk of release of alien species is more or less serious than the discharge of certain chemicals.

Apart from treatment, ballast water exchange (BWE) is an often used option to decrease the amount of invasive species in ballast tanks. Some BWE-techniques, such as the sequential method, have potential ship safety hazards, some seem to be acceptable. Because of existing ballast water regulations in the US, Canada and Australia, BWE has been applied by a large number of ships for many years.

[1] Assessing concepts, systems and tools for a Safer, Efficient and Environmentally Aware and Friendly Maritime Transport.

For the future IMO legal instrument, it is crucial that the "Tool Box" of safe ballast water management options on board is flexible, provided that they comply with performance standards for effectiveness and do not cause unacceptable adverse environmental effects. Another important principle is, that the Convention must give a clear signal to the maritime industry about how and where the problem of alien species introduction by ballast water must be tackled.

With various on-board ballast water management options available and technical progress still developing, it can be stated that a ship directed approach is feasible.

Port side developments

In Certain Areas, the current IMO Convention text states that additional measures such as the provision of port reception facilities can be prescribed. At first, it must be said that the possibility of declaring "more stringent measures" in a certain area is a right that every state has under the United Nations Law of the Sea (UNCLOS). Therefore, with the IMO Convention serving as "baseline requirements", countries are free to design stricter regulations. The Port of Rotterdam is of the opinion that there are more possible measures than port reception facilities. Other possible measures include mandatory BWE prior to port entry or mandatory use of a treatment technique before entering a certain port or sea area. Apart from the basic right of very country to design more stringent measures, the measures itself must be decided on depending on local circumstances.

For the sake of practicality, the Port of Rotterdam has executed a short desk study to visualise and assess the operational, technical and economical implications of the creation of Port Reception Facilities. The following main conclusions can be drawn.

Historical context

The provision of adequate and sufficient Port Reception Facilities (PRFs) has been a global debate for over 20 years. Marpol obligates every state that has ratified the Convention to create and maintain PRF's for oily, chemical and solid waste (garbage, hazardous and cargo-associated waste). For oily and solid waste however, no total ban on discharge in the sea has been established, neither mandatory delivery of waste at a PRF. Also, the inspection regime of the mandatory Oil Record Book has been insufficient.

While some ports and countries still struggle to provide PRFs, within the Port of Rotterdam there have been facilities for twenty years now. Because the lack of a "mandatory use policy", an in adequate inspection regime and high costs, a very low number of ships use the facilities. For ship-generated waste (bilgewater, sludge and garbage) the percentage of ships that use a PRF have fluctuated between 3 and 7 % over the last five years. Fortunately, the European Directive 2000/59 on Port Waste Reception Facilities on Ship-Generated Waste and Cargo Residues is likely to improve this situation. The Directive prescribes indirect financing, mandatory discharge ashore and the design of port waste management plans. The latter must ensure an improvement of the provided service level by PRFs.

However, before the mentioned directive will be implemented, two major Reception Facilities for sludge and bilge water in the Rotterdam Port Area have suffered a financial loss up to 10 million € a year over the years of 2001 and 2002. During 2002, the Rotterdam Port Management was forced to buy out one of these companies and entirely redevelop its site, costing many efforts and financial means. It goes without saying that the Port of Rotterdam does not strive to repeat this scenario.

If the provision of sufficient and adequate ballast water PRFs are made mandatory under the "Special Area" approach in the Ballast Water Convention, this will be also be without any mandatory requirement to use those facilities. This is the same approach that has been followed in the above mentioned Marpol Convention, which obliges ports to provide sufficient and adequate facilities, without any guarantee that they will be used.

Volumes of ballast water to be treated

In view of the high volume of ballast water influx (6 million tonnes annually, Aquasense, 1998), this could mean 0.5 million tonnes per month that has to be treated on shore. This will result in a considerable amount of storage tanks that have to placed on-shore. Apart from storage tanks, also tank space must be available to clean and process this water. If the processed ballast water must be re-used on board, even more tank space is needed for the "clean ballast" to be pumped back into vessels. Adding the space demand resulting from storage, processing and possibly re-use, this might lead to around 10 tanks of 116,000 m^3 (= capacity of one tank at the Maasvlakte Oil Terminal see photo 1). If the ballast water is stored in a basin, this likely also consumes a significant amount of space. This vast space-demand will be very hard to allocate on for example container-terminals (see photo 2).

Per ship, the amount of ballast water varies from 10 to 30 % of DWT. This can lead to from around 10,000 or tonnes (container vessels) up to more than 100,000 tonnes (VLCC's). Apart from the large volumes, the amount ballast tanks can be numerous as well as the location and variation of inlet points. This is likely to result in the need for numerous on shore-connected pipelines as well as barges and vessels. The size of these barges will be far bigger than an average bilge oil vessel. A flexible and expensive infrastructure will be needed to transfer these considerable amounts of collected ballast water to on-shore installations. Besides this, ships continuously aim to decrease the turn around time in port. The strong wish for "zero undue delay" for the shipping industry view to the use of oily and garbage waste facilities will without any doubt re-occur at this debate.

The on shore treatment process

A short desk- and literature study has provided more insight in the needed technical means to treat large amounts of ballast water on shore. The following assumptions were made:

- The treatment process must be able to meet the performance standards for treatment techniques, that is a rate of killing every organism (algae etc.) bigger than 10 µm). At the time of writing this paper, this was stated in the Draft Convention Text;
- Quantities of ballast water that has to be treated varies from 1,000 to 5,000 tonnes (small container ships) to 10,000 to 15,000 tonnes (large container ships);
- The approximate time at the port berth is 12 hours;
- The oil tankers that regularly visit Rotterdam can have up to 100,000 tonnes of ballast water on board. The on shore treatment plant has to also to be able to process such amounts;
- If this water is discharged back into port waters, all non-indigenous fishes, shellfish, plants but also phytoplankton (2-200 µm), zooplankton (50-1000 µm), bacteria's (1-10 µm) and viruses (0.01-0.1 µm) have to be removed. Because of this, the water has to be disinfected.

The resulting cleaning process is presented in Figure 4.

The necessary cost of the technical means (grid filters, hydrocyclone, UV treatment plant and active coal filter) are in the direction of 1, 5 million €. This is based on a flow rate of 850 tonnes per hour. This is a rough initial cost estimate, which does not include:

- Maintenance costs (personnel, machinery);
- On shore infrastructure costs (pipelines etc.);
- Vessel infrastructure (reception barges, trucks etc.);
- Costs because of land/space use (rent).

Such costs must be regarded in comparison what ships have to invest for on board treatment techniques or executing BWE. It is important to realize that if a shore-based treatment approach is chosen, ships will have to pay in numerous ports for such facilities and infrastructure. A point of concern is the requested swiftness of service by the shipping industry. If the given tanker with over

50,000 or even 100,000 tonnes of ballast water arrives, it has to berth along the treatment plant. It will be impossible to discharge such quantities in a mobile vessel.

Above mentioned foreseen problems apply to the reception of ballast water, and not sediment in ballast tanks. For sediments, provision of reception facilities in ship yards and dry docks has been common practice for years. The forthcoming Convention is unlikely to cause any problems in this field. This accounts also for the reception of relatively small volumes of oily ballast water. Because of the regulations of Segregated Ballast Water tanks, this type of waste is likely to decrease to zero in years to come.

In view of the magnitude of volumes, operational, technical and financial implications on both port and ship side, provision of reception facilities for ballast water can be regarded as very complex and .... most likely very expensive. According to the "Polluter Pays Principle", the financial burden will be put on the ship. The important question is whether the shipping industry is willing to pay for the price of these facilities.

The ports escape?

If massive provision of PRFs is regarded as unrealistic, does that exclude ports in general from any involvement in and responsibility for solving the problem of alien species in ballast water? The Port of Rotterdam identifies a range of subjects where port involvement can or must take place.

Incoming ballast water

Although seriously harmful introductions seem not to have taken place yet in the nearby region, there is an urgent need for adequate Risk Analysis. This must lead to an improved knowledge and understanding of the ecological and economic vulnerability of the port, coastal and adjacent sea area to alien species from ballast water discharges. Risk Analysis must provide insight to:

- Location and circumstances of ballast water uptake;
- Description of species in ships' ballast tanks;
- Location and circumstances of ballast water discharge;
- Ecological data on existing habitats and ecosystems (presence of solid substrate, tidal currents, configuration of port basins, water quality);
- Resources that are at risk (biodiversity, fisheries, aquaculture, tourism, port constructions);
- Identification of "high risk" species.

The National institute for Coastal and Marine Management (a branch of the Dutch Ministry of Transport, Public Works and Water Management) has monitored the contents of ballast water tanks of ships entering Dutch ports (NICM management, 2001). This is, in fact, a first step to execute the second above mentioned aspect of Risk Analysis (description of species in ships' ballast water). Although a significant number of (zoo- and phyto) plankton species were found, it is too soon to draw general conclusions.

Further monitoring of the ports' and coastal ecosystem must provide insight in the risks associated with ballast water discharge in the Port of Rotterdam and other Northern-European ports. It is recommended to integrate such research with general ecosystem monitoring that will be executed in the light of the EU Habitat and Bird Directive. National governmental authorities are likely to play a major role in this. On a local level, Port Baseline Surveys might be appropriate to provide specific local data.

Such a comprehensive Risk Analysis must determine whether more stringent measures than the IMO Convention are necessary. These measures might be mandatory use of a treatment technique or

mandatory BWE on mid-ocean before port entry. It is realistic to say that it will take quite some years before all ships comply with the IMO standards. If a non-complying ship arrives in port, planning to discharge ballast water from a suspected area were "high risk species" occur, this might lead to an unacceptable risk. Also, ships might arrive in port that were not able to execute BWE because of sea and weather conditions. These are issues that have to be dealt with. If for such cases the creation of PRFs is considered, the former mentioned economical and operational aspects have to be taken into account.

Export of ballast water

With regard to the outgoing ballast water volumes (as mentioned earlier, approx. 60 million tons from the Port of Rotterdam annually) risks and effects are largely unknown. It is unrealistic to execute a comprehensive Risk Analysis for every sea area that the ballast water is transported to. However, some desk research is recommendable to investigate effects that have already taken place in other port and sea areas.

The last decades, there have been various studies to examine whether fresh water could be pumped in the ballast tanks of oil tankers and transferred to for example the Gulf region, where fresh water has a value comparable to or even higher than the oil transported. With the IMO Convention in sight, the time could be right to seriously consider the start of a pilot-project in this direction.

Operational port involvement

For both incoming as exported volumes of ballast water, it is preferable that Port Authorities design a "ballast water-uptake and discharge policy" in or in the vicinity of their port waters. For example, ships can be advised to avoid ballast water uptake near sewage outlets or water regions that contain much sediment, which could be the case near dredging operations. The latter minimises uptake of species as well as the carriage of superfluous weight when sailing not under ballast.

In the World Port Center, the port's main office, a Harbour Co-ordination Centre (HCC) has been in operation since 2001 (see photos 3 and 4). All ships that enter the territorial waters (or at least at the time of departure from the last port) are obliged to inform the HCC about:

- Any deficiencies and/or accidents with regard to Marpol and/or Solas prior to arrival and during stay in the port;
- The carriage and reporting of dangerous and/or noxious goods.

This intense ship-port interface provides good opportunities to integrate ballast water management procedures. Also, the information provided to the HCC provided by the annual 30,000 incoming ships can provide useful information that is needed when executing a Risk Analysis. For example, the origins of ballast water can obtained from this data.

On board survey by Port Inspectors

The Port of Rotterdam has not waited for the Convention to enter into force in getting pro-active in this field. In the beginning of 2003, an inspection unit of the Rotterdam Port Authority (RPA) has started an on-board survey on the origins, destination of ballast water and management and treatment techniques applied on board. The first results are presented in the following table:

Table 1. *First results of RPA survey.*

	Total no. of ships	***Percentage of total***	***No. of ships that execute BW exchange***
Container vessels	28	44	14
Oil tankers	14	22	2
Chemical tankers	9	14	
Bulk carriers	3	5	1
General Cargo	9	14	3
OBO	1	1	
	64	**100**	

Source: on board survey by inspectors of the Rotterdam Port Authority

Approximately one third of these vessels had exchanged its ballast water prior to port entry. From the BWE methods applied, the sequential method was used most (by 29 vessels), followed by flow-trough (15) and dilution method (3). One vessel, a chemical tanker, declared to have filtering equipment and UV treatment on board. Approximately one third of the examined vessels had ballast water on board which originated from outside the so called OSPAR[2] region, which could be regarded as a sea region in which species migrate freely by natural currents. From 10 % of the vessels, the origin of the ballast water was unknown. Naturally, at a later stage with a higher number of vessels examined, more structural statistical data and trends can be obtained from this on-board survey.

With about 4,000 Marpol-inspections executed per year by the RPA, there is a potential to survey a substantial amount of ships. This inspection role could also be important view to the Port Inspections that will be prescribed in the IMO Convention. The processing of the incoming Ballast Water Record introductions of harmful aquatic organisms by ballast water. For the Port of Rotterdam and most likely many other ports in the world, it is preferable that efforts are made to better analyse, assess and manage the ecological and economical risks of imported as well as exported volumes. Other possible areas of involvement are advising ships view to ballast water uptake and discharge activities in or nearby port areas and the establishment of an effective port inspection regime.

[2] Oslo and Paris Commission, a regional regulatory body for the sea area between Norway and Portugal.

Figure 1. *Map of the Port of Rotterdam Area.*

Figure 2. *Maasvlakte Olie Terminal, Rotterdam.*

Figure 3. *ECT terminal, Rotterdam.*

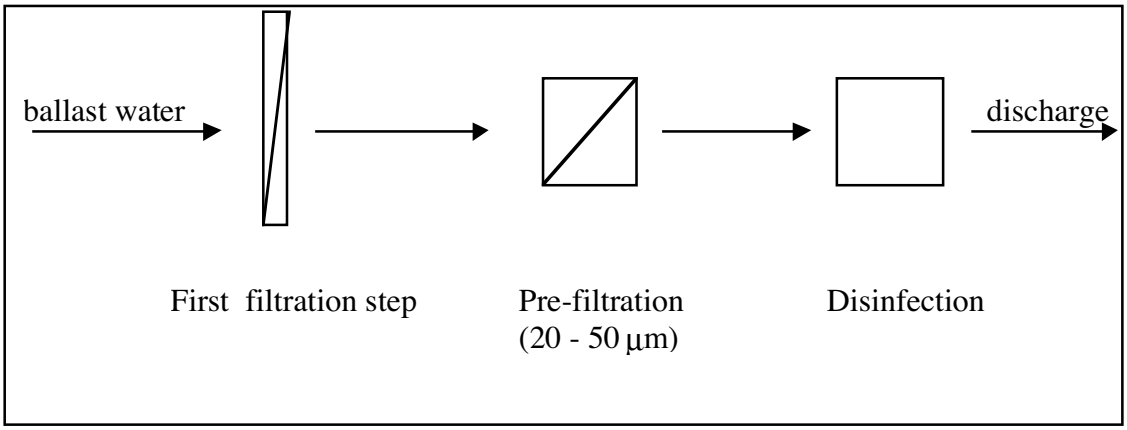


Figure 4. *on shore filtration process*
(source: desk study ballast water treatment by Witteveen & Bos consultants, July 2003).

Figures 5 and 6. *The Harbour Co-ordination Center in the World Port Center, Rotterdam.*

Latest results from testing seven different technologies under the EU MARTOB project - Where do we stand now?

E. Mesbahi

MARTOB Consortium
School of Marine Science and Technology,
University of Newcastle upon Tyne, UK
Ehsan.Mesbahi@ncl.ac.uk

Introduction

MARTOB is a three-year project funded through the Transport and Energy Directorate of the European Commission (GROWTH Programme). The MARTOB project began in April 2001, and it has the dual aims of developing methods for treating ballast water on-board ships and for developing recommendations of best practice for verification and monitoring of compliance of a sulphur cap for marine fuels. Both of these aims are directed towards making shipping operations more environmentally friendly.

The main work components to be carried out as part of the MARTOB project are as follows:

- Collection and assessment of data and information on ballast water management methods and existing relevant legislation, and a review and update of alien species introductions in European waters.
- Development of selected methods for on-board treatment of ballast water through lab-scale testing and in-depth analysis.
- Large and full-scale testing of selected ballast water treatment methods.
- Assessment of the financial, technical and operational effects of a sulphur cap on marine bunker fuel in European waters.

The first phase of the project related to ballast water management was completed in early 2002. This included collection of information on ballast water management methods that are currently used, that have been tested on board ships, or that are in an advanced stage of development. In addition to collecting information on biological effectiveness, information was collected on the safety of methods, environmental effects, and costs. Information was also collected on existing and proposed regulations, to give an indication of future directions for ballast water management requirements.

Techniques tested within the MARTOB project

High temperature Thermal Treatment: This method uses heat to incapacitate and kill organisms in ballast water. Low temperature treatment requires a long time and will not be effective against bacteria and some of the hardier organisms, but will be cheaper to implement as it uses waste heat. High temperature treatment is more expensive as in most cases it needs a dedicated heating system, but is potentially more effective at killing the organisms and requires a much shorter exposure time.

De-oxygenation Treatment: De-oxygenation of ballast water can be achieved mechanically by gas sparging, chemically by adding reducing chemicals, and biologically by adding nutrients. In MARTOB only the latter method has been studied in detail. By adding nutrients into the ballast water, the growth of the naturally occurring bacteria in the water will be stimulated. During the growth they consume oxygen, and the oxygen in the water will be depleted.

Ultraviolet Treatment: Ultraviolet (UV) lamps are used to irradiate the organisms in the ballast water. The UV radiation will induce photochemical changes in the organism; i.e. it will break the chemical bonds in DNA. This can lead to problems should the organisms survive, as it may carry mutations. Furthermore, there is a requirement for pre-treatment of the ballast water, as the performance of the system decreases with the turbidity of the water. Ultraviolet Treatment is well established and proven as a disinfectant in the wastewater treatment sector.

Ultrasonic Treatment: Ultrasound is generated by a transducer, which converts mechanical or electrical energy into high frequency vibration. The ultrasound generates cavitation in liquid (in this case ballast water), which can lead to the cells of organisms rupturing. It has been shown to be effective with bacteria, plankton and other larger organisms. However, ultrasound may have an adverse effect on ship/tank coatings and ship structure and would, therefore, need to be tested. Ultrasonic treatment has been successfully used in water treatment and the food industry to control microorganisms.

Ozonation Treatment: The Ozonation system introduces ozone into the ballast water. As ozone is unstable at atmospheric pressure it must be generated in situ. Ozone has been used in onshore applications, such as swimming pools, disinfecting drinking water and controlling microbiological contamination in various areas. In these applications it has proven to be very effective and a more powerful biocide than chlorine, which has traditionally been used. Ozone is toxic and therefore it will have to be used with care. There is also concern that it may cause increased corrosion in the tanks and pipes.

Oxicide Treatment: The Oxicide method is an electrochemical method, which generates hydrogen peroxide from the oxygen present in the ballast water. This decline in the concentration of oxygen and the presence of hydrogen peroxide is enough to significantly reduce the number of organisms present in the water. It also decomposes in water and will therefore not cause any problems to the environment. Hydrogen peroxide is an irritant and it will have to be used with care and it could possibly lead to increased corrosion.

Advanced Oxidation Technology: Advanced Oxidation Technology (AOT) consisting of a combination of ozone, UV and catalysts. Thus Ozonolytic / Photolytic / Photocatalytic Redox processes are operating simultaneously within a reactor. The unique combination is designed to generate large amounts of radicals, mainly hydroxyl radicals, within the reactor. It is these radicals that destruct / eliminate microorganisms. This water purifier has successfully been used in land-based applications such as purification of swimming pool water, drinking water, water used for irrigation in green houses and water used in fish breeding.

Hurdle Technology: Hurdle technology uses a combination of two or more treatment methods to reduce the number of microorganisms present. This may increase the effectiveness of the treatment and if chosen properly, can also eliminate some of the disadvantages of using the treatment methods alone.

Timeframe of the project

MARTOB project, (On Board Treatment of ballast water (Technologies Development and Applications) and Application of Low-sulphur Marine Fuel, partially funded by European Commission by contract number GRD1-2000-25383, started in April 2001 for a period of 36 months under the coordination of University of Newcastle upon Tyne.

Aims and objectives:

MARTOB's main objectives are:

- To investigate methodologies and technologies for preventing the introduction of non-indigenous species through ships' ballast water.
- To develop design tools and treatment equipment to be used in the further development of ballast water treatment techniques.
- To assess the effectiveness, safety and environmental and economic aspects of current and newly developed methods.
- To develop cost-effective (capital and operating), safe, environmentally friendly on board ballast water treatment methods, which have a minimum impact on ship operations.
- To produce guidelines for crew training and criteria for selecting appropriate ballast water management method.
- To assess the financial, technical and operational effects of sulphur cap on marine bunker fuel in European waters, and propose a verification scheme ensuring compliance with a sulphur cap from all players in the market.
- To help to facilitate the introduction of an important sulphur emission abatement measure without unintentional distortion of competition in the shipping market.

Research methods, test protocols and experimental design:

Laboratory-Scale Testing of Ballast Water Treatment Methods

The purpose of the laboratory-scale testing phase of the MARTOB project was to test a range of ballast water treatment methods using a standard mixture of seawater and target organisms. Specifications for the seawater/organism mixture were developed within the MARTOB project. The test organisms included three species of zooplankton and two species of phytoplankton. By using a standard mixture and analysis method it was possible to measure the biological effectiveness of all methods and to make basic comparisons. In June 2002, laboratory scale testing of selected ballast water treatment methods was carried out at the School of Marine Science and Technology at the University of Newcastle upon Tyne.

In addition to assessing biological effectiveness of the treatment methods, information on safety, corrosion, costs, and potential environmental 'side-effects' is being collected for each method. It is important that the methods are practical, safe for the ship and its crew, environmentally friendly, and economically viable. These characteristics are in addition to the primary requirement that the methods have to be effective at controlling the spread of alien species.

Materials and methods

Standard seawater was prepared for all tests 24 hours before use. Deionised water (supplier) was added to Tropic Marine salt (35g/l) (Aquatics Unlimited, Bridgewater, Wales) in 4 mesocosms of 250 or 450l. Following the addition of water, the mixture was agitated continuously for 24h using compressed air to ensure that all the salt had dissolved. Salinity was checked using a refractometer.

Cultures were supplied in bulk, zooplankton every 2 days and phytoplankton every 5 days. They were stored in CT rooms in the aquarium suite at the Ridley Building, University of Newcastle, at 10 and 15°C respectively.

Information on supplied plankton density was available from the suppliers. Samples were measured out directly from the cultures, each species being stored in a separate bottle. The organisms were mixed with 70L of seawater that had been pumped into a tank, to create a sample of test organisms, the 'soup' (Table 1). This was the agreed minimum volume to be used in the experiments that would

be statistically significant regarding the density of the organisms added as well as being cost effective. However this volume can always be increased in the case larger experiments are wanted to be conducted. After pouring the samples into the prepared seawater the bottles used to carry them were rinsed twice in the same water and added to the mixture.

Prior to pumping the soup into test rigs the mixture was gently agitated to ensure a homogeneous mixture. Following pumping to the test rigs the tank was rinsed with clean seawater to ensure removal of any residual organisms.

Before initiating the treatments, a 10L initial sample was collected from each test rig for laboratory analysis (see below). Treatments were carried out and on completion a 60L sample was taken for analysis.

A control tank containing one sample was set up and left at room temperature. Sub-samples were taken at intervals to monitor background mortality (Table 1). Three replicates were made during three consecutive days (12-14th June)

Table 1. *Times after set-up and sample sizes used for control soup sampling.*

Time of sampling	Size of sample
0 min	10L
30 min	3L
1h	3L
2h	3L
3h	3L
4h	3L
5h	3L
6h	3L
24h	Rest

Biological assessment: *sampling and test protocols*

Within the MARTOB project it was necessary to assess the performance of various ballast water treatment techniques. A standard test protocol was therefore required. Because the standards under discussion at IMO were not finalised, it was necessary to develop a test protocol specifically for this project. The developed protocol is to some extent based on the draft standards, but also other suggested protocols were taken into account.

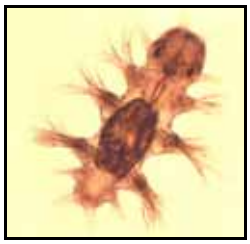
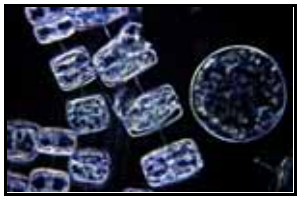
The sampling and test protocol provided standards for:

- water quality,
- species to be used for laboratory tests,
- composition of the test mixture,
- how to assess the biological effectiveness.

The water quality standard specifies the quality and quantity of the artificial seawater (ASW), including salinity, turbidity, pH and temperature. The chosen salinity was 33-35, achieved by adding “Tropic Marine seasalt” to distilled water. Seawater may be turbid due to both inorganic and organic particles. Kaolin was used to simulate the former, while flour was used to simulate the latter. The pH of the ASW was around 8.3, i.e. close to the normal pH of seawater. The temperature was 10-15°C to ensure the survival of the introduced marine organisms.

Five different species, three zooplankton species and two phytoplankton species, were selected as test organisms, and added to the ASW. The zooplanktons were a polychaete (nectochaete larvae of *Nereis virens*), a harpacticoid copepod (*Tisbe battagliai*), and a calanoid copepod (*Acartia tonsa*). The phytoplanktons were a diatom (*Thalassiosira pseudonana*) and a dinoflaggelate (*Alexandrium tamarense*). Densities of the species are given in Table 2.

Table 2. *Artificial Sea Water or MARTOB Soup*

Selected Species	**Maximum field densities (indivs /m^3)**	**Standard mix composition (indivs/ m^3)**	**Standard mix composition of a 70 litre test solution**
 Benthic nectochaete larvae Nereis virens *(700-800µm)*	740	1100	80
 Harpacticoid copepod Tisbe battagliai *(700-800µm)*	807	1100	80
 Calanoid copepod Acartia tonsa *(700-1000µm)*	159,659	2500	200
 Diatom Thalassiosira pseudonana *(4-5µm)*	$30x10^8$	$50x10^7$	$30x10^6$
 Dinoflagellate Alexandrium tamarense *(25-30µm)*	$75x10^6$	$40x10^6$	$24x10^5$

The mix used did not include any fish eggs or larvae. In many countries, including the UK, experiments involving vertebrates require special licenses. For this reason we excluded them from the standard test mix and would propose that separate trials of a mix containing fish eggs and larvae (probably salmon or turbot) be conducted, under licence for the most promising techniques identified in the trials with the standard mix. The mixture composition describes the density of the species to be included in the test mixture. The premise here is that densities should reflect the top end of the natural range for each taxa.

The effectiveness of each individual treatment technique was assessed by determining the number of live and dead organisms of each species after the treatment. This was done by fixing and staining the organisms in a manner that allowed living and recently dead material to be easily distinguished. This will allow the efficiency, expressed as % kill, of each technique for each group of organisms to be reported.

During the first few days of testing, UV, US and Ozone techniques used a high pressure pump for supplying artificial seawater into the treatment system. Analysis of preliminary results showed that the pump itself was eliminating almost all of the zooplankton; therefore a gravity system was used to supply the water for the rest of the tests. Consequently, it was observed that large number of bends, valves and long pipes could contribute as a source of error for these technologies. Since ASW flowrate was now much lower than original pump, it was concluded that some of species were gathered into the slow velocity points, thus altering some of the results. Both living and dead organisms were found to be hidden in the systems. It was therefore decided to flush these systems after each test run, when some of zooplankton species were detected from the sample. This could slightly remedy the source of error but there are still concerns regarding the accuracy of analysis.

Zooplankton fixation and staining

All samples were filtered through a 63 μm sieve. The zooplankton was rinsed from the sieve with clean seawater into labelled pots.

Zooplankton samples were stained with 0.1% Neutral Red solution in the ratio of 3ml stain/100 ml sample. After staining for 60 min, 4 ml of 1N Sodium Acetate solution was added per 100 ml of sample. The specimens were then fixed with 4% Formalin in a volume equal to that of the sample (50/50). Thereafter all samples were stored overnight at 5°C prior to counting.

Following the overnight storage and before examination of the samples, Glacial Acetic Acid was added dropwise to each sample, until the colour of the solution changed to magenta. The sample was filtered through a 48 μm sieve and washed with tap water. During the counting procedure the sample was kept in water. After counting organisms were preserved in 4% Formalin.

Live copepods stained immediately prior to fixation turned a deep magenta after acidification, whereas dead specimens were light pink to white. *Nereis* had to be more carefully observed, as dark staining did not guarantee viability. Some treatments affected the staining in such way that 'live' organisms varied in colour from magenta to orange. Therefore the assessment of individuals also included a morphological examination.

For the counting procedure whole organisms as well as bits were taken into account. The quantity of organisms delivered by the suppliers was a range between two densities therefore we dealt with volumes and not with exact number of organisms to make the soup samples. The percentage of mortality was calculated as the number of dead animals divided by the sum of dead and alive animals found in the after treatment samples. When no material or no whole animals only bits were found a 100% in mortality was recorded.

Framework of evaluation

Environmental assessment

Environmental assessment includes evaluation of the direct environmental impact resulting from the discharge of treated ballast water and consideration of the indirect environmental impact.

Direct impacts on receiving waters can result from discharges of the ballast water systems including that with altered quality, discharge of solids from physical separation methods, and discharge of living organisms that have survived treatment. The treated ballast water will be sampled on discharge for those parameters that are expected to change as a result of the treatment. Data from testing for biological effectiveness will give an indication of the types of organisms that will survive the treatment and be discharged. Indirect environmental effects of ballast water management will be assessed by estimating energy use, and calculating amounts of materials used during both operation and construction of the treatment equipment. Waste generated during operation or through disposal of worn out components and equipment will also be assessed.

Safety assessment

The assessment of safety aspects of treatment methods within the MARTOB project will be based on an evaluation of operational aspects. These include use of hazardous chemicals (either generated or stored on site), hazards related to operation of the equipment, aspects related to the storage and handling of chemicals and residuals required for, or resulting from, the on-board treatment of ballast water; and aspects related to unintentional release on board the vessel of treated ballast water containing residuals. The safety assessment of each method will also consider possible accident scenarios.

Economic assessment

In order to assess the economic viability of treatment options, two basic cost components are relevant, i.e. capital costs and operational costs. An interest rate of 8% over a period of 10 years is recommended to depreciate the investment costs, which fall under capital costs. Material costs, personnel costs and maintenance costs all fall under operational costs and these must be estimated in details for each treatment option. Other cost components like those resulting from training and management issues and those from the economic benefits and disadvantages of treatment options all need to be estimated in detail for each treatment option. All these cost components mentioned above must be estimated based on the same basic data e.g. ship type, ballast water capacity, number of voyages per year, number of ballast pumps, ballast pump capacities etc.

Technical and operational applicability

With respect to on-board ship applicability of treatment options, the options, alongwith their space requirements, capacity, flow rate and time, should be checked on the vessel for effects on stability, visibility, longitudinal strength, overpressure in the ballast tanks, liquid motions in the ballast tanks, thermal stresses, aggressiveness versus materials, corrosion, pressure drop in pumping system, modification of the piping and pumping system, safety of the crew and compatibility with trip duration and crew working load.

Objective assessment

Assessment of ballast water treatment technologies have not been limited to their biological effectiveness only, other criteria such as their compatibility with a particular ship and her route, overall cost, safety, crew, life cycle assessment, corrosion effects and many other factors have been considered here as ranking criteria with their individual weighting in the final assessment. MARTOB has also developed a comprehensive IT based technology to determine attractiveness of a particular ballast water management system for an individual ship travelling at a particular route. Details of the developed objective assessment methodology have been illustrated in Figure2.

Results: biological effectiveness

High temperature thermal treatment

Offers one solution if short heating period is required for the effective elimination of unwanted marine organisms. Treatment during ballasting and treatment at exit (deballasting) are two possible options.

The treatment at exit does not require the water to be pumped from one tank to the other for treatment, or additional tanks for storage, both of which can cause problems with stability of a vessel and/or reduction of the cargo space. There is also no risk of cross-contamination of the treated ballast water, once treated water is discharged. A possible problem for this system is that the equipment reliability is critical as the water is not stored and there is therefore no backup.

The effects of temperature on phytoplankton and zooplankton have successfully been tested under laboratory conditions. This has allowed us to obtain a correlation between kill rate and temperature for *Acartia* sp., *Nereis* sp. and *Tisbe* sp., three zooplankton species commonly found in ballast water. For the phytoplankton *Alexandrium* sp. and *Thalassiosira* sp., it was stated that all the temperatures that were used for thermal treatment resulted in a reduction of chlorophyll a. However, experiments carried out at lower temperatures (40 and 45°C) resulted in a significantly lower reduction of chlorophyll a. It would therefore appear that temperatures of 55°C and above were more effective at reducing phytoplankton biomass. However, there was no significant effect between the results for treatments at 55, 60 and 65°C, which would seem to indicate that increasing the temperature above 55°C does not result in a corresponding reduction of chlorophyll a. Combining the results from the zooplankton and phytoplankton we have been able to deduce a treatment temperature for the high temperature thermal treatment system of between 55 to 60°C. Figure 3 shows laboratory scale equipment for High Temperature Thermal Treatment.

Biological de-oxygenation

The solubility of oxygen in water is low. Biological de-oxygenation is based on the fact that addition of nutrients to ballast water will stimulate the growth of the indigenous bacteria in the ballast water. The growth of the bacteria will consume the available oxygen in the water, and when the ballast water becomes anoxic, organisms that require a steady supply of oxygen will die. The aim of the studies was to develop a de-oxygenation process that could be applied in large scale, and to test the efficiency towards selected organisms in the mesoscale trials in Newcastle. See Figure 4.

The time it takes to consume all the oxygen in seawater decreases with increasing temperature. At 4°C it will take 3-4 days, at 10-20°C, 1-2 days and above 20°C less than 1 day to obtain anoxic conditions.

Biological de-oxygenation was tested in meso-scale in 50 litre polypropylene vessels covered with black plastic bags to simulate the darkness in a ballast tank. The efficiency of the treatment was tested against three species of zooplankton, two copepods (*Acartia tonsa* and *Tisbe battagliai*) and one polychaete (nectochaete larvae of *Nereis* virens), and two species of phytoplankton, a dinoflagellate (*Alexandrium tamarense*) and a diatom (*Thalassiosira pseudonana*).

Biological de-oxygenation of the seawater killed all the added zooplankton species. The killing rate increased with increasing time under anoxic conditions. After 4-6 days of anoxia, more than 95% of all the tested organisms were dead.

The killing effect on phytoplankton of de-oxygenation was limited as measured by the change in the concentration of chlorophyll a. On average, the chlorophyll concentration decreased by 33%, but there was no significant difference between the treated tanks and the non-treated controls. The reduction in chlorophyll may therefore be due to the fact that the micro algae in all cases were incubated in darkness.

Corrosion effect estimated with FMECA analysis identified the following issues: a slight decrease of the pH with possible consequences on metal corrosion, coatings and gaskets, a slight increase of CO_2 with possible consequences on metal corrosion and gaskets, the production of H_2S with possible consequences on metal corrosion, coatings and gaskets, the addition of inorganic substances with possible consequences on metal corrosion, coatings and gaskets, the addition of organic substances with possible consequences on coatings and a significant increase of the bacteria concentration with possible consequences on metal corrosion, coatings and gaskets.

Ultraviolet light treatment (UV)

UV irradiation is used for the disinfection of potable, process, aquaculture and waste waters. It achieves disinfection by inducing photochemical changes of biological components within micro-organisms, and more specifically by breaking chemical bonds at the DNA and RNA molecules and proteins in the cell. In the majority of UV disinfection applications, low-pressure mercury arc lamps have been chosen as the source of UV radiation. Approximately 85% of the output from these lamps is monochromatic at a wavelength of 253.7 nm. This corresponds to the short wave portion of the UV spectrum which in all spans from 200-280 nm, and is referred as UV-C. The sensitivity of micro-organisms to UV radiation depends on the wavelength. Microorganisms are sensible to UV radiation between 210 and 320 nm, with a peak at 265 nm. See Figure 5.

Maximum reduction rate of 78% with phytoplankton was achieved and regarding zooplankton the UV method did not inactivate more than 56%. With UV treatment, the greatest percentage change of chlorophyll *a* concentration achieved was a 56% reduction.

UV light causes a slight increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets.

Ultrasound treatment (US)

Ultrasonic treatment is a relatively new technology in ballast water treatment. Ultrasonic liquid treatment uses high frequency energy to cause vibration in liquids to produce physical or chemical effects. Ultrasound, from 20 kHz to 10 MHz, is generated by a transducer that converts mechanical or electrical energy into high frequency acoustical (sound) energy. The sound energy is then fed to a horn that transmits the energy as high frequency vibrations to the liquid being processed. The action of ultrasound is thought to be mediated through various responses that may be fatal to marine organisms. These are heat generation, pressure wave deflections, cavitation and possibly the degassing effect of ultra-sound causing removal of much of the oxygen. Cavitation, the formation of gas cavities within liquids, is affected by the frequency of the ultrasonic, power level, volume of water, temperature of the water and concentration of dissolved matter and gases. Higher frequencies, warmer temperatures and lower concentrations of dissolved matter have been found to increase the effect of ultrasound pulses. Plankton mortality has also been observed in the presence of ultrasound and is considered in part to be attributable to the cavitation process.

The mortality attained by the US treatment was always below 40% for zooplankton for all the tests. The highest percentage change of chlorophyll *a* levels achieved with US was a 71% reduction.

No risk of increased corrosion with respect to coating and gaskets was identified regarding the US method.

Ozone treatment

O_3 is the triatomic form of oxygen which is a gas at room temperature. Marine applications of ozone include depuration of shellfish, oxidation of colour producing organics and toxins, improvement of filtration, control of microbiological contamination in aquaria and aquaculture, and control of biofouling in cooling water systems. Ozone is a fairly powerful but unstable agent which rapidly destroys viruses and bacteria, including spores, when used as a disinfectant in conventional water treatment. Salt-water ozone reactors are currently used for salt-water aquariums and fish hatcheries. The three modules of an ozone treatment system are a generator, ozone contact chamber, and ozone destructor. In the contact chamber ozone is introduced to the water stream. Biological effectiveness is a function of concentration and exposure period. The longer the ozone-contact time, the higher the mortality. Industrial systems use a “bubble contractor” chamber that maximises ozone exposure. A bubble system was also selected to the ozone device utilized in the Martob project. See Figure 6.

Mortality rates increased rapidly with increasing contact time. The highest value for the O_3 treatment was 89%, eliminating *Nereis*. Phytoplankton results showed that O_3 reduced chlorophyll *a* levels with a 97.2 percentage change against samples taken before treatment.

O_3 method caused a significant increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets. The production of O_3 (short term effect) with possible effects on metal corrosion, coatings and gaskets was also identified.

Oxicide treatment

Hydrogen peroxide is an oxidising compound and can be produced in-situ by means of an electrochemical conversion of dissolved oxygen. This new process, the Oxicide process, is carried out in a specially designed and patented electrochemical reactor. H_2O_2 destructs plankton and microorganisms in the ballast water. Hydrogen peroxide is known to be of limited risk to humans, especially at low concentrations. It decays within a period of days or a few weeks, resulting in harmless compounds: water and oxygen. Hydrogen peroxide has various applications, among others treatment of swimming pool water, as an alternative to chlorine based disinfectants. A first design of the Oxicide cell has been built and tested under laboratory conditions at a scale of 100 dm^3 water per hour. It contained three Oxicide cells in series, each with contactors for supplying oxygen to the sea-water, the source of which is either pure oxygen or air. The seawater runs along a 3 dimensional electrode (cathode), where the oxygen is transformed to hydrogen peroxide. The anode compartment is fully separated from the seawater compartment by means of a conducting membrane. It was found that the maximum achievable concentration of hydrogen peroxide in seawater is determined by kinetics and depends on the concentration of dissolved oxygen, temperature, electrical current and cell voltage. The H_2O_2 concentration follows a logarithmic trend in batch operation. The highest concentration of H_2O_2 achieved at ambient condiments was approx. 400 mg per liter (using pure oxygen gas) or 150-180 mg per liter (using air). The initial current efficiency (CE) was 70-80%. The pH of the seawater decreases because of some migration of H+ ions from the anode compartment through the membrane. The maximum observed pH drop in a batch operated Oxicide cell was from pH 8.4 to pH 6.5. The 3-dimensional electrode of the Oxicide module showed no plugging or irreversible retention of particles in tests with kaolin, wheat flour and algae, i.e. particles < 100 µm. See Figure 7.

H_2O_2 is efficient against selected organisms: 100% of *Nereis* and ≥ 90% of *Acartia* were removed in all experiments at 10-15 mg H_2O_2/dm^3. *Tisbe* proved more difficult, but was also removed by at least 85% at higher concentrations of H_2O_2 (> 28 mg/dm^3). Furthermore, a reduction in chlorophyll *a* levels of 50% was achieved by Oxicide treatment at 10-15 mg/dm^3, although some of the other test results with phytoplankton were inexplicable.

Elevated temperature (up to 35°C) seems to improve the efficiency of H_2O_2, especially zooplankton. A literature study and additional tests revealed that some organisms need much higher concentrations (>100 mg H_2O_2/dm^3) to destruct or inactivate; this especially holds for large organisms.

In summary, various organisms are destructed or inactivated at relatively low concentrations of hydrogen peroxide (10-30 mg H_2O_2/dm^3). A treatment time of at least 24 hrs is required for H_2O_2 to take full effect. However, a combination of Oxicide with other techniques should be considered, because of the relatively high resistance of some organisms to hydrogen peroxide.

In terms of corrosion assessment, the production of H_2O_2 and the significant increase of the Redox potential of the water (several hours to a few days) may have consequences for the metal corrosion, coatings and gaskets. In addition, it is recommended to consider the electric isolation of the DC equipment, because of the risk of unexpected current return paths and significant local metal corrosion.

Advanced Oxidation Technology (AOT)

AOT consists of a combination of ozone, UV and catalysts. Thus Ozonolytic / Photolytic / Photocatalytic Redox processes are operating simultaneously within a titanium reactor to generate large amounts of radicals, mainly hydroxyl radicals, which will destruct and/or eliminate microorganisms. This technology has successfully been used in land-based applications such as purification of swimming pool water, drinking water, water used for irrigation in green houses and water used in fish breeding. The water was circulated through the water purifier. Tests were taken after 1 – 10 cycles. Some tests were carried out with 100 µm filter upstream the water purifier. The combination of AOT and the 100 µm filter could achieve over 95% killrate of zooplankton. See Figure 8.

In the samples after treatment with the water purifier and filter the number of dead and alive zooplankton are low (1.4 - 17% of the number initially included in test water). Organisms are obviously caught in the filter. Also in the samples after treatment with the water purifier and no filter the number of zooplankton are low (down to 4% of the number included in test water). This indicates that organisms are eliminated by the water purifier. It could be that some organisms are left in the pipes or in the tank. But compared to the number of zooplankton left after a test with only the pump (35-52% of the number included in test water) some may have been lost.

The combination oxidation technology together with the 100 µm filter achieved a 40-70% reduction in chlorophyll *a* compared to samples taken before treatment. This indicates that there has been a reduction in the phytoplankton biomass. It is possible that the filter caught some of the phytoplankton.

In terms of corrosion assessment a moderate increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets and a slight increase of CO_2 with possible consequences with respect to metal corrosion and coatings were recommended for careful scrutiny.

Hurdle Technology

Combining disinfecting technologies offer the option of eliminating the limitations of individual techniques as well as the advantage of using the synergy of different methods. From the food industry it is known that combinations of two disinfecting techniques have more effect than the sum of individual conservation methods. One well known application of hurdle technology in ballast water treatment is the combination of filter technology (hydrocyclons) and UV disinfection.

During the MARTOB trials various combinations were tested, based on the expected synergistic effects, i.e. the combination of mechanical filter + US + UV, filter + UV + oxicide (H_2O_2), H_2O_2 + UV, thermal treatment + de-oxygenation and H_2O_2 + heat treatment.

From the results of the hurdle technologies, the treatment that worked best was the low temperature thermal treatment (40°C) + de-oxygenation, which had 100% efficiency for *Tisbe* and *Nereis*, and 97% for *Acartia*.

Comparing the efficiency of UV+H_2O_2 with and without filter (150 µm), the results showed that the filter did affect the survival of the organisms, as the percentage removal increased for *Acartia* and *Nereis* when the filter was used.

The combination of US and UV achieved a 68% reduction of chlorophyll *a* levels compared to samples taken before treatment. The combination of filter, US and UV achieved a 57 % reduction of chlorophyll *a* level.

Regarding the phytoplankton results, it is difficult to be certain which of the combinations of technologies are the most effective. It would appear that combinations of low heat with de-oxygenation or hydrogen peroxide were not effective at reducing chlorophyll *a*. The remaining four treatments were all based on combinations of UV and hydrogen peroxide, sometimes with the added

combination of a filter. On two occasions this reduced the chlorophyll *a* by over 70%, on another occasion the reduction was less than 20% and the fourth run resulted in an increase in chlorophyll *a*. It is therefore impossible to say with any certainty whether this combination of technologies is effective.

Results: Environmental impacts, Risk and Safety and Economic aspects

In the laboratory testing phase of the MARTOB project, information from the laboratory scale test reports and from information provided by system designers for ballast water treatment on a case study ship formed the basis of the evaluation. Evaluation criteria developed within the MARTOB project were used to assess each of these effects for each of the methods tested at laboratory scale. To provide a consistent basis for comparing the individual ballast water treatment techniques, a theoretical case study approach was used. Data on the case ship and sample voyage were specified and provided to the technical developers in the project, as well as a list of data needed for assessing cost, environmental effects, and hazards.

Table 2. *Case study SHIP details.*

Basic Ship Information		
Ship type	Pure Car and Truck Carrier (PCTC)	
DWT (Dead Weight Tonnage)	14841	
Length Overall	199.1 m	
Voyages per year	50	
Route	Southampton – New York	
Ballast water capacity	8076 m^3 (total volume of all ballast water tanks)	
Volume of Ballast Water to be treated per trip	2000 m^3	
Number of ballast pumps	4	
Capacity of ballast pumps	500 m^3/h	
Additional Data Selected for Economic Assessment		
Parameter	**Details**	**Specified for case study**
Power consumption of pumps	Energy use per hour per pump	50 kW
Fuel Type	Fuel type used for BW pumps	MDO
Energy content of fuel	Standard factor	42.5 MJ/kg
Fuel notional costs	Have to be standard for all comparative calculations	0.4 €/kg
Fuel conversion efficiency (diesel to electricity)	Standard factor	30%
Fuel conversion efficiency (diesel to steam)	Standard factor	66%
Depreciation period	Period in years used to annualise capital costs	10 year
Interest rate	Interest rate used to annualise capital costs	8%
Fuel cost	Cost per litre MDO	0.4 €/kg
Personnel cost	Average cost per hour	25 €/h

Risk and safety effects

For the risk and safety assessment of ballast water treatment methods, hazard identification was carried out and some recommendations for potential risk control measures were provided. Hazards can be considered from the perspective of safety/survivability of the vessel and safety of the crew during ship operations. Categories of hazards related to operation of the ballast water treatment methods tested in MARTOB include physical hazards such as heat, electrical hazards, ultraviolet or

ultrasound radiation hazards, and chemical hazards from gases or hazardous liquids used or generated during treatment. The major hazards associated with most of the treatment methods, including thermal treatment, UV, US, Oxidation, and Oxicide, were confined to the location of the equipment installation. None of the on-board treatment methods have the potential to threaten ship structural integrity in the manner of empty-refill ballast exchange. For biological de-oxygenation and ozone, ballast water is treated in the ballast tanks, so the hazard would encompass a larger area of the ship.

Most of the ballast water treatment methods, with the exception of biological de-oxygenation and ozone, require the ballast water to be pumped through treatment systems. This additional piping means that there is an additional risk for pipe breaks and leaks of treated or untreated ballast water. However, this is expected to be a minor risk as most additional pipe work would be in a very localized area.

Other hazards associated with ballast water treatment include the potential for a spill of hazardous material stored or being used within the treatment system. The UV and AOT treatment systems both use UV lamps that contain mercury or amalgamated mercury. The oxicide method uses nitric acid as an anolyte and requires sodium nitrate salt to be stored on board. All of these could result in damages if accidentally released.

With all methods, there is the potential to reduce risks through appropriate training and safety procedures. If these systems are installed on new ships additional safety features could be considered during ship design.

Environmental effects

Environmental impact categories used to assess the effects of each of the ballast water treatment technologies tested in the MARTOB project included:

- Direct Impact through Discharge to Receiving water:
  - Discharge of water with altered quality with respect to the following parameter types:
    Physical parameters
    Metals
    Nutrients/Oxygen Demand, Low D.O.
    Biocide residuals
  - Discharge of surviving organisms
  - Discharge of solids (organisms and sediments)
- Other Environmental Impacts
  - Energy Consumption (treatment systems, additional pumping, filtration)
  - Potential for spill of treatment chemicals
  - Materials use (both for consumables and for construction of treatment equipment)

Although some of the treatment methods will result in the discharge of ballast water with altered quality, none of the discharges will include substances that are identified as ‘priority hazardous substances’ (under the European Union’s Water Framework Directive), or that have the potential to bio-accumulate. Ballast water quality will undergo the most change with the biological oxygen removal method, which will produce a discharge that is low in dissolved oxygen and that has increased concentrations of nutrients and bacteria. The Oxicide and advanced oxidation methods will both lower the dissolved oxygen concentration of the ballast water. Increased temperature of the ballast water discharge will occur after thermal treatment and ultrasound treatment. UV treatment has no effect on ballast water quality.

For all methods, the ballast water discharge will include some form of organic matter in the form of dead organisms, but this will vary depending on whether filtration is used, treatment type, and the

concentration of organisms within the intake ballast water. The potential of this would be much less than if live non-indigenous species are released, but could be of minor concern in eutrophic waters. All but two of the treatment methods would be operated using a filter as pre-treatment. Biological de-oxygenation and ultrasound treatment do not require the use of a filter. Methods using the filter as pre-treatment will need to discharge the filtered material to the receiving environment, which could cause some turbidity.

All treatment methods require the use of some energy, and this will result in environmental effects from fuel consumption and associated emissions. Energy use is lowest for biological oxygen removal and high temperature thermal treatment is the most energy intensive method (although the energy used is dependent on the selected treatment temperature and the temperature of the ballast water before treatment).

Stainless steel and titanium are the most commonly used materials for constructing the treatment systems. Materials used for construction of the treatment equipment will be further refined in the next phase of the project when the treatment systems are constructed for full scale testing. It should then be possible to have more detailed information to assess life cycle impacts of these methods.

Economic aspects

Installation of an on-board ballast water treatment system will lead to changes in ships' capital costs, changes in annual operating costs, and possibly will lead to extra training and management costs and economic benefits or disadvantages. Generally, the cost calculation results highly depend on some basic data associated with shipping trade and ballast water treatment. This may include type and characteristic of the vessel, sailing and trading pattern, including aspects like route, distances, speed, sailing and harbour time, and number of voyages per year, volume of ballast water, number of ballast pumps and their capacities, type of fuel used, type of treatment and treatment capacity. Costs can be easily compared when they are calculated based on the same type of dependants mentioned above. The theoretical case study approach provided a consistent basis upon which to compare costs.

Table 3. *Preliminary calculations for costs*

Cost Type	**Details**	**Thermal Treatment**	**De-Oxygen.**	**UV**	**US**	**Ozone**	**Oxicide**	**AOT (average)**
Capital costs		€	€	€	€	€	€	€
TOTAL capital costs (for 10 years)	one time investment costs (including investment, installation, testing, & commissioning)	110,000	50,000	60,500	130,000	105,000	1,552,000	125,000
Capital costs/year	10 year depr. at 8% interest	16,393	7,451	9,016	19,374	15,648	231,294	18,629
Operational costs		€/year	€/year	€/year	€/year	€/year	€/year	€/year
*** Material costs**	Costs of all materials needed in the course of system operation, including fuel.	38,764	2,629	1,434	1,672	3,501	2,837	2,943
Maintenance costs	Including materials and labour	0	0	75	7,000	2,200	0	1,813
Training and management costs	Including training, management, certification	0	0	200	200	575	360	75
Total costs (€/year)	All costs annualised.	**55,157**	**10,081**	**10,726**	**28,245**	**22,124**	**234,491**	**23,459**
Costs per m^3 BW (€/m^3 BW)	All costs calculated towards costs per tonne ballast water treated.	0.55	0.10	0.11	0.28	0.22	2.34	0.23

From the preliminary cost calculations it can be concluded that there are still some data gaps to be filled in. For some treatment methods the potential cost and cost factors are already quite transparent, for some other systems there is still a lot of data to be estimated. The differences are partly related to the status of development of the method. It is expected that during scaling-up of the systems and the large-scale trials more data will become available. In addition more research into tank cleaning costs, cost of corrosion control, certification cost, average wages of on-board personnel, total shipping cost to be able to calculate the impact of ballast water treatment on the total cost of shipping, needs to be done.

The preliminary cost of treatment of ballast water on "the case study ship" varies considerably, ranging from €0.10/m^3 in the case of biological de-oxygenation up to €2.34/m^3 for oxicide. Nevertheless, it should be kept in mind that not all data were available for the techniques, and some were preliminary.

Results: evaluation of corrosion risk of the treatment methods

In ships, an important problem is the corrosion of the hull structure, the piping system and the ballast water handling equipment. Therefore it has been decided to identify if the installation and operation on board of the considered in the MARTOB project ballast water treatment systems will modify the water properties in such a way that it could increase the corrosion risk of the ship structure and ballast water piping network. The target of this study was not to perform a detailed analysis of the corrosion risk link to each system which will require information about the ship on which they will be installed, but to provide a warning to the designers and classification societies which will have to approve the installation on board, on the main possible new risks with respect to corrosion attached to each system. This approach was carried out utilising FMECA grid support and ranking tables developed by MARTOB's expert group.

The parameters considered in the analysis with indication of the variation or consequences which induce a corrosion risk increase were water properties, water content and circuit content. The resistance list for the chosen coating is important. It appears that the manufacturers of the coatings, linings, seals, Dresser couplings, pumps, etc. should be asked to provide a resistance list for their product. The coating maker will have to investigate the resistance of the coating where the ballast tanks contain treated water.

Therefore, it is possible that the chosen ballast water treatment method needs to be specified first so that the materials with the best corrosion resistance and coatings compatible with the water content can be chosen for the detailed specification of coating, piping, pump, valve, seals and alloys etc., based on the treatment method.

All risk increases are acceptable considering today's knowledge and can be managed for new ship design with existing techniques and methods. In existing ships, some treatment systems may be not acceptable due to the treated water, incompatibility with the existing piping, gaskets or coatings materials.

Full/large scale trials

Strategy for full scale is based on the experience gained from laboratory scale test trials. High Temperature Thermal Treatment, de-oxygenation and oxidation technologies will be tested onboard a Care and Truck Carrier. Ultraviolet, ultrasound, ozone and oxicide methods will be tested with large scale facilities.

In the large scale test phase of US and UV the duration of test runs will be longer in order to minimise the technical sources of errors, i.e. piping, fittings, valves and small amount of water. The use of sea

water enables the access to unlimited amount of water and thus the error caused by the small amount of water can be reduced. Also the link to the actual marine environment is evident. The strategy with ozone has also been changed. The contact time will be extended with modification of the device in order to monitor ozone dosage per amount of water versus contact time. Various ozone dosages and contact times will be studied, and long term test runs might also be carried out.

To assess biological effectiveness of treatment systems, similar procedures as laboratory tests will be followed. Standard sieves of size ranging from 10 µm (for phytoplankton) to 50 µm (for zooplanktons) will be used onboard the ship. A large volume of Ballast Water (1000 litres) will be tested at each sampling period to ascertain true representative of individual Ballast Water tanks. The effect of time spent in the ballast water tank on species' survival will also be studied.

Conclusions and recommendations

During last two years, MARTOB has gained valuable expertise in the field of Ballast Water treatment technology, assessment of biological effectiveness (large and small scale), development of test protocols and procedures and overall objective assessment.

MARTOB believes that all key criteria in the development of Ballast Water technologies should be weighted and considered accordingly.

MARTOB believes that given time and adequate funding, there are technologies which have the capability of reaching high standards for Ballast Water treatment. Setting up a high standard of "No harmful discharge" and deciding on realistic time horizons to achieve such goal, could urge technology developers to seek more effective solutions. Considering the existing level of expertise, a primary standard of "No discharge of live species larger than 50 µm" seems justifiable. More stringent standard (i.e. No discharge of 10-20 µm live species) could be introduced in a 3 or 5 year time and after re-visiting the level of technological developments.

During last few years, significant progress has been made by various projects all around the world; MARTOB strongly suggests that additional Research and Development funds through appropriate channels at national, continental and international levels should be provided to enable technologists and scientists proceed with further development.

MARTOB Partners

University of Newcastle upon Tyne (Coordinator, UK)

Abo Akademi University (FIN)

VTT Industrial Systems (FIN)

Environment, Energy and Process Innovation (NL)

Institute for Applied Environmental Economics (NL)

SINTEF Applied Chemistry (NO)

Fisheries Research Services (UK)

T V/den Heuvel Watertechnologie BV (NL)

The International Association of Independent Tanker Owners (UK)

Souter Shipping Ltd. (UK)

SSPA Sweden AB (S)

Three Quays Marine Services (UK)

International Chamber of Shipping (UK)

Bureau Veritas (F)

French Research Institute for the Exploitation of the Sea (F)

Association of Bulk Carriers (UK)

Alfa Laval AB (S)

Berson Milieutechniek B.V. (NL)

Environmental Protection Engineering S.A. (EL)

(MARINTEK) Norwegian Marine Technology Research Institute (NO)

Shell Marine Products (NO)

Wallenius Wilhelmsen Lines (SW and NO)

MAN B&W (DK)

Fueltech AS (NO)

Norwegian Shipowner Association (NO)

Acknowledgements

MARTOB is partly funded by the European Commission under the 5th Framework Programme for Research, Technological development and Demonstration activities, Programme GROWTH, and is managed by the Direction-General for Energy and Transport.

References

All materials presented in this paper are extracts from publicly available MARTOB reports. Please visit our website:

http://www.marinetech.ncl.ac.uk/research/martob/Public%20Reports.htm

where all detailed technical and scientific references may be found.

Figure.1 *Preparation of MARTOB Soup.*

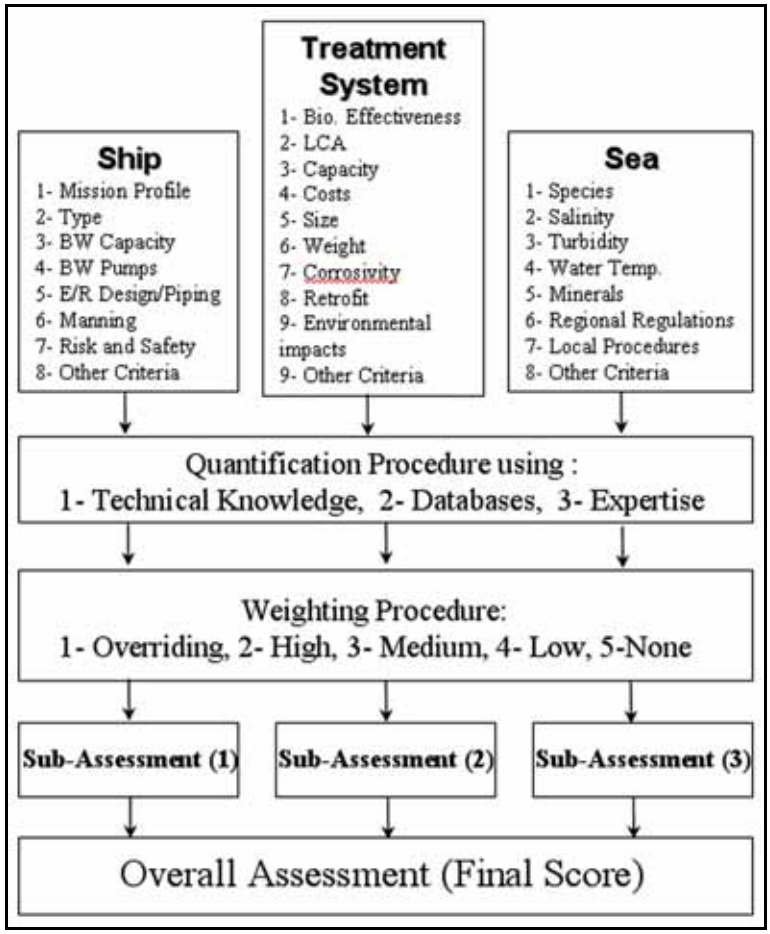


Figure 2. *Objective assessment flowchart.*

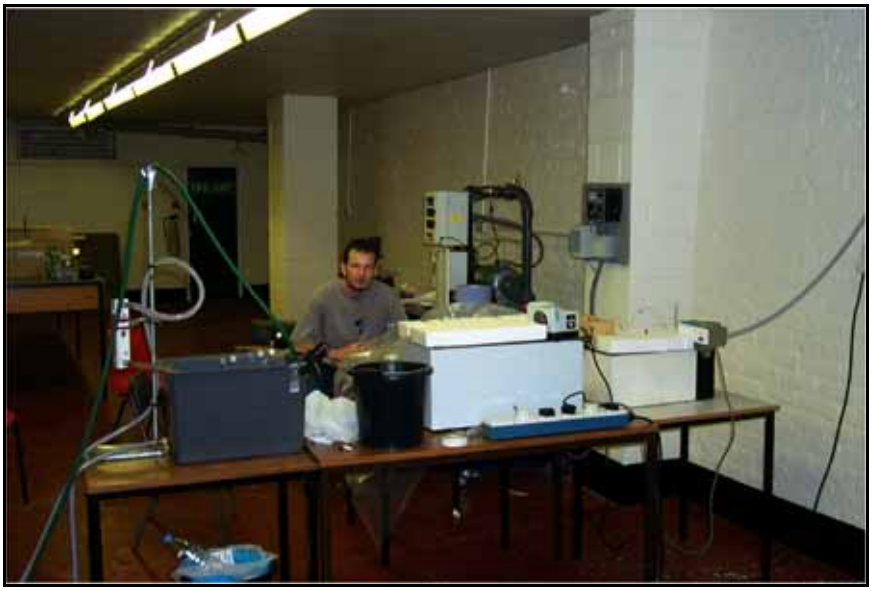


Figure 3. *High Temperature Thermal Treatment, Laboratory Scale.*

Figure 4. *Laboratory scale De-oxygenation technique.*

Figure 5. *Laboratory scale equipment for UV and US systems.*

Figure 6. *Laboratory Scale Ozone treatment.*

Figure 7. *Laboratory scale Oxicide treatment system.*

Figure 8. *Laboratory Scale Advanced Oxidation Technique.*

The TREBAWA ballast water project

K. Hesse[1], Mike Casey[2], P. Zhou, F. Aslan[3], E. Schmid, A. Leigh[4] & A. Santos[5]

[1]*Reederei Klaus Hesse GmbH*
info@reederei-hesse.de

[2]*Department of Naval Architecture and Marine Engineering,*
Universities of Glasgow and Strathclyde
mcasey@strath.ac.uk and
peilin.zhou@na-me.ac.uk

[3]*Technologie-Transfer-Zentrum Bremerhaven*
faslan@ttz-bremerhaven.de and
schmid@ttz-bremerhaven.de

[4]*Willand U.V. Systems Ltd tony.leigh@atgwilland.com.*

[5]*ISQ-Instituto de Soldadura e Qualidade*
acsantos@isq.pt

Treatment options being researched

The TREBAWA project is based on a primary mechanical treatment to remove larger organisms and suspended solids, followed by an ultraviolet (UV) light irradiation to inactivate the remaining organisms, disinfect the ballast water and make it suitable for discharge.

Timeframe of the project

TREBAWA is a European CRAFT project included in the 5th Framework Programme of the European Commission started on the 1st of July 2002 and will end on the 31st of June 2004.

Aims and objectives of the project

Ballast water is of great importance for maintaining a ship's stability and limiting share forces and tensions. During the loading of ballast water, large volumes of sediment are sucked from the water columns or the harbour floor into the ballast tanks. The movement of some 10 billion tonnes of ballast water in ships internationally each year has been responsible for the settlement of about 100 million tons of sediments. Its cleaning and the disposal of the ballast sludge produced involve enormous costs, as well as job hazards and time. Besides these economic aspects, ballast water has been recognised as a major vector for the translocation of aquatic species across biogeographical boundaries, which may prove ecologically harmful when released into a non-native environment. It is estimated that as many as 3,000 alien species of plants and animals are transported per day in ships around the world.

The Marine Environment Protection Committee is working on developing draft new regulations for ballast water management to prevent the transfer of harmful aquatic organisms in ballast water. The working group has confirmed that ballast exchange on the high seas is the only widely used technique currently available to prevent the spread of unwanted aquatic organisms in ballast water and its use should continue to be accepted. However, it has been stressed that this technique has a number of limitations.

The conclusions are that development of alternative treatment technologies might produce techniques that were substantially more reliable and that ballast water exchange is an interim solution. There is considerable demand for efficient ballast water treatment alternatives, and thus, a great market

potential for the development of such a system, besides the environmental benefits that it would report.

TREBAWA is a European CRAFT project included in the 5th Framework Programme of the European Commission. Its objective is the development of a new technically and economically competitive ballast water treatment system, based on a primary mechanical treatment to remove larger organisms an/or suspended solids, followed by a ultraviolet (UV) light irradiation to inactivate the remaining organisms, disinfect the ballast water and make it suitable for discharge.

Seven European SMEs from every sectors of marine field will participate in this project in a cooperative research, joining their capacities and expertise in the multidisciplinary areas involved in the development of TREBAWA system. Meanwhile, three RTD performers will participate in order to carry out the research and development of the system.

The experimental focus of the proposed work, consisting of 5 interdependent work packages, is a pilot-scale system, which will be constructed to obtain the required data using in-situ analysis techniques. It will then be installed on board in order to develop the field tests leading to the validation of the prototype. Critical points are the achievement of:

(i) a high degree of separation of in seawater suspended particles,

(ii) a high performance for the UV system in inactivating and killing all the in water remaining organisms,

(iii) an integrated prototype compact in size which fulfil the space requirements of a wide range of existing ships,

(iv) an economically and operational efficiency for the final system.

Research methods, test protocols and experimental design

The main techniques which have already been assessed or are currently being investigated for application in the treatment of ballast water are:

- Mechanical separation: is a good ballast water pre-treatment and should in fact be applied on every ship to reduce residuals.
- Chemical separation: addition of chemicals is no good option in connection with negative effects to the environment.
- Heat treatment: heating is a big energy consumer, what brings negative effects to the surroundings; application of UV treatment appears to be an effective disinfection method. Its application on board needs further research.

Most of these potential technologies haven't yet been demonstrated in a full-scale shipboard environment.

It can be concluded that effective method can be achieved by using a combination of existing technologies together, using the hydrocyclone as a primary treatment to remove larger organisms and/or suspended solids, and UV as a secondary treatment, to inactivate the remaining organisms, disinfect the ballast water and render it suitable to discharge.

The two most feasible treatment technologies for primary solids separation are filtration and cyclonic separation. Filter has operational problems regarding high-pressure drops and a strong tendency towards clogging and a low operational dependability.

In contrast to filtration, spin particle separation is a relatively simple and inexpensive way of removing larger particles and organisms from ballast water.

Cyclonic separators are utilized in various industries such as chemical, coal mining and handling, metal mining, rock products, plastics and wood products. Their relatively simple construction and absence of moving parts mean that their capital and maintenance costs are lower than those of other control devices that are available.

The most viable option for secondary treatment at the present time is considered to be ultraviolet (UV) light irradiation. It has been the subject of laboratory testing on a range of marine organisms with positive results and it has already been used in other marine applications for many years. Based upon currently available information, UV radiation preceded by a primary clarification stage by cyclonic separation appears to be the method that will provide the best combination of effectivity and feasibility.

The research method includes computer modelling, laboratory tests, pilot tests and field evaluation. The work programme has been formulated to address the key technical issues which must be understood/solved in order to optimise the performance of the ballast water treatment system and allow for its development. It includes fundamental hydrodynamic studies to measure the dispersion coefficients and the separation performance as a function of critical parameters not available in literature for solid ballast water components, such as particle size, aspect ratio and separator loading. The subsequent data and the CAD/CFD (Computational Fluid Dynamics) model developed will provide the basis for the design and detailed economic analysis of the system for commercialisation.

The experimental focus of the proposed work is a pilot-scale system which will be constructed to obtain the required data using *in-situ* analysis techniques. It will then be installed on board in order to develop the field tests leading to the validation of the prototype. The biological effectiveness of the technology under consideration will be measured by comparing zooplankton, phytoplankton and microbial concentrations with and without ballast water treatment. The deliverable of this project will be the TREBAWA prototype for the on-board treatment of ballast water which is suitable for demonstration on a wider basis.

Theoretical studies

Several commercial software tools have been successfully employed to carry out CFD in cyclonic separator and UV chamber design. These include 'PHOENICS'[1] 'CFX'[2] and 'Fluent'[3]. Fluent was adopted for the current work and its effectiveness was assessed in meeting the main objectives. Numerical meshes representing each of the separator and UV chamber geometries were created using Fluent's GAMBIT preprocessor. Unstructured (tetrahedral) elements were employed to model the geometry. These elements were found to model the separator and UV chamber components more accurately than structured elements. The total number of computational cells making up a mesh typically ranged from 150,000 for straightforward single pipe geometries up to 500,000 for more complicated geometries. All the simulations were run on a Dell GX260 Pentium 4 PC machine and the convergence times varied from two to several hours depending on the mesh size. The fluid flow properties for each of the simulations involved typical values for sea water at 50F (ρ=1027.9 kg/m^3 and μ = 0.0014 kg/m-s).

A selection of separator geometries has been investigated. CFD predictions were carried out on several centrifugal separators. Some designs were based on those previously constructed and successfully employed onboard ship by OptiMarin [4].

The main objectives of the simulation work associated with the primary system were:

- To simulate the physical flow characteristics within various proposed designs and assess the effects on the flow field when modifying various geometric components.
- To assess the efficiency of various designs in removing particles of varying size by introducing them at the inlet and predicting their movement towards the outlet and drain exit.
- To provide the group with design recommendations based on the predictions obtained.

Ultraviolet light has been employed for many years to treat contaminated water due to its ability to have a detrimental affect on the DNA of harmful micro-organisms that may be present. It is essentially an environmentally friendly process without damaging side effects to the treated water. It is for this reason that UV light has been considered as a viable treatment for ballast water for many years. The main objectives of the secondary UV system investigation were:

- To produce a practical and efficient prototype UV treatment system to be employed in conjunction with a primary separation system for use onboard ship.
- To carry out design optimisation by taking a wide range of possible UV system geometries and simulating the physical flow characteristics within them using CFD.
- To focus on the most efficient system (or systems) and undertake construction and physical testing of the prototypes under laboratory conditions.
- To undertake sea trials of the chosen prototype system.

Experimental tests

First ballast water characterization procedure was prepared in order to identify all the required parameters for assessing the system performance. Analyses were made to the ballast water and the ballast tank sediments. Those ballast water analyses were performed by diffraction of laser beam, using samples from MV Jambo (Reederei Hesse) and from MV Roaz (Vinave).

An experimental platform has been designed and with the delivered cyclonic separators by OptiMarin several tests have been carried out. The experimental platform was tested with two different feeds:the harbour water in Bremerhaven and diatomaceous earth ($\rho = 2.6$ kg/m^3).

The feeding water passes through the centrifugal pump that transforms the pressure charge into velocity charge, allowing the centrifugal movement of the flow inside the separator. The feeding flow rate can be controlled by means of the rotameter and the bypass, so that it can be fixed at the wished value. The inlet flow passes through the cyclonic separator were it is separated in two streams: the sludge (separated solids) and the outlet of clean water. This separation always involves a pressure drop. The pressure is measured before the separator and after it, for both outlet streams, in order to determine the pressure drop.

Water samples have been collected during each test for two different intermediate values of the flow, after a stabilisation time: sample of clean water and sample of sludge. The samples were analysed in the laboratory in order to determine the particles separation efficiency .

Results

The results of the ballast water characterisation show (tables 1-2 and figures 1-4) that the *average particle diameter* for the samples analysed is placed in between 19 and 30 μm, while the values for the *sauter average* diameter are placed between 8 and 11 μm. In general, those values are smaller than foreseen and could present serious difficulties for the separation of the particles with the existing cyclonic separators, which can not separate particles with low density, such as ballast water particles, smaller than 50μm.

To ensure conditions, showing the characteristics of real ballast water, it was planned to conduct the experimental tests in the harbour of Bremerhaven, Germany.

Different types of cyclonic separators are under experimental tests in order to improve the performance of the separators as our aim is to remove the smaller particles.

Table 1. *Average diameter size of samples collected in MS* Roaz *(5/11/02).*

Sample	D[4.3] µm	D[3.2] µm
Sample 1- Bottle 1	19.66	10.10
Sample 2- Bottle 1	18.58	10.19
Sample 1- Bottle 2*	23.17*	10.93

Table 2. *Average diameter size of samples collected in MS* Jambo *(5/11/02)*

Sample	D[4.3] µm	D[3.2] µm
BW Sample	22.63	9.12
Sediments Sample	33.22	8.59

D[4.3] volume average diameter and D[3.2] Sauter average diameter (diameter in the surface)

Regarding the performance of cyclonic separator, the first tendencies are:

- the efficiency of removing particles >150 µm is very good
- the performance of the separator decreases by particles <50 µm. The performance is between 15 – 40 %.

The experimental tests results comply with the findings of the simulated cyclonic separators.

Over 20 separator simulations and over 75 UV chamber simulations were carried out (see figures 5 and 6). Simulations were obtained for designs similar to those that are currently commercially available and for designs that were proposed through collaboration with Willand UV Systems Ltd by drawing on their expertise in UV chamber design.

The CFD design optimisation has provided a useful insight into the possible behaviour of the separator and UV system when the geometry is modified. Modification is of little benefit however unless a proposed design can be practically employed onboard ship. For example, a 15° separator head angle necessitates a tall unit that is likely to be impractical for fitting onboard ship. Similarly, a 70° separator head angle would require a significant space requirement and material costs would increase significantly compared to the original 35° design.

The experimental tests are still running as the most efficient separator and UV system has to be found for the TREBAWA prototype. At this stage additional serious detailed results can not be published. Developments on the most important two units have been carried out but both units have not been tested together. After the implementation of the TREBAWA prototype more optimization will be needed, which will be done by conducting tests and a CFD simulation of the whole prototype.

Conclusions and Recommendations

CFD was proved to be a useful tool in the design optimisation of a ballast water treatment system for use onboard ship. The ‘Fluent’ package was proved to be a robust and easy to use tool for the current study. CFD has enabled the TREBABWA group to evaluate a wide range of centrifugal separator and UV chamber designs under varying conditions and to focus on the most favourable thus avoiding the need to construct numerous physical prototypes. This approach has helped to speed up the design optimisation process and reduce the overall project cost. A number of points can be made from the centrifugal separator optimisation:

- For separators to effectively move a large percentage of particles to the drain exit it is essential that they are employed at the correct scale and at the correct flow rate when installed onboard ship.

- CFD has effectively highlighted possible practical improvements that can be made to the original designs e.g. the movement of the flow restrictor and the positioning and size of the drain outlet.
- The simulations have highlighted geometric modifications that are likely to be detrimental to the separator design.
- The simulations have provided predictions of pressure drops for each design to enable running costs to be estimated.

Several conclusions were drawn from the UV chamber optimisation:

- The steady state, RTD and UV intensity map calculations have indicated that the 'inline' designs are likely to be the most favourable for use by the TREBAWA group and represent the most practical and economic solution for a UV chamber design.
- CFD has effectively highlighted possible unfavourable flow conditions such as short-circuiting and areas of stagnation.
- CFD has successfully shown the effects on the flow caused by changing the chamber geometry and by changing the lamp configuration.
- The simulations have provided useful comparisons of the pressure drop values between different designs enabling a comparison to be made of the possible running costs of each system.

In summary the experimental- and simulation results have shown promising results for the further development of the TREBAWA system. It is expected that the removal of the smaller particles can be achieved through the compilation of experimental and simulation results for the construction of the TREBAWA unit.

References

Holdo, A. 2001. Simulation of Ballast Water Treatment. *1st International Ballast Water Treatment R&D Symposium, IMO London 26-27 March 2001: Symposium Proceedings*. GloBallast Monograph Series No 5. IMO London. pp 151-161.

Wright, N.G. & Hargreaves, D.M. 2001. The use of CFD in the evaluation of UV treatment systems, *Journal of Hydrodynamics* Vol 3, pp. 59-70.

Lawryshyn, Y. A. & Dong Ming, L. 1999. Reactor Design: Its more than putting a lamp in a pipe, *Water Conditioning and Purification*, February 1999.

Nilsen, B., Nilsen, H. & Mackey, T. 2001. The OptiMar Ballast System, *1st International Ballast Water Treatment R&D Symposium, IMO London 26-27 March 2001: Symposium Proceedings*. GloBallast Monograph Series No 5. IMO London. pp. 126-136.

MALVERN INSTRUMENTS **MASTERSIZER X**

Version 1.2b — Tue, 12 12e Nov 12e 2002

ISQ/TREBAWA 5/11/02 :Run Number 2

Amostra frasco 1

Source: Analysed

Measured on: Tue, 12 12e Nov 12e 2002 1

Presentation: 2OHD
Polydisperse model

Volume Result

Focus = 300 mm.

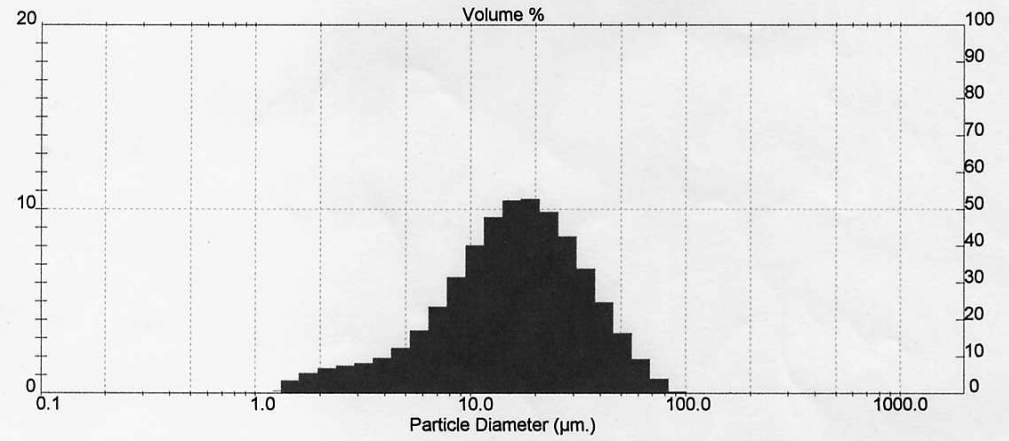
Residual = 0.175 %
d (0 .5) = 16.13 µm
D [4, 3] = 19.66 µm
Sauter Mean (D[3,2]) = 10.10 µm
Specific Surface Area = 0.5941 sq. m. / gm

Concentration = 0.020 %
d (0.1) = 4.94 µm
Span = 2.12

Obscuration = 14.27 %
d (0.9) = 39.10 µm

Mode = 17.20 µm
Density = 1.00 gm. / c.c.

Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
0.50	0.16	1.32	0.16
1.32	0.68	1.60	0.84
1.60	1.10	1.95	1.94
1.95	1.35	2.38	3.29
2.38	1.50	2.90	4.79
2.90	1.64	3.53	6.43
3.53	1.92	4.30	8.35
4.30	2.47	5.24	10.82
5.24	3.40	6.39	14.22
6.39	4.71	7.78	18.93
7.78	6.30	9.48	25.24
9.48	8.03	11.55	33.27
11.55	9.57	14.08	42.84
14.08	10.48	17.15	53.32
17.15	10.56	20.90	63.88
20.90	9.84	25.46	73.71
25.46	8.53	31.01	82.24
31.01	6.78	37.79	89.02
37.79	4.94	46.03	93.96
46.03	3.28	56.09	97.23
56.09	1.86	68.33	99.09
68.33	0.79	83.26	99.88
83.26	0.12	101.44	100.00
101.44	0.00	123.59	100.00
123.59	0.00	150.57	100.00
150.57	0.00	183.44	100.00
183.44	0.00	223.51	100.00
223.51	0.00	272.31	100.00
272.31	0.00	331.77	100.00
331.77	0.00	404.21	100.00
404.21	0.00	492.47	100.00
492.47	0.00	600.00	100.00



Malvern Instruments GmbH.
Herrsching Germany

MasterSizer X Ver. 1.2b
Serial No. 6543

p. 2
12 Nov 02 14:57

Figure 1. *Report of particle size distribution.*
Samples collected in MV ROAZ (Aveiro Harbour, 05.11.02).

MALVERN INSTRUMENTS **MASTERSIZER X**

Version 1.2b — Tue, 12 12e Nov 12e 2002

ISQ/TREBAWA 5/11/02 :Run Number 2

Amostra 2 frasco 1

Source: Analysed

Measured on: Tue, 12 12e Nov 12e 2002 1

Presentation: 2OHD
Polydisperse model

Volume Result

Residual = 0.433 %
d (0 .5) = 14.30 µm
D [4, 3] = 18.58 µm
Sauter Mean (D[3,2]) = 10.19 µm
Specific Surface Area = 0.5891 sq. m. / gm

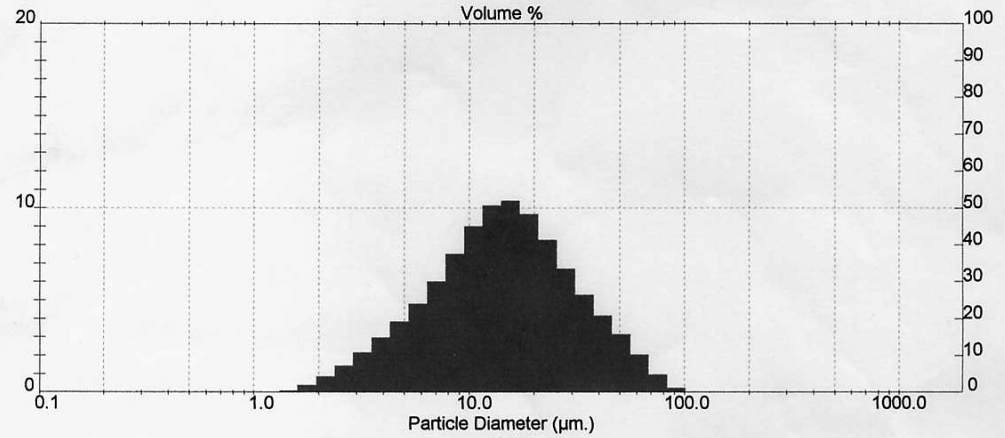
Concentration = 0.012 %
d (0.1) = 4.82 µm
Span = 2.37

Focus = 300 mm.

Obscuration = 8.41 %
d (0.9) = 38.67 µm

Mode = 14.95 µm
Density = 1.00 gm. / c.c.

Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
0.50	0.00	1.32	0.00
1.32	0.08	1.60	0.09
1.60	0.39	1.95	0.48
1.95	0.85	2.38	1.32
2.38	1.45	2.90	2.77
2.90	2.17	3.53	4.94
3.53	2.97	4.30	7.91
4.30	3.83	5.24	11.74
5.24	4.79	6.39	16.54
6.39	6.00	7.78	22.54
7.78	7.49	9.48	30.03
9.48	9.00	11.55	39.03
11.55	10.13	14.08	49.16
14.08	10.39	17.15	59.55
17.15	9.67	20.90	69.22
20.90	8.26	25.46	77.49
25.46	6.69	31.01	84.18
31.01	5.28	37.79	89.46
37.79	4.16	46.03	93.62
46.03	3.15	56.09	96.76
56.09	2.04	68.33	98.80
68.33	0.96	83.26	99.77
83.26	0.23	101.44	100.00
101.44	0.00	123.59	100.00
123.59	0.00	150.57	100.00
150.57	0.00	183.44	100.00
183.44	0.00	223.51	100.00
223.51	0.00	272.31	100.00
272.31	0.00	331.77	100.00
331.77	0.00	404.21	100.00
404.21	0.00	492.47	100.00
492.47	0.00	600.00	100.00

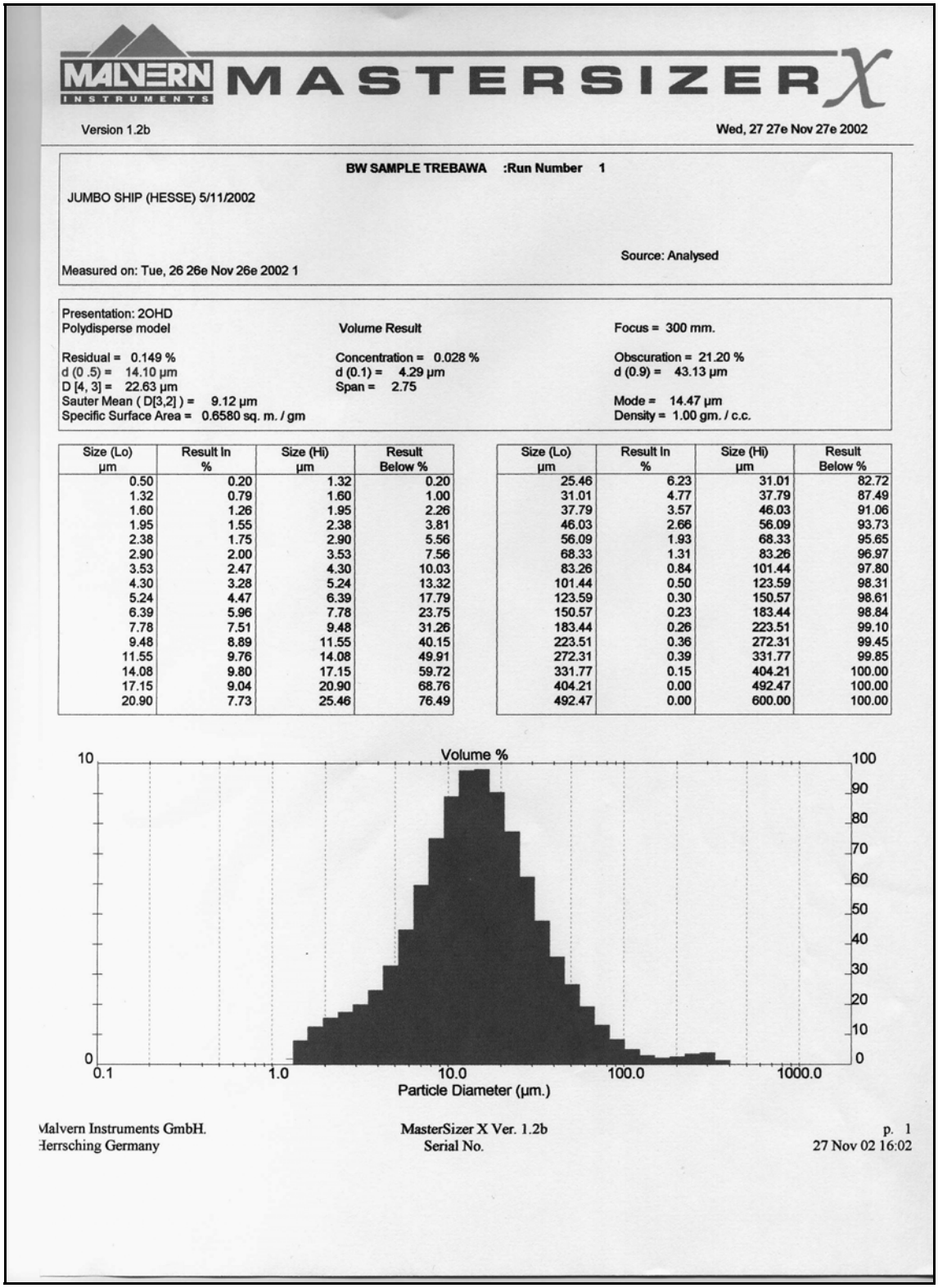


Malvern Instruments GmbH.
Herrsching Germany

MasterSizer X Ver. 1.2b
Serial No. 6543

p. 3
12 Nov 02 15:43

Figure 2. *Report of particle size distribution.*
Samples collected in MV ROAZ (Aveiro Harbour, 05.11.02).



MALVERN INSTRUMENTS MASTERSIZER X

Version 1.2b — Wed, 27 27e Nov 27e 2002

BW SAMPLE TREBAWA :Run Number 1

JUMBO SHIP (HESSE) 5/11/2002

Source: Analysed

Measured on: Tue, 26 26e Nov 26e 2002 1

Presentation: 2OHD
Polydisperse model

Volume Result

Residual = 0.149 %
d (0 .5) = 14.10 µm
D [4, 3] = 22.63 µm
Sauter Mean (D[3,2]) = 9.12 µm
Specific Surface Area = 0.6580 sq. m. / gm

Concentration = 0.028 %
d (0.1) = 4.29 µm
Span = 2.75

Focus = 300 mm.

Obscuration = 21.20 %
d (0.9) = 43.13 µm

Mode = 14.47 µm
Density = 1.00 gm. / c.c.

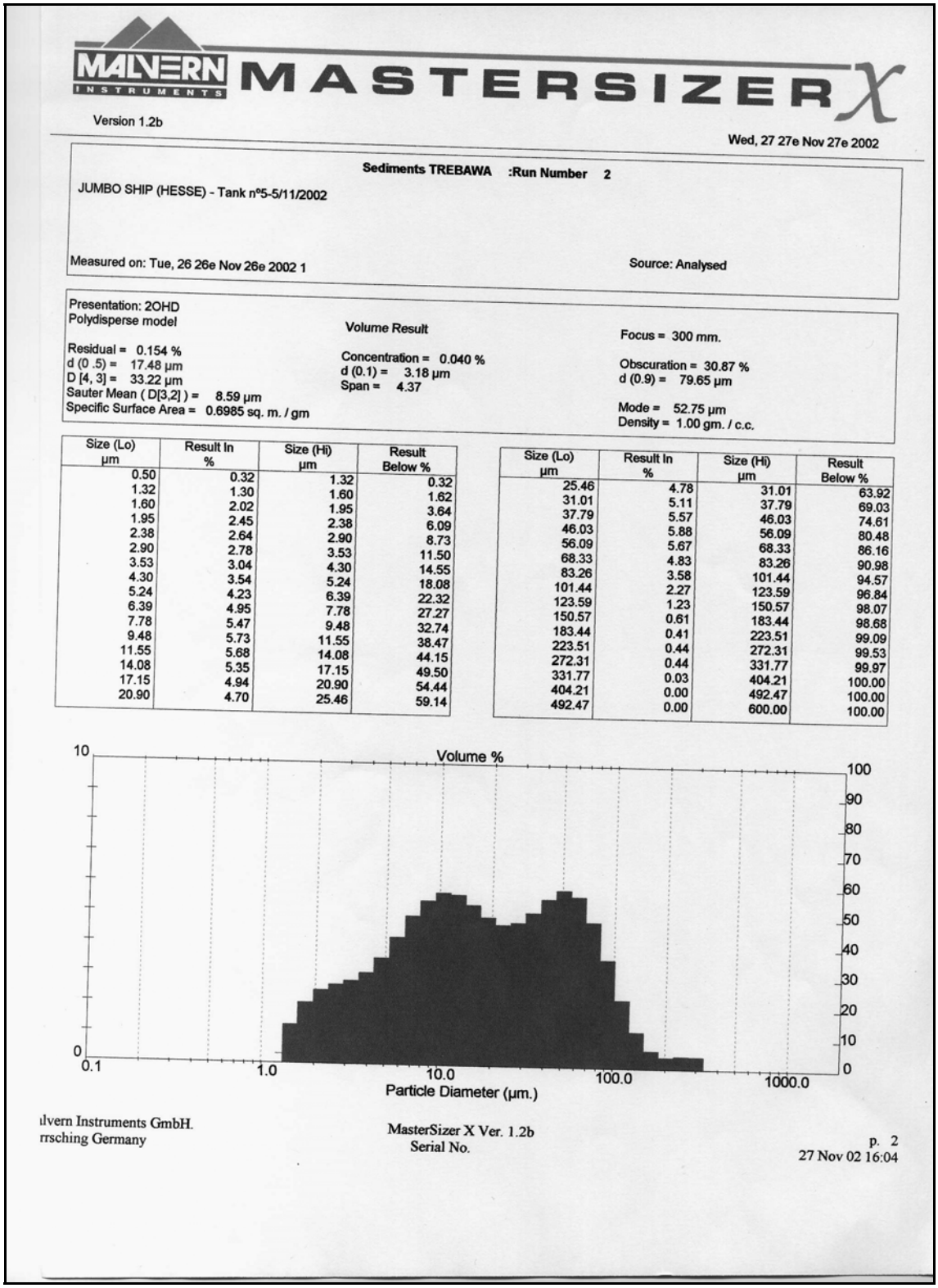
Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
0.50	0.20	1.32	0.20
1.32	0.79	1.60	1.00
1.60	1.26	1.95	2.26
1.95	1.55	2.38	3.81
2.38	1.75	2.90	5.56
2.90	2.00	3.53	7.56
3.53	2.47	4.30	10.03
4.30	3.28	5.24	13.32
5.24	4.47	6.39	17.79
6.39	5.96	7.78	23.75
7.78	7.51	9.48	31.26
9.48	8.89	11.55	40.15
11.55	9.76	14.08	49.91
14.08	9.80	17.15	59.72
17.15	9.04	20.90	68.76
20.90	7.73	25.46	76.49
25.46	6.23	31.01	82.72
31.01	4.77	37.79	87.49
37.79	3.57	46.03	91.06
46.03	2.66	56.09	93.73
56.09	1.93	68.33	95.65
68.33	1.31	83.26	96.97
83.26	0.84	101.44	97.80
101.44	0.50	123.59	98.31
123.59	0.30	150.57	98.61
150.57	0.23	183.44	98.84
183.44	0.26	223.51	99.10
223.51	0.36	272.31	99.45
272.31	0.39	331.77	99.85
331.77	0.15	404.21	100.00
404.21	0.00	492.47	100.00
492.47	0.00	600.00	100.00

Malvern Instruments GmbH.
Herrsching Germany

MasterSizer X Ver. 1.2b
Serial No.

p. 1
27 Nov 02 16:02

Figure 3. *Report of particle size distribution.*
Jambo ship (Hesse) - Tank n°5 - 5/11/02 - BW Sample.



MALVERN INSTRUMENTS MASTERSIZER X

Version 1.2b

Wed, 27 27e Nov 27e 2002

Sediments TREBAWA :Run Number 2

JUMBO SHIP (HESSE) - Tank nº5-5/11/2002

Measured on: Tue, 26 26e Nov 26e 2002 1

Source: Analysed

Presentation: 2OHD
Polydisperse model

Residual = 0.154 %
d (0 .5) = 17.48 µm
D [4, 3] = 33.22 µm
Sauter Mean (D[3,2]) = 8.59 µm
Specific Surface Area = 0.6985 sq. m. / gm

Volume Result

Concentration = 0.040 %
d (0.1) = 3.18 µm
Span = 4.37

Focus = 300 mm.

Obscuration = 30.87 %
d (0.9) = 79.65 µm

Mode = 52.75 µm
Density = 1.00 gm. / c.c.

Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
0.50	0.32	1.32	0.32
1.32	1.30	1.60	1.62
1.60	2.02	1.95	3.64
1.95	2.45	2.38	6.09
2.38	2.64	2.90	8.73
2.90	2.78	3.53	11.50
3.53	3.04	4.30	14.55
4.30	3.54	5.24	18.08
5.24	4.23	6.39	22.32
6.39	4.95	7.78	27.27
7.78	5.47	9.48	32.74
9.48	5.73	11.55	38.47
11.55	5.68	14.08	44.15
14.08	5.35	17.15	49.50
17.15	4.94	20.90	54.44
20.90	4.70	25.46	59.14

Size (Lo) µm	Result In %	Size (Hi) µm	Result Below %
25.46	4.78	31.01	63.92
31.01	5.11	37.79	69.03
37.79	5.57	46.03	74.61
46.03	5.88	56.09	80.48
56.09	5.67	68.33	86.16
68.33	4.83	83.26	90.98
83.26	3.58	101.44	94.57
101.44	2.27	123.59	96.84
123.59	1.23	150.57	98.07
150.57	0.61	183.44	98.68
183.44	0.41	223.51	99.09
223.51	0.44	272.31	99.53
272.31	0.44	331.77	99.97
331.77	0.03	404.21	100.00
404.21	0.00	492.47	100.00
492.47	0.00	600.00	100.00

ılvern Instruments GmbH.
rrsching Germany

MasterSizer X Ver. 1.2b
Serial No.

p. 2
27 Nov 02 16:04

Figure 4. *Report of particle size distribution.*
Jambo ship (Hesse) - Tank nº5- 5/11/02 - Sediments Sample.

Figure 5. *Selection of Centrifugal Separator geometries.*

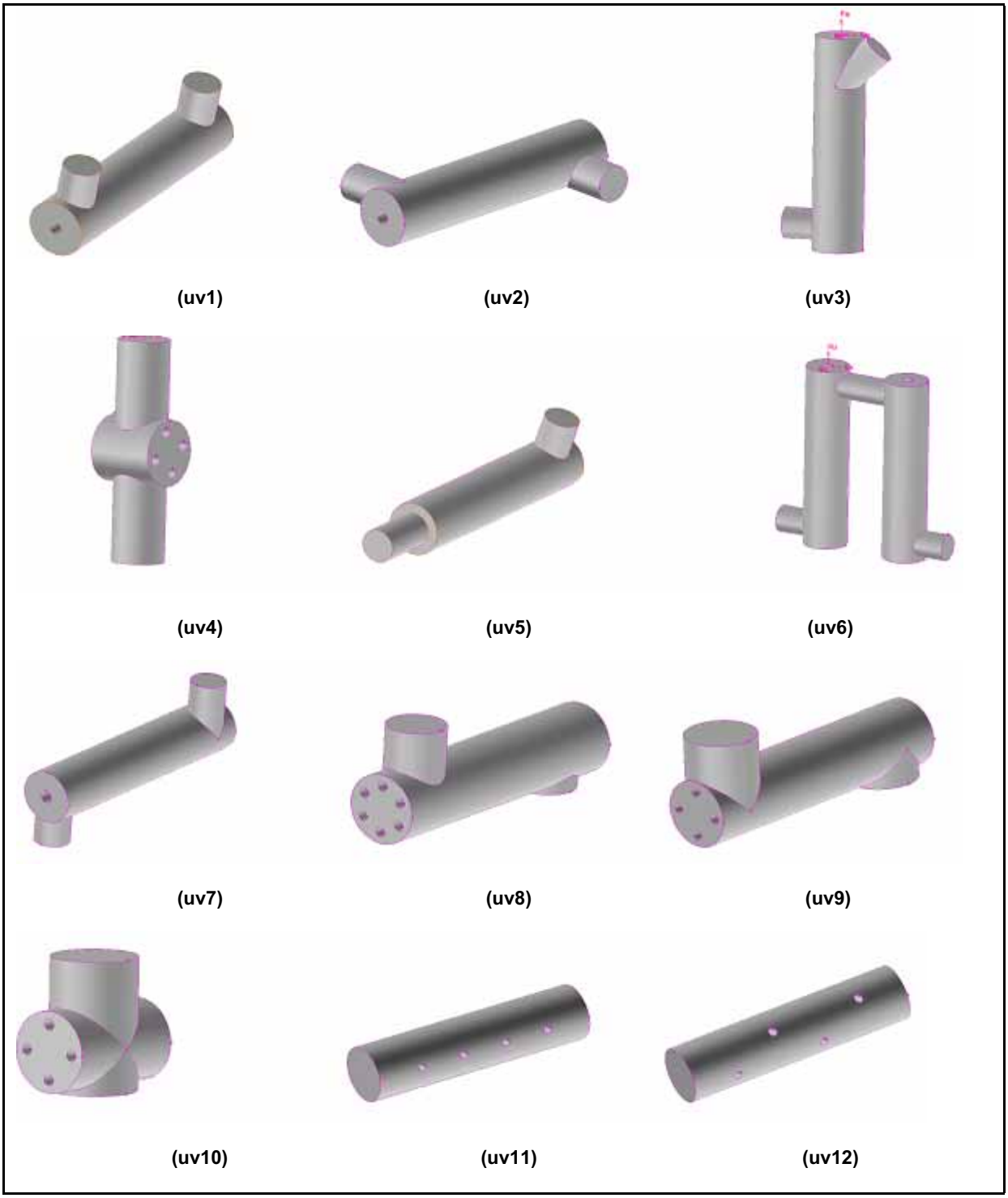


Figure 6. *Selection of UV chamber geometries.*

Some shipboard trials of ballast water treatment systems in the United States

D. A. Wright[1], R. Dawson[1], T. P. Mackey[2],
H. G. Cutler[3] & S. J. Cutler[3];

[1]*University of Maryland Center for Environmental Science, USA*
wright@cbl.umces.edu

[2]*Hyde Marine, Inc., USA*

[3]*Mercer University School of Pharmacy, USA*

Abstract

Full-scale ship trials of potential ballast water treatments were conducted aboard the Cape May, a ship of the U.S. reserve fleet under the auspices of the U.S. Maritime Administration (MARAD). The Cape May was berthed in Baltimore Harbor, near the Chesapeake Bay, on the east coast of the United States. Two biocides and an ultraviolet (UV) irradiation system were each tested singly. With correct dosing, biocide treatments resulted in the total eradication of zooplankton and phytoplankton. All three technologies were capable of effective removal (>95%) of planktonic organisms without the need for any primary treatment. This testing led to the development of two commercial ballast water treatments, one using one of the biocides (SeaKleen®) and the other using the UV technology in combination with a filtration primary treatment technology (tested separately).

Both systems will be further evaluated, both singly and in combination, in full-scale (3000 gpm) ship trials aboard the Cape Washington, a MARAD vessel located in Baltimore Harbor. Particular emphasis is being placed on demonstration of additive or synergistic effects of UV/biocide combinations and the ramifications for cost effectiveness. In addition, primary treatment of filtration to 50 microns is being examined to ascertain if economies may be realized in the use of biocide or UV. Further evaluation of the filtration/UV combination will be tested aboard Princess Cruises' Coral Princess.

Treatments

Mechanical: Separation, Filtration
Physical: UV irradiation
Chemical: Biocides
Hybrid systems: Multiple treatments used in combination

Timeframe

Present phase underway from 2001-2005

Objective

The purpose of this project is determination of the efficacy of various ballast water treatment technologies when used alone and in combination. Emphasis is on the identification of a comprehensive, versatile, effective and economical system that is of immediate practical use to the shipping industry.

Methodology

The experimental design of this project is intended to evaluate various ballast water treatment technologies under 'real world' conditions. After preliminary evaluations are performed in a laboratory setting, treatment technologies are placed aboard operational commercial vessels for rigorous and thorough analysis. The work described here is designed to test the efficacy of a primary mechanical treatment consisting of either separation or filtration, and secondary treatments consisting of ultra-violet (UV) irradiation either alone or in combination with various biocides.

Laboratory analysis is conducted at the University of Maryland's Chesapeake Biological Laboratory, a fully equipped research facility located in Solomons, Maryland. Shipboard trials are conducted aboard a variety of vessels including vessels belonging to the U.S. Maritime Administration (MARAD), and passenger cruise ships. Project vessels are selected for their potential to provide ballasting conditions representative of typical shipping operations in both scale and difficulty.

The sampling design is based upon the following treatments: A) primary treatment only, B) primary treatment + UV, C) primary treatment + biocide, D) UV only, E) biocide only, F) UV + biocide, G) primary treatment + UV + biocide. The test system incorporates multiple sampling ports providing the capability to simultaneously sample pre-treatment (raw) water, post-treatment water, and between-treatment water. Water samples are drawn before and after each stage of treatment and directed to triplicated banks of 200L polyethylene mesocosms, installed in the machinery space of the vessel, to be held for 24 and 48 hours. All samples from the mesocosms are compared with triplicate untreated controls. Treated and untreated water is also directed into different ballast tanks. The sampling and biological endpoint determinations determined below are those used aboard the MARAD ship *Cape May* in 2001 trials. See Figures 1 and 2. Some modifications to these methods were made for cruise ships and ongoing MARAD ship trials (e.g. no mesocosms: ballast tank sampling only).

Sampling protocols

Mesocosm and ballast tank samples

Mesocosms are filled from sampling ports located at strategic points in the treatment system and designed to supply water of different treatment status. They are maintained under dark conditions to simulate ballast water storage. Water samples are collected at 24 and 48 hour intervals following initial ballasting/treatment. All mesocosms are thoroughly mixed with a compressed air wand immediately prior to sampling. Ballast tanks are sampled either by lowering containers into the tanks or using submersible pumps. A 1L sample is taken for phytoplankton analysis, and 260 ml. taken for bacterial analysis (10 ml. for AODC and 250 ml. for culturable bacteria). The remainder (40-100 L) is filtered (20 μm) for zooplankton analysis. Another sample is analyzed for standard water quality parameters (salinity, temperature, pH, oxygen concentrations) as well as suspended particulate size distribution analysis using an Accusizer laser obscuration particle analyzer. Control samples are carried through the complete trial and analyzed for biological endpoints following dark storage.

Biological endpoint determinations

Zooplankton

Samples for zooplankton analysis are concentrated to obtain approximately 50 organisms per ml. subsampled in a circular, 'one-time' counting chamber. Selected subsamples are preserved in 0.1% Lugol's solution for possible further taxonomic identification. Representative organisms from at least 5 taxa are sized using a calibrated reticule eyepiece and records are made of live/dead counts. The efficiency of a treatment is determined by comparing counts of taxonomic groups with an untreated control sample. Overall removal efficiencies are calculated on the basis of total number of organisms counted vs. controls.

Phytoplankton

Extractable chlorophyll *a* fluorescence determination in treated and untreated ballast water is the core of the phytoplankton analysis. The fluorimeter used for analysis (Perkin Elmer 650-10 S) is equipped with monochromators for specific wavelengths (436 nm ex., 680 nm emm.) that read only emissions from chlorophyll *a* (Welschmeyer 1994). Whole water samples from ballast tanks are prefiltered through a 200 µm screen to remove larger zooplankton. Post-treatment and control water samples (500 ml.) are illuminated for 24 hours to examine capacity for cell doubling as determined by repeated extraction and measurement of chlorophyll *a*. The instrument is calibrated daily with accurate concentrations of chlorophyll *a* in ethanol.

Bacteria

Assessment of ambient bacterial populations are made using Acridine Orange Direct Counting (AODC), together with standard plate counts of cultural bacteria. Colony counts are made on treated and untreated samples following up to 72 hours incubation on Petri Pads impregnated with marine broth.

ATP analysis

(introduced in 2003 for cruise ship tests and ongoing studies aboard the *Cape Washington*).

Adenosine triphosphate (ATP) is an obligate constituent of all living organisms and analysis of ATP has long been performed by biologists to assess live (usually microbial) biomass. ATP is related to total microbial biomass by determining ATP and applying a well established, laboratory-derived conversion factor. Following death, ATP is rapidly converted to other phosphorylated compounds. Therefore ATP would be expected to be at a maximum prior to UV inactivation. In these studies ATP present in organisms is analyzed by filtration of the biota through a Whatman glass fiber filter and immediate extraction with boiling Tris buffer. ATP levels in UV-irradiated and control samples are determined using the firefly luminescence technique with the Deltatox analyzer operated in ATP mode (Karl 1993).

Particle size analysis

Particulate size distribution is determined by Fraunhofer laser diffraction using an optical particle sizer (Accusizer 770) fitted with a syringe injection sampler (Accusizer 770/SIS). Triplicate syringe pulls of 25 ml. volume from a vigorously stirred beaker are counted and averaged to display the particle size distribution either over the entire size range of the sensor (2 µm - 1000 µm) or selected size ranges at 5 µm intervals. Particle concentration distributions are expressed as counts per ml. All samples are analyzed aboard the vessel within two hours of sampling. The optical sensor is factory calibrated with NIST traceable standards and may be recalibrated on site if necessary.

Laboratory studies

In parallel with 2003/04 shipboard trials, laboratory studies are being carried out to test the hypothesis that combination of UV treatment and chemical biocide can lead to economies and benefits in the treatment of ships' ballast water. A benchtop UV system is used to irradiate seawater samples and organisms. The UV dose delivered at 254 nm is measured with a spectral radiometer. Calibration points include the following doses: 35 mWatt sec^{-1} cm^{-2} (the standard germicidal dose for many bacteria), 50 mWatt sec^{-1} cm^{-2} (usually sufficient to inactivate phytoplankton), 100, 150, and 200 sec^{-1} cm^{-2} (the range over which zooplankton and fish larvae are killed, based on data from previous studies, including the *Cape May* trials). Test organisms include *Vibrio fischeri*, a luminescent bacterium congeneric with *Vibrio cholera*, the basis of the Deltatox test (Azur International), a toxic strain of the dinoflagellate *Prorocentrum minimum*, the estuarine copepod, *Eurytemora affinis*, and sheepshead minnow (*Cyprinodon variegatus*) larvae.

Various analytical techniques are employed to determine degree of inactivation and/or mortality associated with these tests including acridine orange direct counts, chlorophyll *a*, and ATP analysis.

In parallel experiments, the chemical biocide SeaKleen® (primary active ingredient menadione) will be tested with the same species and employing the same end-points to obtain dose response curves and toxic thresholds. Once minimum lethal doses, of UV and biocide, have been established for the different test species, a matrix of combinations will probe synergistic effects. The order of treatment will also be a variable, i.e. experiments will be performed with UV irradiation either preceding or following chemical biocide treatment.

Shipboard studies

Based upon results of laboratory investigations, shipboard tests are performed aboard the MARAD ship *Cape Washington*, utilizing the most effective UV/biocide combination where UV irradiation precedes biocide dosing and the most effective biocide/UV combination where biocide dosing precedes UV irradiation. The experimental design follows that used in the 2001 shipboard experiments, with the addition of the ATP determination described previously.

In the absence of a successful trial of a primary treatment system in 2001, a depth filter (Arkal Inc.), supplied and installed by Hyde Marine Inc., will be tested as the primary treatment system. The experimental design allows for evaluation of UV or biocide treatments with and without 50 μm depth filtration.

Results

Note on centrifugal separator:

The centrifugal separator failed to operate during the 2001 test period. Reported to have been corrected, the separator is scheduled for re-testing in the fall of 2003. The focus of the 2001 investigation shifted to a determination of the maximum efficacy that could be provided by the secondary treatments alone. The question posed was: what was the minimum chemical or UV dose required to achieve the maximum kill rate without the assistance of any other technology?

A summary of the major findings from the 2001 portion of the project is given below, although a more detailed description of preliminary data appears in a November 2001 Interim Report to Maryland Port Administration, and a more extensive report is in preparation.

Peraclean Ocean® experiments

Zooplankton

Three experiments with Peraclean Ocean® were conducted during June 2001. The first experiment applied Peraclean Ocean® at doses of 400 ppm and 200 ppm, which resulted in > 95% zooplankton mortality. The second experiment applied Peraclean Ocean® at doses of 100 ppm and 50 ppm, which resulted in complete mortality of zooplankton with both doses. Repeat experiments at doses of 100 ppm and 50 ppm, using different ballast tanks, resulted in overall mesocosm mortalities of 98% and 100% at 100 ppm and 50 ppm respectively. See Figures 3a-f. Overall ballast tank mortalities were 96% and 54% for 100 ppm and 50 ppm respectively. Much of the inconsistency between experiments 2 and 3 was due to incomplete mortalities in protozoans seen in experiment 3. This taxon was not recorded in experiments 1 and 2.

Phytoplankton

Exposure of phytoplankton to Peraclean Ocean® doses of 400 ppm and 200 ppm resulted in complete bleaching of the chlorophyll *a* pigment with no growth whatsoever.

Bacteria

Success was achieved in controlling bacteria and will be presented in more detail by Dr. Fuchs at this symposium. See Table 1.

Table 1. *Peraclean Ocean® and culturable bacteria*

Colony Counts of treated and untreated (control) ballast water samples. *(TNTC = too numerous to count)*		
	Colony Count (24h)	Colony Count (48h)
Peraclean 400 ppm		
Straight mesocosms	2	0
Straight ballast tank	3	3
Control mesocosms	TNTC	TNTC
Control ballast tank	TNTC	TNTC
Peraclean 50 ppm		
Straight mesocosms	7	6
Straight ballast tank	TNTC	TNTC
Control mesocosms	TNTC	TNTC
Control ballast tank	TNTC	TNTC

SeaKleen® experiments

A synopsis of the results obtained with the biocide SeaKleen® is presented below; a more complete data set appears in the aforementioned reports.

Zooplankton

Three experiments on SeaKleen® were conducted during 2001. SeaKleen® was applied to mesocosms and ballast tanks, at doses of 1ppm and 5ppm. Dosing at 5ppm SeaKleen® resulted in complete mortality of all zooplankton examined after 24 hours. See Figure 4a. All developmental stages of copepod crustaceans showed 100% mortality at 1 ppm SeaKleen® after 24 hours, however other taxonomic groups showed incomplete mortality at this dose. See Figure 4c. Dosing with 2 ppm SeaKleen® resulted in overall zooplankton mortalities of 99% and 100% after 24 hours and 48 hours, respectively. See Figure 4b.

Phytoplankton

SeaKleen® was shown to be effective in controlling phytoplankton irrespective of cell densities at all concentrations tested. See Table 2.

Table 2. *SeaKleen® toxicity to phytoplankton*

Effect of SeaKleen® on phytoplankton. Chlorophyll a expressed as µg Chl a L-1 ± S.D.						
	Controls 24h	Controls 48h	1ppm SeaKleen 24h	1 ppm SeaKleen 48h	5 ppm SeaKleen 24h	5 ppm SeaKleen 48h
Before fluorescent illumination	34.2 ± 0.7	27.9 ± 2.5	12.6 ± 0.32	9.7 ± 0.3	12.3 ± 0.4	5.1 ± 0.3
After 24h fluorescent illumination	30.6 ± 1.1	26.4 ± 2.6	6.8 ± 0.3	5.1 ± 0.3	6.5 ± 0.6	4.4 ± 0.6

Bacteria

Laboratory studies have shown that low ppm concentrations of menadione are effective in controlling several microorganisms, including *E.coli* and *Vibrio fischerei,* as well as impacting overall acridine orange direct counts (Cutler pers. com., Wright/Dawson Cape May results).

Samples analyzed from mesocosms and ballast tanks, based on plate counts, did not present a clear picture largely due to the latent release of bacteria from decaying phyto-zooplankton.

Ultraviolet irradiation experiments

Zooplankton

Two experiments were completed at a nominal UV dose rate (200 mW sec^{-1} cm^{-2} at 1450 gpm). The ambient estuarine water in Baltimore Harbor was measured for UV (254 nm) transmission periodically, and was always in excess of 90%, measured over a 1 cm path length. True dosing was seen to be closer to 180 mWatt sec^{-1} cm^{-2}, when corrected for UV transmission). At this dose zooplankton mortalities averaged better than 95% in both mesocosms and ballast tanks. See Figures 5a-d.

Phytoplankton

UV irradiation at 180 mWatt sec^{-1} cm^{-2} resulted in greatly reduced phytoplankton growth relative to unexposed control water. Results are presented for water samples taken immediately following treatment and for samples taken after a 24-hour illuminated grow out period. See Table 3.

Table 3. *UV treatment of phytoplankton*

Effect of UV irradiation on phytoplankton. Chlorophyll a expressed as µg Chl a L-1 ± S.D.				
	Controls 0h	Controls 24h	UV 0h	UV 24h
Before fluorescent illumination	6.1 ± 0.1	5.0 ± 0.2	5.6 ± 0.2	4.2 ± 0.2
After 24h fluorescent illumination	9.2 ± 0.2	7.5 ± 0.1	4.6 ± 0.1	3.6 ± 0.1

Bacteria

Counts of cultural bacteria were usually much higher in UV-treated samples compared with untreated (control) samples. We concluded that the increase in bacterial numbers resulted from the destruction of phytoplankton and zooplankton providing increased nutrient levels for both free-living bacteria and endogenous bacteria released from decomposing metazoan organisms. See Table 4.

Table 4. *UV and culturable bacteria*

Colony Counts of UV-treated and untreated (control) ballast water samples. (TNTC = too numerous to count)		
	Colony Count (24h)	Colony Count (48h)
Test No. UV1		
UV-treated mesocosms	ca. 5000	ca. 3000
UV-treated ballast tank	ca. 2000	ca. 1330
Control mesecosms	18	76
Control ballast tank	185	ca. 2000
Test No. UV2		
UV-treated mesocosms	TNTC	TNTC
UV-treated ballast tank	100	270
Control mesecosms	340	20
Control ballast tank	800	510

Conclusions and recommendations

Biocides

There have been two distinct classes of biocides proposed to treat ballast water. These can best be described as inorganic oxidants (H_2O_2, Cl_2, peracetic acid, Br, O_3, $K_2S_2O_8$) and organic oxidants such as quinones (e.g. menadione; active ingredient in SeaKleen®). The first class can be classified as indiscriminate oxidants because they react with carbon and organic matter in general and, to varying degrees, with metals. Peracetic acid (Peraclean Ocean®), used in trials aboard the *Cape May*, is a good example of the first class. While it was evident that in mesocosm tanks (plastic), levels of biocide of 100 ppm and lower were effective in controlling zooplankton, data from ballast tanks (metal) indicated a slightly lower degree of effectiveness and, analogous to chlorination practices, it is clear that residual oxidant levels are important in metal ballast tanks. Organic oxidants, such as the menadione (vitamin K3) used in the SeaKleen® formulation, are selective for cellular structures and, via futile redox cycling reactions, repeatedly oxidize tissues and membranes (O'Brien 1971). In fact, many such organic oxidants, particularly the quinones, have been investigated in tumor and cancer research because of their unique targeting properties. SeaKleen® does not seem to be consumed via oxidation of metals and corrosion studies (results not included here) have shown SeaKleen® in seawater to be no more corrosive to bare steel than seawater alone.

Measurement of growth potential through chlorophyll *a* determination represents a robust and convenient method for assessing the efficacy of a particular ballast treatment in controlling natural phytoplankton assemblages. While a healthy phytoplankton population might be expected to double in a 24-48 hour period, a substantially lower rate of doubling indicates inhibition resulting from toxicity or a limiting resource. In the experimental design used here, untreated samples serve to control for any limiting resource unrelated to the ballast water treatment itself. However, dark exposure itself probably contributes to lack of growth potential depending on the initial densities of phytoplankton. Interestingly, control water samples taken after 24 hours and subjected to further irradiation showed no sign of growth. In the SeaKleen® experiment reported here, control phytoplankton standing crop declines 18% and 42% between 24 and 48 hours, respectively. Control samples collected at 24 and 48 hours showed no capacity for growth under fluorescent light (10.6% and 5.3% loss in chlorophyll *a* respectively). It may be concluded from these results that, even without treatment, a dark ballast tank represents an inhospitable environment for free-living phytoplankton. And certainly, following biocide treatment, natural phytoplankton populations are much more severely inhibited than controls. Also, there is little difference between the effects of SeaKleen® on phytoplankton whether sampled in ballast tanks or dark mesocosms.

UV Irradiation

UV irradiation has been the subject of laboratory and pilot testing on a range of marine organisms with relatively positive results (Wright and Dawson, 2000). UV works by damaging parts of organisms' DNA. The biological effect depends on the dose, expressed as mWatt sec^{-1} cm^{-2} and is dependent on power, exposure surface, flow rate and distance from the UV source. With the correct dose of UV, viruses, bacteria, and most types of zooplankton and phytoplankton can be killed or rendered nonviable.

The results of UV irradiation testing, without pretreatment, indicate that medium pressure UV (200 mWatt sec^{-1} cm^{-2}) reduced viable zooplankton by better than 95%. Phytoplankton growth was arrested relative to untreated control water. With the addition of effective pretreatment to remove larger, more UV resistant organisms, consistent mortality of organisms in excess of a 95% standard should be possible.

Development of commercial Ballast Water Treatment (BWT) systems

As a result of the research and testing on both SeaKleen® and medium pressure UV irradiation conducted aboard the *Cape May* , and of separate full-scale testing of solids separation and UV

systems and components aboard several ships and a barge, two commercial ballast water treatment systems have been developed. The SeaKleen® biocide is undergoing EPA registration and is awaiting testing approval from several states in the U.S. It is expected that full-scale testing on operating tank vessels will begin in 2003. A Hyde Marine BWT system, incorporating disk filtration (Arkal) and medium pressure UV (Aquionics), was recently installed aboard Princess Cruises' *Coral Princess*. Testing of the system is expected to commence in the fall of 2003.

Performance of shipboard BWT systems is based upon biological effectiveness, cost effectiveness, and adaptability to the ballast pumping and piping systems on ships. SeaKleen®, is intended for ships with large ballast water volumes such as bulk carriers and tankers. The filtration and UV irradiation BWT system is intended for ships with ballast water flow rates up to approximately 1000 m^3/hr. Larger flow rates are possible, but the system would consume a very large amount of electrical power and could be subject to space limitations. The development of both systems continues as part of a University of Maryland research program designed to improve both performance and economic effectiveness. Testing of SeaKleen® will include determining the benefits of pretreatment by filtration, UV irradiation and other technologies to reduce the chemical dosage required. Testing of the filtration and UV system will attempt to determine the most synergistic combination of filtration level and UV dose to improve efficiency and adaptability to new and existing ships.

Development of SeaKleen® treatment system

SeaKleen® can be used without pretreatment. Testing to date has indicated it will be effective at dosage rates of 1.5 ppm to 2 ppm. Application requires mixing with water just prior to use, as biodegradation of SeaKleen® begins as soon as it is mixed with water. Injection of precise amounts of SeaKleen® would be accomplished using conventional dosing pumps to feed the chemical at proportional rates to the ballast water flow into the ballast pump(s) discharge piping. Sediments do not greatly affect the performance of SeaKleen® (particularly compared with indiscriminant inorganic oxidants and hydrophobic compounds) and it is not corrosive. No special materials are required for the dosing system, and many ships already meter chemicals into their ballast tanks. The environmental degradation of SeaKleen® has been the subject of several investigations (and will be presented by Dr. Cutler) and was a regulatory requirement of the Cape May study. See Figures 9a-f.

It is expected that the cost of SeaKleen® will be 10-20 cents per tonne of ballast water treated. For ships with very large ballast volumes and relatively frequent ballasting and deballasting, this could lead to significant costs over the lifetime of the ship, in addition to a low initial capital expenditure. Future research on the application of SeaKleen® will focus on pretreatment methods to reduce the required chemical dosage. Shipboard trials of SeaKleen®, aboard bulk carriers working in Puget Sound, Washington, are planned for late 2003.

Development of filtration and UV systems

Independent of the Cape May testing, three full-scale Ballast Water Treatment (BWT) Systems were installed on cruise ships, one on a Panamax container ship and one on a parcel tanker during 2000 and 2001. These systems ranged from 200 to 350 m^3 hr^{-1} ballast water flow rate and included cyclonic separation of solids as a pretreatment during ballasting and low pressure UV treatment (100 to 125 mWatt sec^{-1} cm^{-2}) during both ballasting and deballasting. Testing both on board ship and aboard the Great Lakes Ballast Technology Demonstration Project (GLBTDP) test barge indicated that cyclonic separation is not an effective means of removing larger organisms from ballast water. Additional information on such systems may be found in: Parsons and Harkins 2001, Parsons 2003; Cangelosi et al. 2001; Mackey 2001. The current design philosophy for modern UV/filtration systems is further described in Mackey and Wright (2002).

There has been a widely held belief that particle separation by filtration or centrifugal separation may improve UV transmission and several projects have sought to compare the effect of UV treatment with and without separation. Turbidity is rarely the limiting factor for UV transmission, although it can be during an extreme red tide event. Molecular absorbance of dissolved organic matter, on the

other hand, can have dramatic impact on UV penetration (ex: Duluth Harbor) and no amount of physical separation will improve transmission. Efforts to remove particulates using back-flush filter screens, voraxial separators, or hydrocyclones have shown little or no success. Efforts to reduce turbidity in hopes of aiding secondary treatment of either UV or biocide, have not demonstrated significant results. Several modern biocides have a low affinity for binding with particulates, therefore the argument that turbidity consumes these biocides seems misguided. No currently available separators remove small zooplankton or phytoplankton.

In the case of UV treatment, there does not seem to be a strong correlation between UV treatment effectiveness and organism size, however, shelled organisms (bivalves) and those with highly protective carapace pigments (some crustaceans) are noticeably more resistant. The argument may be made that effective filtration (e.g. down to 50 μm) might remove a substantial fraction of organisms in this category, however, attempts to demonstrate complimentary benefits of physical separation and secondary treatment have been confusing, given the current state of available technology. It is also clear that a quantum leap in the performance of UV systems is necessary to effectively and economically achieve the doses required to treat ballast water flow rates in excess of 3,000 gpm. In the future, this may be possible with the use of higher efficiency excimer UV systems (Coogan et al. 1999) but expense remains an issue, particularly if multiple units are employed. The current test platform, MARAD's *Cape Washington,* has ballast pumps rated at 3,000 gals min^{-1}. These pumps will be used in 2004/05 to test the efficiency of two 32 kW UV systems mounted either in series or in parallel. In series mounting will test the as yet unproven concept that UV irradiation can be additive where higher ballasting rates and multiple systems are involved.

Combination UV/biocide treatment systems

To our knowledge, there have been no serious attempts to combine UV and chemical biocide treatments in order to examine synergistic or complimentary effects, although waste-water and pulp mill effluents have been successfully treated with a combination of UV and peroxide. This combination increases the oxidation potential via formation of hydroxy radicals. In the case of organic biocides, we have a little or no information as to whether a UV toxic stress to an organism results in enhanced susceptibility to chemical toxicity or conversely if sublethal biocide toxicity compromises an organism's susceptibility to UV. An additional benefit of a combination biocide and UV treatment may result in an enhanced degradation of the biocide post treatment and, hence, a reduction in the holding time prior to safe discharge. In view of foregoing considerations, a comprehensive appraisal of UV/biocide combinations is the focus of our 2003/2004 studies. We hypothesize that exposure to one treatment may sensitize organisms to the other treatment and that such combination treatments may offer economies in both UV dose and biocide application. Initial laboratory studies are well underway at the time of writing. Planned ship-scale test platforms include two MARAD vessels; the *Cape Washington*, recently returned from the Middle East and currently berthed in Baltimore and a fully refurbished liquid containment barge, presently located in Virginia but available for relocation to Baltimore.

References

Cangelosi, A et al., *GloBallast Symposium and Workshop Submission*, March 26-30, 2001.

Cooghan, J.C. Byssing, A., Morgan, G.L., Barracato, J., Dawson R. & Wright D.A. 1999. *UV disinfection of ballast water: effects of organism size on system scaling*. National Conference on Marine Bioinvasions. Massachusetts Institute of Technology, Cambridge, MA. January 24th - 27th, 1999.

Karl, D.M. 1993. Total microbial biomass estimation derived from the measurement of particulate adenosine-5? -triphosphate. In: Kemp, P.A., Sherr B.F. & Cole J.J. (eds.). *Handbook of Methods in Aquatic Microbial Ecology*. Lewis Publ., Boca Raton, Fl.

Mackey, T.P. 2001. Ballast Water treatment Technologies: Including a review of Initial Testing and Lessons Learned Aboard the Regal Princess, *Marine Environmental Technology Symposium 2001: Engineering for a Sustainable Marine Environment* CD ROM Session A2, May 31 – June 1, 2001.

Mackey, T.P. & Wright, D.A. 2002 *A Filtration and UV based ballast water treatment technology: Including a review of initial testing and lessons learned aboard three cruise ships and two floating test platforms*, ENSUS 2002, Marine Science and Technology for Environmental Sustainability, Univ. of Newcastle upon Tyne UK and EU MATOB Project, 16, 17 and 18 December 2002.

O'Brien, P.J. 1971. Molecular mechanisms of quinone toxicity. *Chem. Biol. Interactions*. 80, pp. 1-41.

Parsons, M.G. & Harkins, R.W. 2002. Full-Scale Particle Removal Performance of Three Types of Mechanical Separation Devices for the Primary Treatment of Ballast Water, *Marine Technology*, Vol. 39, No. 4, pp. 211-222.

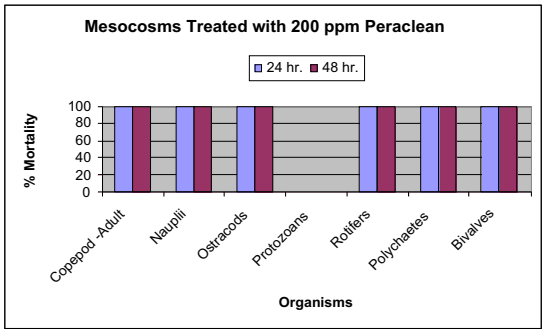
Parsons, M.G. 2003. Considerations in the Design of the Primary Treatment for Ballast Systems, *Marine Technology*, Vol. 40, No. 1, pp. 49-60.

Welschmeyer, N.J. 1994. A fluorescence based approach for determination of chlorophyll a without interference from phaeopigments. *Limnol. Oceanogr* 39: pp. 1985-1992.

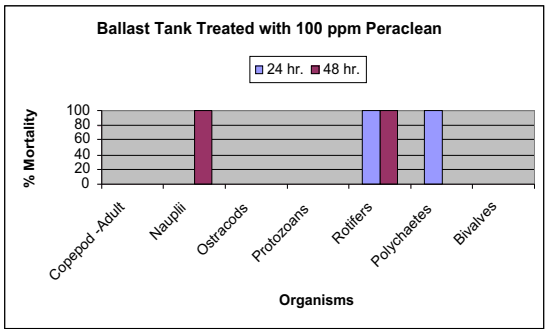
Wright, D.A. & Dawson, R. 2000. *International control of non-indigenous species*. Presentation at 3rd International Congress of the Society for Environmental Toxicology and Chemistry. Brighton, England. May 21st - 25th, 2000.

Figure 1. *Cape May.*

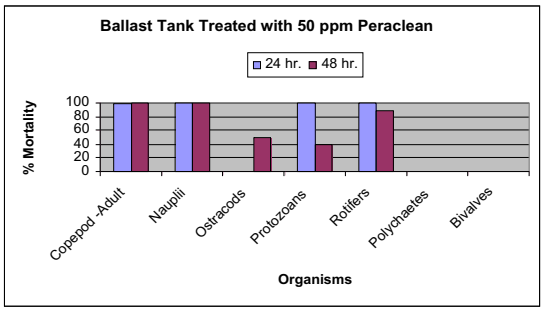
Figure 2. *Cape May.*



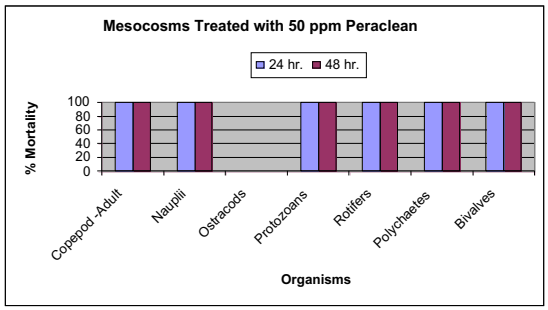
(a)



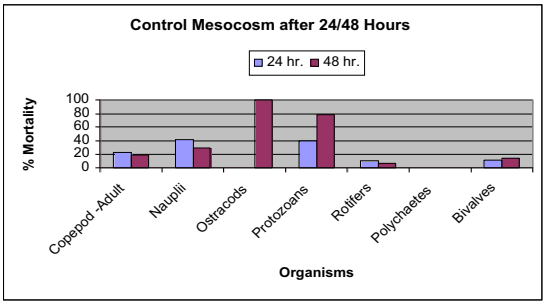
(b)



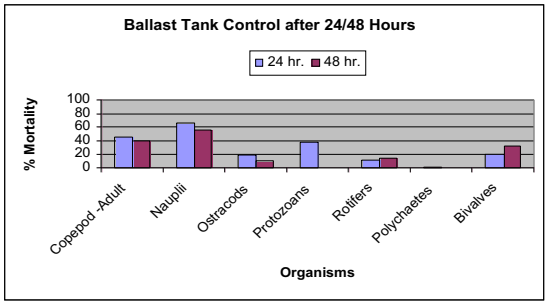
(c)



(d)



(e)



(f)

Figure 3. *Effect of Peraclean Ocean ® on zooplankton.*

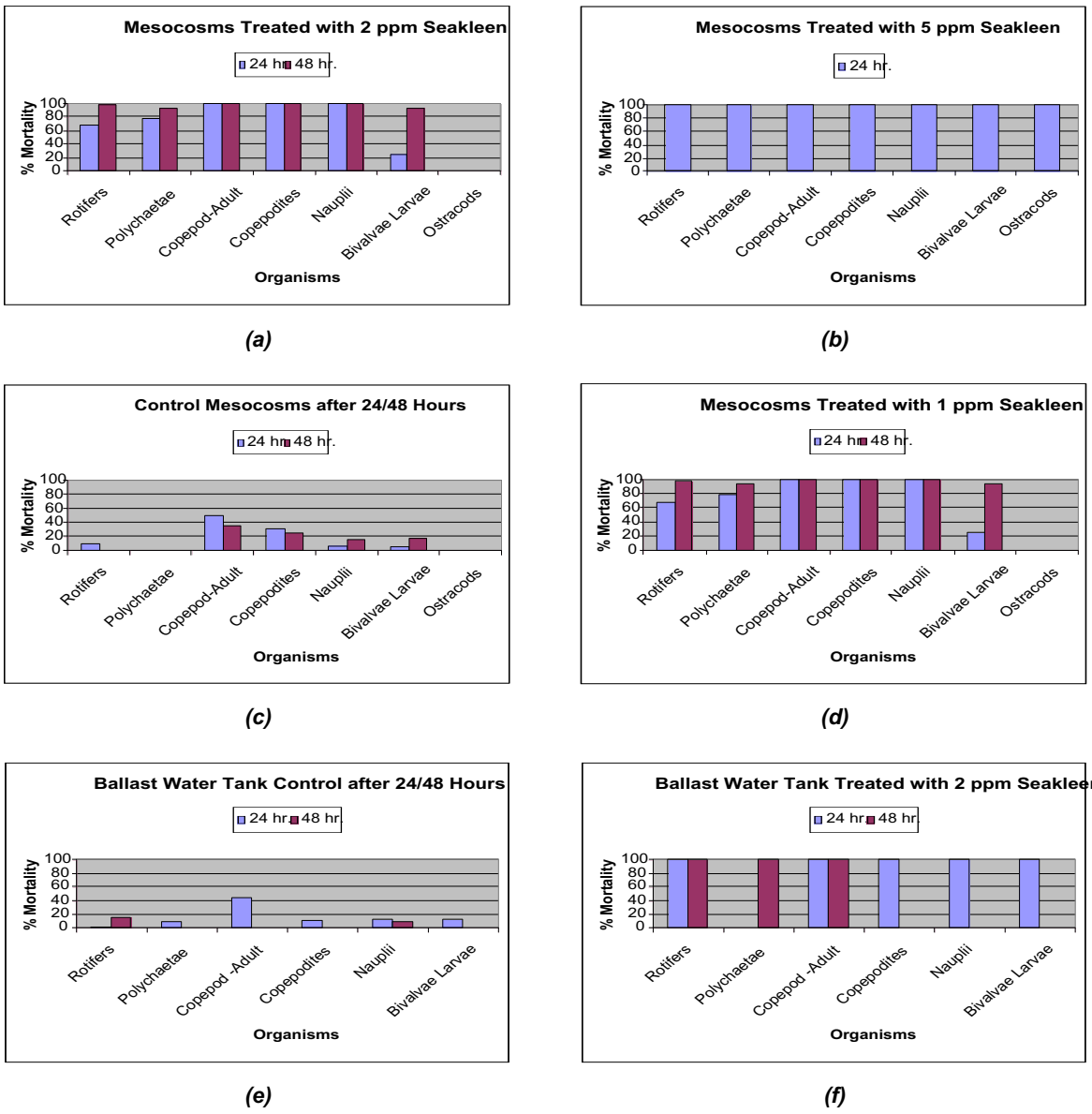


Figure 4. *Effect of SeaKleen® on zooplankton.*

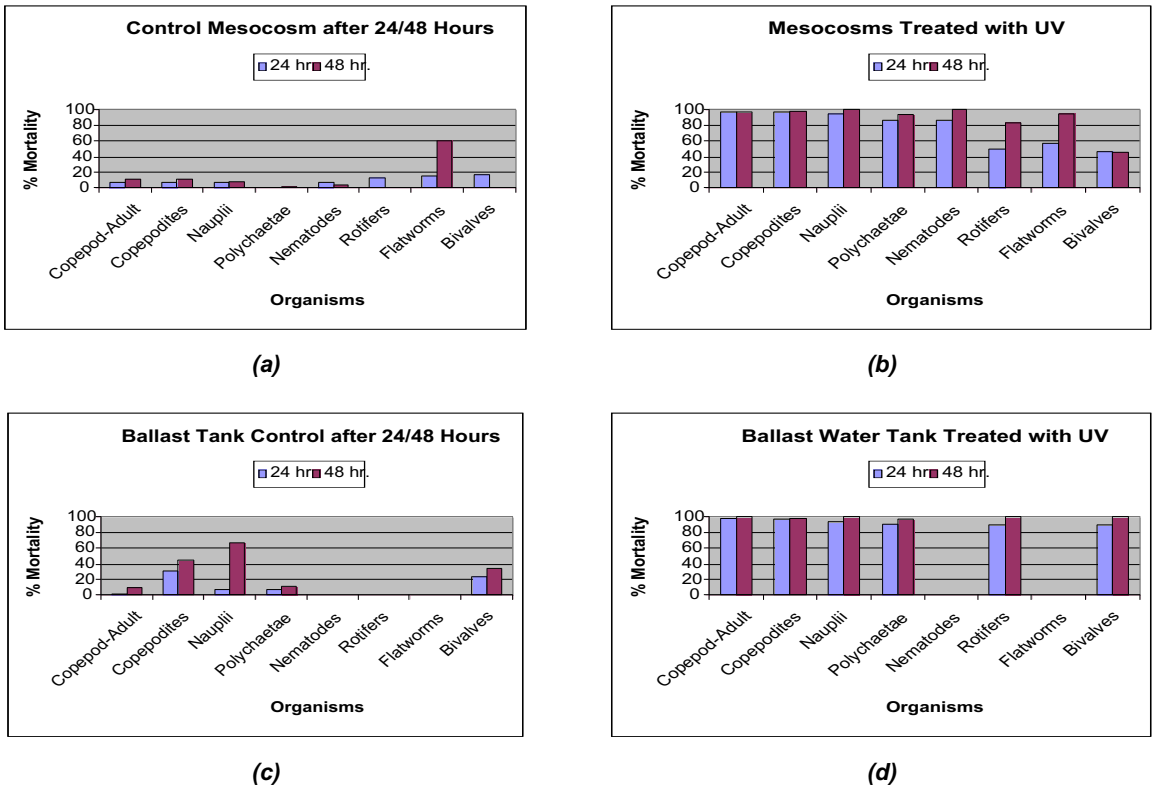
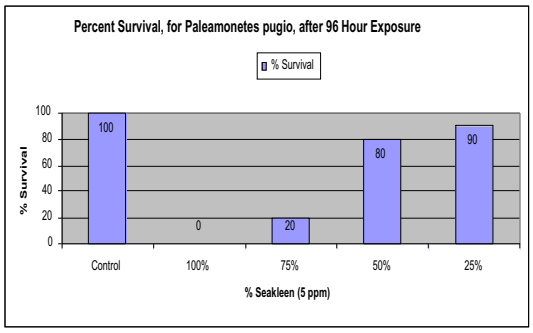


Figure 5. *Effect of UV on zooplankton.*

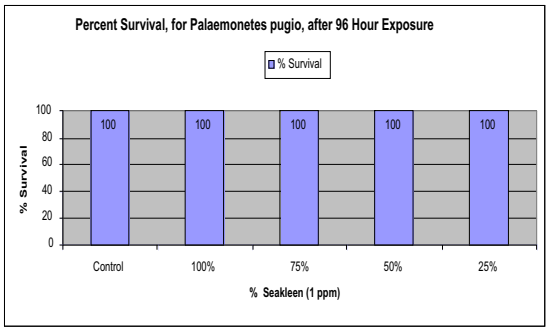
Figure 6. *Coral Princess.*

Figure 7. *Arkal Galaxy Filter, Coral Princess.*

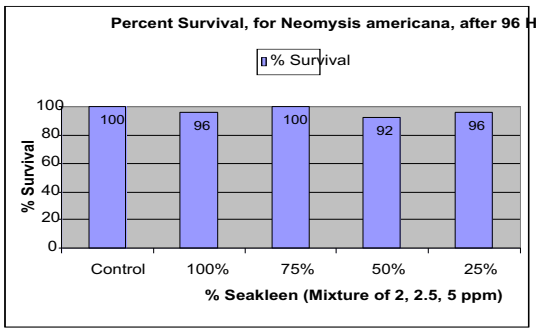
Figure 8. *Aquionics UV Chamber, Coral Princess.*



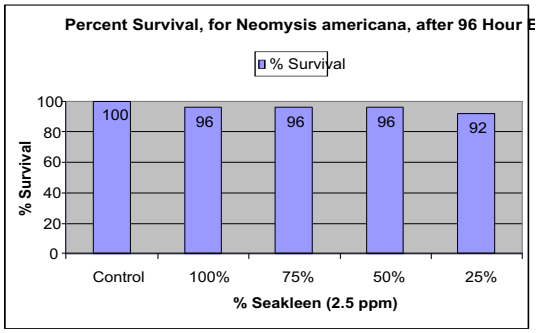
(a)



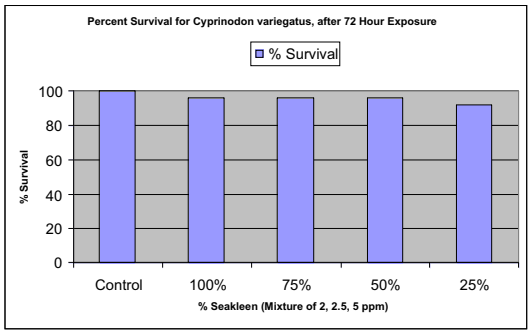
(b)



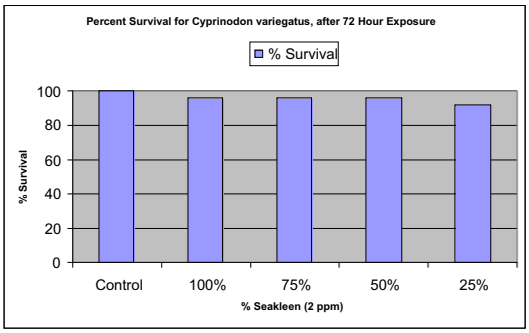
(c)



(d)



(e)



(f)

Figure 9. *Regulatory discharge survival assay.*

Figure 10. *Cape Washington.*

Figure 11. *Liquid containment barge.*

Development and design of process modules for ballast water treatment on board

A. Kornmueller

Berkefeld Water Technology, Germany
a.kornmueller@berkefeld.de

Treatment options being researched

Various processes have been suggested for ballast water treatment (BWT) in the last years (IWACO 2001). Overall solutions are hard to meet due to the complexity in design specifications, which are caused predominantly by the variation in the water quality, the technical demands and the specific requirements by different vessels. Berkefeld Water Technology and its subsidiary RWO Marine Water Technology are developing new ballast water treatment systems for use onboard ships, which include particle separation and disinfection steps. Intentionally a concentration on just one treatment solution is avoided. Different treatment options are investigated, which enables a modular design and adaptation to each kind of vessel in accordance with the biological, chemical and technical constraints. Besides the prevention in the introduction of harmful aquatic species, the BWT solves the problem of sediment accumulation in ballast water tanks by a mechanical separation as the first step.

Timeframe of the project

In the scope of the program "Shipping and marine technology for the 21st century" the R&D-project is under investigation since Oct. 2002 and will be funded by the Ministry for Research and Technology (Germany) until the end of 2004.

Aims and objectives of the project

The R&D-project is entitled "Basic examinations of the biological, chemical and physical characteristics and loadings of ballast water and the design of process modules for its treatment and disinfection onboard". The aim of the project is the development of efficient and cost-effective modular process combinations for ballast water treatment onboard. Therefore, a parallel approach is applied by basic evaluation and practical examinations. The basic evaluation includes the biological/aquatic and chemical/physical water characterization, and sets a special focus on the basic conditions by different vessels (such as type, construction and operation). A comprehensive survey of these influencing parameters results in the definition of requirements on BWT and the development of system specifications. After the identification and comparison of different treatment options, which are available in the market and research, suitable processes are studied experimentally for sediment and organism removal followed by disinfection. From the beginning a modular design is considered, which is a precondition for the adaptation of BWT systems to each kind of vessel.

Research methods, test protocols and experimental design

The following methodologies are applied in preliminary basic evaluation, which includes the desk based review like:

- literature and internet inquiry,
- communication with organizations, authorities, research institutes and companies,
- field examinations (like ballast water sampling) to complement existing data

- and the assignment of different research institutes and companies to attribute their special expertise.

Within the scope of the experimental examinations a test plant for sediment removal is designed, which will be upgraded stepwise to different BWT options and described later in detail. Two parallel test lines are installed to examine the reproducibility of the same equipment and the direct comparison of different processes. A significant statistical component is necessary in the test procedure and water analysis for the assessment of test data. In particular, time profiles have to be determined, because the water used as influent to the plant is varied by the tide. Due to the different water qualities and salt contents found globally, the performance of the test plant has to be verified at different locations reflecting these variations.

This project takes part in an expert group of participants from German R&D-projects, which works on land-based type approval tests for BWT systems (Voigt at al. 2003). Certainly its outcome resulted in our own testing protocols, such as sampling procedure, selection of test organism and test water characteristics.

Results

Ballast water treatment is limited by specific characteristics and conditions. Its complexity is given by the global variation in the biological and chemical/physical water characteristic, the high technical demands and efficiencies, the requirements by vessel construction and operation as well as different national and international regulations and legislations.

Chemical and physical water characterization

Very small information is available on the chemical and physical characteristic of water used as ballast. This includes fresh, brackish and sea water depending on the location of ballasting and the vessel route. The concentrations of some water parameters are known by en-route and end-point sampling of ballast water tanks or by monitoring of harbour water. A comprehensive and publicly available database does not exist yet. Monitoring programs often concentrate only on few, mainly physical water parameters. Therefore it has to be stressed, that various water parameters and impurities may have an influence on the performance of different treatment processes. For example the iron content is normally not included in monitoring programs, but has an important influence on the efficiency in disinfection due to precipitation on UV-lamps. Even extreme water conditions, like algae blooms or dispersed sediments by vessel propellers nearby intake, have to be accomplished by a BWT system. Therefore, the influence of different water parameters is defined on the performance of possible treatment processes within this R&D-project. Concentrations of decisive water parameters are collected from the literature and authorities to give a comprehensive, global overview in their variations and to define limitations on treatment performances. This data collection is ongoing and will be published later.

Biological water characterization

The biological basics of organisms and their invasion have been under investigation for years. The influences of the diverse organisms properties are important on the performance evaluation of different treatment processes. While the size distributions of main organisms are known and compiled (e.g. IWACO 2001), only single data are available on the concentration of organisms in water used as ballast. Based on these organism densities and sizes, limit values have to be concluded for performance standards. These standards are urgently needed and discussed internationally at the moment. This is an international task, which cannot be solved by a single R&D-project. Nevertheless, from a plant manufacturers perspective the knowledge about organism properties and standards is decisive for designing BWT systems and for achieving its future required overall efficiency.

Requirements by vessel

In this R&D-project one main focus is set on the requirements by various vessels, which comprise the vessel routes and therefore the water quality ballasted, the vessel operations and construction of the vessel itself and its ballast water system. Figure 1 shows a comparison in vessel number of passenger ships, oil tankers and bulk carriers over the dead weight tonnes (dwt) – size class. While passenger ships feature a high vessel number at low dwt, oil tankers show a more even distribution over the whole dwt-range. In opposite bulk carriers have a main maximum in vessel number at 30,000 dwt – size class. In accordance with the different vessel sizes and transport functions a great variation can be found in the layout of the ballast water system, vessel routing and operation. Passenger ships have a more flexible routing, which often occurs near the coast at a regional mode, while oil tankers show a fixed and recurred routing on a global scale. Ballast water tanks vary in number and sizes having different total ballast water capacities and flow rates at ballasting/deballasting. The later normally range from around 200 m^3/h for cruise ships up to 6,000 m^3/h for Very Large Crude Carriers. A cruise ship is continuously ballasting at a low rate in order to compensate for the consumption of consumables (like fuel). Because of its mode of operations at touristy sites, the water quality used as ballast water is better compared to the intake of harbour water by other kind of vessels, which are ballasting at the time of unloading.

Conception and design of treatment options

In general three different overall options can be distinguished for the BWT onboard:

- Treatment at intake during ballasting
- Treatment during voyage
- Treatment at discharge during deballasting.

If the treatment concentrates solely on the prevention of non-indigenous species, a treatment at intake would be the right one and most effective to choose. Additionally the BWT offers the possibility to avoid simultaneously the problem of sediment accumulation in ballast water tanks. Sediment is deadweight, which makes the trim and stability of a vessel harder to rate, and causes additional costs due to loss of cargo, energy consumption and tank cleaning at shipyard. Additionally sediments in ballast water might hide and protect smaller organisms from disinfectants. Therefore, a BWT including a mechanical separation of particles during intake provides many advantages for the vessel operation and maintenance and the prevention of biological invasions. Besides the inorganic (mostly sediment) particles a part of the organisms is likewise removed by mechanical separation. This facilitates the following disinfection step resulting in advantages like a lower disinfectant dose and footprint. Likewise the disinfection step can be carried out as an in-line treatment during ballasting or can be operated later during the voyage in a bypass to the ballast water tanks. The second options has the advantage, that lower flow rate can be applied at longer treatment times. Unfavourably inhomogeneities and incomplete mixing effects result in unstable and insufficient treatment efficiency. These are caused by the present design of ballast water tanks, which contain a large number of fixtures for the structural strength of tanks, like longitudinals, intercostals and floors (Taylor and Rigby 2001).

A possible design of a ballast water treatment system is shown exemplary in Figure 2 for a container vessel. The treatment modules are set in the main ballast water line, whereas each can be located independently. For ship safety the BWT system can be bypassed. The treatment takes place during ballasting using only the two ballast water pumps. For discharge via valves in the hull the stored ballast water is pumped out of the tanks using the ballast water pumps again. As discussed in details below, an additional disinfection might be affordable at deballasting, if the disinfectant used during ballasting does not prevent a regrowth of organism in the ballast water tanks during voyage.

Like mentioned above, some vessels run on fixed routes giving an easier assessment of the water quality to be treated onboard. Ballast water treatment on vessels with more flexible routes affords a higher reliance in treatment efficiency and therefore a more redundant and effective treatment

combination, which can be obtained by installing modular multi-step processes. The basic treatment by an one-step mechanical separation followed by a disinfection can be upgraded in the case of higher loadings in water quality. Another separation module can be integrated in the basic two-step BWT giving relief to the original one. By applying a different second disinfectants a short- and long-term deactivation or a supplementary chemical oxidation can be combined. Depending on the characteristics of the disinfection process used two different process options are possible. A disinfectant, which provides a depot effect in the ballast water tanks, can guarantee a continuing disinfection until discharge. In the other case a replicated disinfection is necessary at deballasting due to a possible regrowth of organisms during voyage.

The potential for various treatment processes is restricted by some constraints, like the high flow rate and volume to be treated and the low footprint available at ships. Therefore all basic processes in mechanical, chemical and physical treatment are identified quantitatively by specific parameters, like the

- maximal volume flow rate being treatable
- footprint and height
- removal efficiency
- energy consumption
- acquisition costs
- operation expenses.

As an example, some data of different filter types, which are theoretically applicable in the first treatment step of mechanical separation, are shown in Table 1.

Table 1. *Example of some specific parameters for different filters used in the quantitative process assessment (based on a volume flow rate of 500 m^3/h).*

Filter type	Specific velocity [m/h]	Δ p [bar]	Overall height [m]
Pressurized gravel filter	15 - 30	0.1 - 0.5	4.5 - 5.5
Cartridge filter	5 - 40	0.2 - 2.5	2 - 3
Edge filter	400 - 600	0.5 - 1.0	1.5 - 2
Disc filter	100 - 200	0.5 - 1.0	1.7

After quantitative data collection and the consideration of qualitative parameters, like safety and environment issues, a comprehensive survey is carried out by combining all relevant biological, chemical, physical and technical parameters for designing BWT systems. Hereby, a setting of priorities is necessary. For example, the effectiveness of a sufficiently long sand passage is known for cyst removal from drinking water, but sand filtration is not a treatment option for shipboard use due to the enormous space and time requirement.

After the identification and comparison of different treatment options, which are available in the market and research, suitable processes are studied experimentally for particle and organism removal and disinfection. Intentionally alternative processes are examined and optimised for mechanical separation and for disinfection, which can be used as complementary or replacing components and facilitate a modular design.

In a test plant the performance of single and combined processes will be optimised including the above mentioned specific parameters. For instance, filtration using a filter fineness of 20 µm is effective in removing zooplankton and the cysts of toxic dinoflagellate algae (Oemcke and van Leeuwen, 2003), but certainly smaller organisms like phytoplankton, bacteria and virus are not removed in this step. Published results of experiments using different filters indicate, that the lowest achievable filter fineness is around 50 µm for BWT at this time (Parsons and Harkins 2003). An

optimum has to be determined between the lowest filter fineness giving relief to the post-disinfection and the increasing footprint of the filtration system with decreasing filter fineness.

At the end of June 2003 a test plant was started to run on river water in order to investigate different mechanical separation options (results will be available later). Focussing on sediment removal the performance of different suitable filter are studied first of possible options. Later the pilot plant will be upgraded stepwise to test and optimise different BWT options followed by designing and testing onboard.

Conclusions and Recommendations

- BWT systems exhibit a complexity in design specifications, which has to compromise the requirements by biological, chemical/physical and technical parameters together with the ones by different vessels (such as type, construction and operation).
- Therefore different optimised processes should be available in BWT design giving the choice for the most adequate and efficient treatment system in accordance with the requirements.
- For onboard treatment an adaptation of BWT systems to each kind of vessel has to be achieved by its modular design.

Acknowledgement

The research project is funded and supported by the Federal Ministry for Research and Technology of Germany under registration number 03SX169.

References

ISL. 2001. Shipping Statistics Yearbook 2001. Institute of Shipping Economics and Logistics (ISL). Bremen. December 2001.

IWACO. 2001. Standards for ballast water treatment. Report for the Ministry of Transport and Public Works, North Sea Directorate. Netherlands. February 20, 2001.

Oemcke, D. J., van Leeuwen, J. (H). 2003. Chemical and physical characterization of ballast water – part I: Effect on ballast water treatment processes. Journal of Marine Environmental Engineering Vol. 7. 47 - 64.

Parsons, M. G., Harkins, R. W. 2003. Full-scale particle removal performance of three types of mechanical separation devices for the primary treatment of ballast water. Marine Technology Vol. 39 – No. 4. pp. 211 – 222.

Taylor A. H., Rigby G. 2001. Suggested designs to facilitate improved management and treatment of ballast water on new and existing ships. Proceedings of the First International Conference on Ballast Water Management – Best Practices and New Directions. November 1-2, 2001. Singapore.

Voigt, M., Gollasch, S., Kornmüller, A., Röpell, H., Kerschek, O., Bahlke, C. 2003. Proposed land-based type approval tests for ballast water treatment systems. Oral presentation at the International Conference and Exhibition on Ballast Water and Waste Water Treatment Aboard Ships and in Ports, June 11-13, 2003, Bremerhaven, Germany.

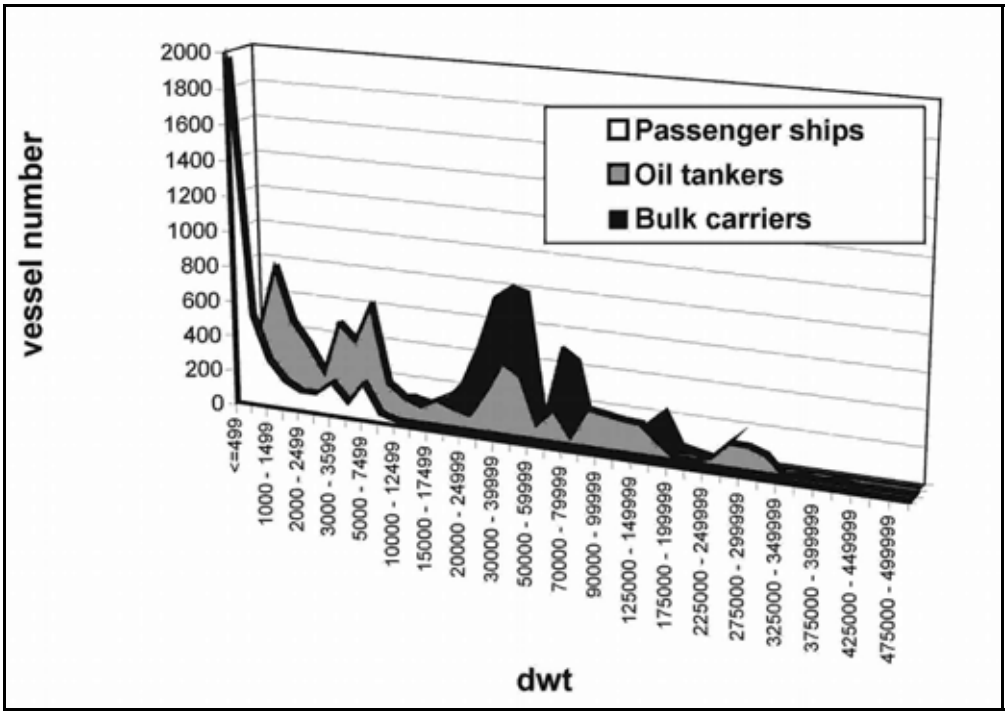


Figure 1. *Vessel number of passenger ships, oil tankers and bulk carriers over dwt-size class (based on statistics by ISL 2001).*

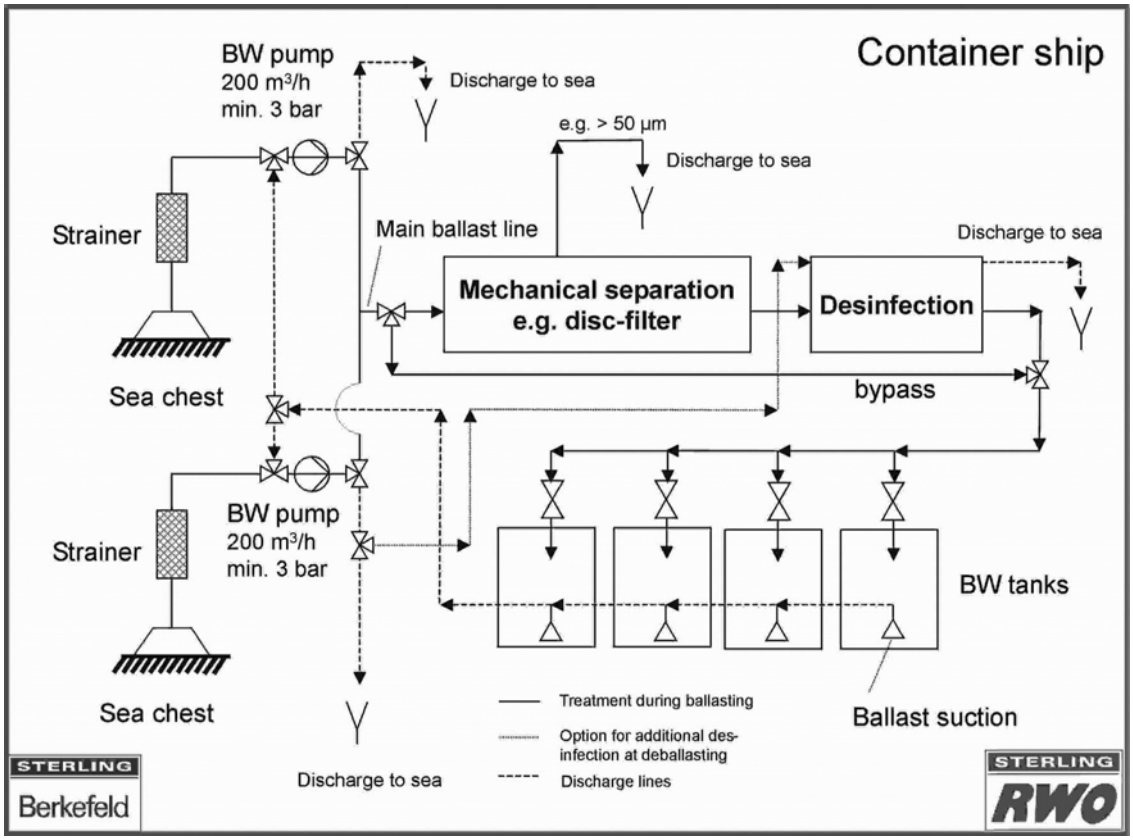


Figure 2. *Exemplary design of a ballast water treatment system on a container vessel providing full treatment at ballasting and additional disinfection at deballasting.*

Hydrodynamic transonic treatment and filtration of ship ballast water

A. Andruschenko, A. Dukhanin, V. Rabotnyov,
Y. Skanunov & S. Tishkin

TRANSZVUK, Ukraine
transsound@paco.net

Introduction

A well-balanced and thoroughly researched choice of method, or complex of methods, for treating ships' ballast water is an important goal. Surveys of work previously done in this field, as published in the *Ballast Water Treatment R&D Directory August 2002* materials, do not cover all possible methods for treating ballast waters.

The goal of our research is to develop a technical solution for treating ship ballast waters that would comply with criteria set forth in the materials of the *Marine Environment Protection Committee 48th session (MEPC 48 / WP.15.10 October 2002. Regulations E-1 ... E-4).*

This research is being conducted under the auspices of the GEF/UNDP/IMO/GloBallast Program.

The goals of the research are:

1. developing and putting together a pilot version of a ship-mounted autonomous processing complex;
2. conducting experiments to determine the effectiveness of the hydraulic transonic method of decontamination combined with filtering procedures;
3. examining the effects of hydraulic transonic decontamination of seawater combined with filtering on any macro and microorganisms, including bacteria and etc.;
4. reconciling research results with regulations set forth in the materials of the *Marine Environment Protection Committee 48th session (MEPC 48 / WP.15.10 October 2002. Regulations E-1 ... E-4);* and
5. assessment of specific energy consumption of the project.

At the time of writing this paper, the first phase of our work has been completed – a complete set of project and engineering documentation has been created that will allow us to manufacture the pilot version of an autonomous ship-mounted processing plant. The device is engineered for testing scenarios both on shore and in actual ship environments. The materials and devices used, the technologies used to manufacture the processing plant and its various parts, and the operating parameters are nearly all compliant with corresponding regulations of the Ukrainian Shipping and Navigation Register for auxiliary equipment installed in seagoing ship machine rooms.

Hydrodynamic transonic decontamination of liquids is based on a complex localized high-intensity exposure of the liquids processed to a combination of physical energy fields, specifically, a field of ultrasonic wave influence, appearing during high-speed phase transfers and the nearly instant (approximate timing is 10^{-4} to 10^{-6} seconds) pressure shifts in the system. These field effects are achieved without using expensive electronic ultrasound generators, electric oscillators, and no heat energy is used as input in the process. Spontaneous gassing occurs in the pressure shift zone, and, with certain conditions met, fairly high-intensity ultrasound is also generated due to several hydrodynamic effects. Ultrasound generated within a narrow segment of the liquid flow destroys the structure of macro and microorganisms. Additionally, during the second sharp pressure shift from

vacuum conditions to very high pressure, the so-called pressure jump phenomenon occurs. Gas bubbles collapse within the area affected by this phenomenon, which means a lot of mechanical influence is applied to the liquid medium. The bactericidal effect of the ultrasonic vibrations depends on the specific form of the microorganisms, the durability of the chemical composition of organism cell walls, the presence of a cell capsule, the age of the culture, the intensity of influence, the frequency of the ultrasonic waves, and the length of the exposure. It is known that the most lethal effect is produced by ultrasound with a wavelength roughly the same as the size of the target organisms.

The draft regulations set forth at the *Marine Environment Protection Committee 48th session (MEPC 48 / WP.15.10 October 2002. Regulations E-1 ... E-4)* specifically stipulate:

Regulation E-2 Ballast Water Management Standard

Option 2: Ships conducting Ballast Water Management in accordance with this Regulation shall discharge no detectable quantities of viable organisms above [100] μm in size, and discharge no more than [25 viable individuals of zooplankton per litre, 200 viable cells of phytoplankton per ml26] smaller than [100] μm in size.

The more recent draft of the regulations produced by the *Marine Environment Protection Committee 49th session* significantly reduce the dimensions of organisms to control, raising the bar of quality for ship ballast water treatment.

Regulation E-2 Ballast Water Performance Standard

Ships conducting Ballast Water Management in accordance with this Regulation shall discharge no more than [25] viable individuals per litre of zooplankton greater than [10] μm in size; and no more than [200] viable cells per ml of phytoplankton greater than [10] μm in size; and discharge of a specified set of indicator microbes shall not exceed specified concentrations.

Regulation E-3 Additional criteria for Ballast Water Management systems

Ballast Water Management systems used to comply with the Convention must be:

#	***Criteria***	***The level of compliance of the trans-sound ballast water treatment technology to the additional criteria***
1.	Safe in terms of the ship and its crew;	Safe for ship and crew members
2.	Environmentally acceptable, i.e., not causing more or greater environmental impacts than it solves;	Do not provide secondary pollution to the treated environment, environmentally safe
3.	Practicable, i.e., compatible with ship design and operations;	Contain equipment common for ships
4.	Cost effective, i.e., economical; and	Assessment of economical parameters will be carried out after installation testing
5.	Biologically effective in terms of removing, or otherwise rendering inactive Harmful Aquatic Organisms and Pathogens in Ballast Water.	Effective on all living forms contained in water

In order to validate the proposed technical solution, during the first phase, a working model was created based on the TCA/3/B-1 processing plant, with a throughput capacity of 0.35 m^3/hour and a maximum water pressure of 10 MPa. A basic installation schematic for the TCA/3/B-1 is shown in Figure 1.

The preliminary testing studied the effectiveness of the processing plant's influence on zooplankton organisms living in the waters of the Odessa Bay. Among the principal technical benefits of the processing plant, which make its use practical on a variety of ship types, are small dimensions,

productivity, energy economy, safety and easy maintenance. The initial material was a plankton sampling living in water drawn from "Peschananya Gavani" of the Odessa Port. During the experiment, seawater was passed through the TCA/3/B-1 processing plant, running the following operational parameters:

- Water pressure before processing point: 20 bar
- Water pressure in the working area: 0.05 bar
- Water pressure on exit: 5 bar
- Input water temperature: 19.7°C
- Output water temperature: 20.1°C

A control sampling of the original seawater was taken before each series of experiments, and the populations of the various zooplankton organisms were assessed. The volume of water that passed through the processing plant during each experiment equaled approximately 10-30 litres of water.

After processing, another sample was taken, and the remaining plankton debris was condensed with the use of special gauze filters (#60 and #70).

Table 1. *Species content and basic dimensions of zooplanton.*

No	Organism Species	Dimensions (microns)
Aztropoda Type, Crustacea Class		
Brachiopoda Subclass		
Cladocera Order		
Podonidae Family, Podon Genus		
1	*Pleopis polyphemoides*	400
Daphniidae Family, Daphnia Genus		
2	*Daphnia magna*	2000-4000; 1500 average
Copepoda Subclass		
Calanoida Order		
Pseudodiaptomidae Family, Calanipeda Genus		
3	*Calanipeda auae dulcis*	1000-1200; 1000 average
Acartiidae Family, Acartia Genus		
4	*Acartia clausi*	1170-1750; 1000-1500 average
Cyclopoida Order		
Oithonidae Family, Oithona Genus		
5	*Oithona minuta*	500-700; 400-600 average
Harpacticoida Order		
Canuellidae Family, Canuella Genus		
6	*Canuella perplexa*	900-1300; 800-1000 average
Harpacticidae Family, Harpacticus Genus		
7	*Harpacticus flexus*	600-700
8	*Harpacticus sp.*	200-300
9	*Copepoda, nauplii*	50-240
Cirripedia Subclass		
Balanomorpha Superfamily, Balanidae Family, Balanus Genus		
10	*Balanus, nauplii*	40-130
Nematoda Type, Rotatoria Class		
Monogononta Order		
Brachionidae Family, Brachionus Genus		
11	*Brachionus plicatilis*	60-315
Synchaetidae Family, Synchaeta Genus		
12	*Synchaeta sp.*	50-200

In determining the species of the organisms that survived or were killed, living/dead percentages were detailed for each type of organism, as well as their sizes; various samples of debris were examined and their possible origins were accounted for.

Preliminary processing of the samples was performed without fixing. Then the samples were fixed with 10-percent formaldehyde solution to conduct further laboratory analysis.

Calculation, content determination and zooplankton measurement was performed with binocular lens MBS-10.

In order to identify the zooplankton forms, *Black and Azov Sea Fauna Guide* was referenced.

Species content and basic dimensions of zooplankton organisms are given in Table 1.

The first series of tests

Samples were condensed through gauze No.60

Control: The number of zooplankton organisms was 560 per liter. The basic taxonomic groups present in samples are *Rotatoria* (wheel animalcules), *Cirripedia nauplii*, *Copepoda nauplii*, *Harpacticoida*, *Cladocera* (crustaceans), *Nematoda* (worms), *Polychaeta* larvae. Among them, wheel animacules (36%), *Cirripedia nauplii* (25%) and *Harpacticoida* (21%) were prevalent in the total number. Many *Infusoria* could be observed. Natural departure of organisms has not been detected.

After processing with the TCA/3/B-1 plant: We detected 9 and 11 (i.e. 0.9 and 1.1 per liter) *Cirripedia nauplii* with dimensions of 50-90 microns in 2 analyzed samples, respectively. Processing efficiency, i.e. death rate, for this kind of species amounted to 99.3%. Representatives of other organism groups were not detected. The efficiency is 100%. There are neither *Infusoria*, nor zooplankton fragments in the water.

The second series of tests

Samples were condensed through gauze No.60

Control: Zooplankton content is similar to that of the first test series. The number of organisms is 400 per liter.

After processing with the TCA/3/B-1 plant: We detected 14 *Cirripedia nauplii* (i.e. 1.4 per liter) with dimensions of 40 to 80 microns. Processing efficiency, i.e. death rate, for this kind of species amounted to 98.6%. The processing efficiency for other species is 100%. The water is clean, suspended matter and *Infusoria* are not present.

The third series of tests

Samples were condensed through gauze No.70

Control: The number of organisms is 3200 per liter. The species are *Rotatoria*, *Cirripedia nauplii*, *Copepoda nauplii*, *Calanoida*, *Harpacticoida*, *Cladocera*, *Polychaeta larvae.* Among them, *Calanoida* (34%), *Harpacticoida* (22%) and *Cirripedia nauplii* (19%) were prevalent. Many *Infusoria* could be observed.

After processing with the TCA/3/B-1 plant: We detected 7 *Cirripedia nauplii* (i.e. 0.7 per liter) with dimensions of 40-100 microns. Processing efficiency, i.e. death rate, for this kind of species amounted to 99.9%. The processing efficiency for other species is 100%. The sample contains many fragments of crustaceans, some non-destructed chitinous covers are also met. *Infusoria* are not observable.

The fourth series of tests

Samples were condensed through gauze No.70

Control: The number of organisms is 6000 per liter. Their species are *Rotatoria*, *Copepoda nauplii*, *Calanoida*, *Harpacticoida*, *Cladocera*. *Cladocera* crustaceans and wheel animalcules were predominant.

After processing with the TCA/3/B-1 plant: Living zooplankton organisms were not found in any of the samples taken while the plant was operated. The plant performance efficiency is 100%.

Conclusions

1. Under conditions in which these experiments were performed, passing sea water through the TCA/3/B-1 processing plant provides for practically complete destruction of zooplankton organisms. *Cirripedia nauplii* proved to be the organisms most resistant to effects produced by the processing plant. Their survival rates observed in three series of tests turned out to be 0.7%, 1.4% and 0.1%, respectively, which can possibly be explained by inadequate cleanliness of the processing tract before the experiments.

2. Transonic decontamination technologies are one of the potential solutions to the ship ballast water treatment problem – they are characterized by the simplicity of the equipment used, ease of maintenance, transfer no secondary pollution to the liquid being processed, and are based mostly on equipment commonly found on ships.

More research on the effectiveness of ballast water transonic decontamination is planned for this year on the experimental autonomous processing plant created during the first phase of the project. A schematic of the experimental processing plant is provided in Figure 2. The device complex includes:

1. Reservoir for input water to be processed.
2. Tank to mix and store chemical disinfection reagents
3. Peripheral pump
4. Mechanical filtration module
5. Gas saturation module, part of the filtered air / water ejector segment
6. Holding tank for aerated water under pressure
7. Multistage centrifugal pump
8. Transonic hydrodynamic module
9. Degasification module
10. Reservoir to hold processed water

The processing plant is equipped with a thermometer to measure the temperature of the water being processed, as well as a manometer and flow meter. The basic installation allows for both successive processing of the water by all modules, as well as selective processing, with different combinations of modules. The whole device complex is mounted on a common framework.

The purpose of the chemical reagent tank is to provide means of preliminary decontamination of the hydrodynamic tract. If necessary, the position and hookup of the tank allows routing controlled doses of reagent solution directly into the water medium being processed.

The peripheral pump provides a pressure increase in the water being processed, up to 1 MPa. Control of the pump output pressure is achieved with a bypass valve. Water volume passing through the mechanical filter can be measured by the flow meter.

The mechanical filtration module can use a number of different filtering materials with an effective mesh of no more than 100 micrometers.

The processing plant can function with or without the presence of a filtering material in the mechanical filtering module.

The purpose of the ejector is to force filtered air into the water being processed, raising the pressure of the mix and pumping it into the holding tank. The layout of the processing plant also allows it to function without air input.

The purpose of the holding tank is to saturate the water being processed with air under pressure, and is equipped with a water level gauge glass, an emergency valve and a device for maintaining the needed water level. Extra air is released automatically into the atmosphere.

The purpose of the multistage centrifugal pump is to further raise the water pressure to 2.5 MPa. Output pressure is controlled via a bypass valve. The device complex installation scheme allows for operation without the centrifugal pump. In that case, a section of pipe is installed in its place.

The hydrodynamic transonic module destroys zooplankton present in the water. This module was engineered to be easily interchangeable, to allow testing both high-pressure and low-pressure modes of water treatment. The low-pressure mode uses only the peripheral pump. Maximum water pressure in this mode is 1 MPa. The high-pressure mode uses both the peripheral and the centrifugal pumps. Maximum water pressure in this mode is 2.5 MPa.

The degasification module removes gases released in the water by the hydrodynamic cavitational treatment, and lowers dissolved gas content in the treated water to levels lower than the input water. Extracted gases are released into the atmosphere. After going through the degasification module, processed water is collected in a final reservoir.

Preliminary analysis of the results allows us to make the following conclusions:

- Treatment of seawater by a TCA-type processing complex can result in a near absolute elimination of zooplankton and phytoplankton organisms.
- Transonic decontamination technologies are one of the potential solutions for treating ship ballast waters. They are characterized by the use of simple and reliable technical components, ease of maintenance, no secondary processing pollution, and are based on technology that is commonly found on most ships.

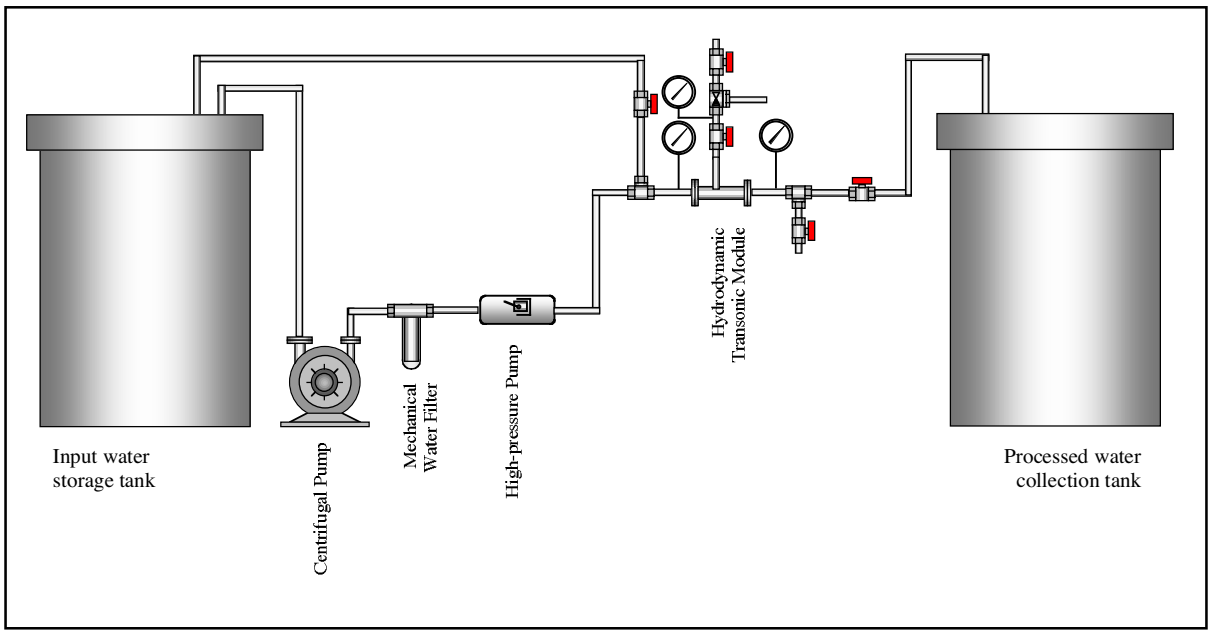


Figure 1. *Basic schematics of model setup of TCA/3/B-1 processing plant.*

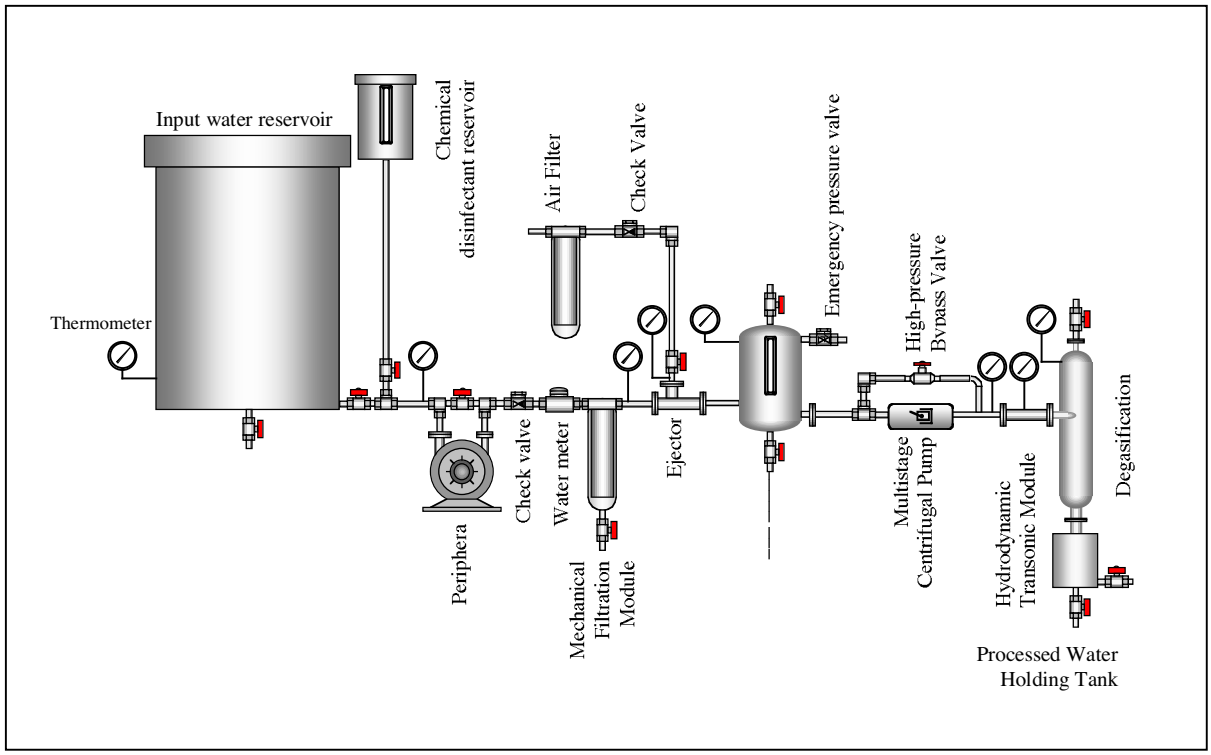


Figure 2. *Composition schematic of hydrodynamic water.*

A new modular concept for the treatment of ships ballast water - the Hamann project

H. Röpell & T. Mann

Hamann Wassertechnik GmbH, Germany
HaukeRöpell@HamannWassertechnik.de

Abstract

This paper presents the new ballast water treatment option of Hamann Wassertechnik GmbH, Germany. The system is based on a modular concept which includes a two-step physical separation (hydrocyclone and 50 µm self-cleaning filter) as well as a secondary treatment with an oxidising agent (Peraclean® Ocean). Due to the modular approach, the Hamann ballast water treatment option is flexible in adopting different ships' requirements such as space available, location of ballast water system on board ship, capacity of ballast water pumps, and others. Furthermore, it can adjust to different ballast water management scenarios (changing flow rates of ballast water pumps, serving all ballast water tanks from double bottom to top wing, varying flow rates of ballast water pumps).

Hamann's ballast water treatment option has been tested at full scale flow rates of 135 m^3/h to 210 m^3/h. The tests were carried out at a number of different land based location with different water qualities (e.g. Baltic Sea, Lower Elbe River and Port of Hamburg). The Artemia Testing System (ATS) was applied to produce reliable and reproducible test results.

Introduction

The key-objectives of the project were the identification of suitable combinations of treatment steps / methods for various types of ships and ballast water management scenarios as well as the design of a full scale treatment plant for land-based tests and evaluations. The time frame of the project was 3 years (2000 to 2003). The project was funded jointly be the Federal Ministry Of Research (through *Arbeitsgemeinschaft industrieller Forschungs-vereinigungen*, Otto von Guericke e.V., AIF) and the industry.

At this stage, a practicable combination of treatment steps has been identified and a full-scale test unit has been produced for land-based tests. The tests of this treatment plant were carried out at different locations and different flow rates.

Technical description of the test treatment plant

The test treatment plant has a modular design, which gives the most possible flexibility in addressing different ballast water management scenarios and different types of ship. The modular design concept allows the installation of individual treatment steps at different locations on the ship where room is available, which makes the system suitable even for refits. Furthermore, new modules can be integrated or added to an existing system as technology improves or regulations change.

The modular system that was tested consisted of the following treatment steps / modules:

1. A physical separation which included two treatment steps:
    a. A new developed **hydrocylone** which was specially designed for ballast water applications. It significantly reduces the sediment load of the ballast water and also removes some of the organisms. The small size of the individual hydrocylone allows installation on a single deck.

The number of hydrocyclones needed (35 m^3 to 45 m^3/h each) depends on the flow rate of the ballast water pump.

b. A **fine filtration** with a mesh size of **50 µm**, which serves two functions:

   1) It removes nearly all organisms with a body length > 100 µm,

   2) It increases the stress imposed on the organisms present in the ballast water, resulting in physical damage of the organisms as well as increased sensitivities towards the secondary treatment.

2. A chlorine free oxidising agent (Peraclean®Ocean) was used as a secondary treatment, which was dosed to the ballast water after the physical treatment at concentrations of only 150 ppm. The selected oxidising agent is fully bio-degradable and has no corrosive impact on the ballast water system of the ship.

Test-conditions

The tests were carried out at different locations with different types of water:

a. In the **inter-tidal zone of the lower Elbe River near Brunsbüttel**. This location is characterised by changing salinities due to tidal influence and high turbidity with high loads of suspended solids.

b. In the **Baltic Sea (Kiel),** at constantly brackish water conditions (salinity about 13 ppt).

c. Currently more tests are on the way in the **Port of Hamburg** at freshwater conditions.

All tests were carried out at flow rates of 135 m^3/h to 210 m^3/h. The duration of the tests varied between 4 weeks (Kiel) and 16 weeks (Brunsbüttel). During the tests, the treatment plant was operated at the above flow rates for an average of 8 to 10 hours of continuous operation during working days.

Furthermore, the biological efficiency of the treatment plant was evaluated at each of the test sites. The evaluation was based on the removal/inactivation of the plankton present at the testing sites and surrogate organisms, respectively. Different life-stages of *Artemia salina* were used as surrogate organisms and the ATS (Artemia Testing System) test protocol was applied.

A total of 7 tests have been conducted with the plankton present at the test sites and 6 experiments were carried out according to the ATS test protocol. The results of the tests are summarised below.

Results of full-scale land-based tests

- The treatment plant performed during the test cycles without mechanical problems, giving good continuous flow conditions at each of the testing sites.

- The biological efficacy was evaluated for each treatment step separately. The different qualities of the water at the testing sites had no influence on the biological efficacy.

- Great differences occurred in the separation rates of both, the hydro cyclones and the 50 µm filter, according to the different sizes and physical properties of the test organisms.

- During all tests, the Hamann Modular Ballast Water Treatment plant was dosed with 150 ppm of Peraclean® Ocean, which is equivalent to 15 l of Peraclean® per 100 m^3 of ballast water.

- After 24 hours of exposure time to Peraclean®Ocean, no living organisms were detected in any of the samples. The test results are summarized in the following table.

Numbers of frequently found organisms during the experiments; single findings were not regarded	Mean numbers of organisms per litre	Range of organisms per litre	average removal by cyclone	average removal cyclone + 50µm filter	kill rate after 24 hrs exposure to 150 ppm Peraclean®*
ATS experiments	n=6		n=6	n=6	
Artemia salina nauplii	15,8	3 – 47	58%	81%	**>98%**
Artemia eggs in development	64,8	10 - 231	62%	93%	**>98%**
Artemia soaked cysts	159,9	17 - 220	60%	97%	**>98%**
Artemia dry cysts	28,0	7 - 65	81%	97%	**>98%**
in-situ plankton organisms	n=7				
Copepod (Cyclops sp.)	4,9	2 - 10	52%	86%	**>98%**
Daphnia sp.	0,5	0 - 2			**>98%**
Copepod nauplii	4,1	1 - 14	29%	40%	**>98%**
Rotifer	9,8	1 - 41	45%	62%	**>98%**
Ciliate	3,4	0 - 13	(50%)**	(36%)**	**>98%**

*no living organisms were detected in any of the samples after 24 hrs exposure to 150ppm of Peraclean® Ocean.
**the observed differences between the removal rates of the cyclones and the removal rates of the cyclones + fine filter were not significant, because of the high variance of the input values.

Conclusions and remarks

The Hamann modular BWT addresses all of the following criteria:

- compliance with short term regulations that are currently discussed by IMO and
- options for upgrading to future requirements
- the type of ship and the individual ballast water management plan
- space requirements (footprint of set-up)
- risks involved: safety and handling, environmental risks (aquatic toxicity)

The current treatment modules include a physical separation in two steps, the Hamann Hydrocyclones and a 50 µm fine filtration unit plus a disinfection with a chlorine free oxidising agent (Peraclean® Ocean).

Test results showed a removal of:

- 97% of all organisms > 100 µm in smallest dimension;
- 80 % of all organisms of < 100 µm in smallest dimension; and
- a killing/inactivation of all organisms, no living organisms were detected after 24 hrs of exposure.

Further full-scale tests will be carried out in the port of Hamburg and onboard ship's with updated testing procedures according to currently developed national and international test standards.

A portable pilot plant to test the treatment of ships' ballast water

S. Hillman, F. Hoedt & P. Schneider

CRC Reef Research Centre
James Cook University, Australia
steve.hillman@jcu.edu.au

Aims and objectives of the project

The objective of project is to build a pilot treatment plant based on existing technologies and off-the-shelf equipment. The pilot plant uses various technologies, as well as chemicals on a 'plug and play' basis. The medium to longer term aim is to develop a system that will be scaled up and used aboard ships.

Research methods

Concept

The overall concept of the pilot plant is to treat ballast water using a variety of techniques individually or in series as described by Oemcke (1999 (1)), Oemcke and Hillman (2001). They suggested that the use of filtration followed by ultra-violet radiation would be efficacious in treating a large number of known ballast water pest species with the notable exception of encysted dinoflagellates. To address the need to treat ballast water for encysted organisms, the pilot plant incorporates an ultra-sonic shear device as well as the capability of injecting measured doses of chlorine dioxide.

The pilot plant has been constructed in a 20 foot container and is designed so that it can be used under laboratory conditions or be moved to different ports for testing under various port environmental conditions, such as temperature, salinity and sediment load. It can also be put aboard ships for testing of ballast water treatment in transit.

We consider the best time to treat ballast water is during loading by the ship. This has the benefit of leaving filter backwash material at the port of origin and ensures all ballast water passes through the treatment system. Recognising that the quality of discharged ballast water is the essential criteria, the use of the system to treat water during discharge may be necessary to kill or inactivate organisms that may have recovered during the voyage. The pilot plant is, therefore, designed to treat water as it passes through the system. Design flow rate for the pilot plant is between 2 and 3 litres per second (up to 11 tonnes per hour). This balances our ability to sample the water effectively with the need to demonstrate pilot plant perfomance. It also investigates treatment at reasonable flow rates, which we feel can be scaled up to meet required full scale throughputs. A schematic of the pilot plant is found at Figure 1.

Pilot plant operation

Fresh seawater can be stored in two 27,000 litre tanks. Test water can then be gravity-drained to the 10,000 litre dosing tank, where it is inoculated with the organism of choice. This tank is mixed using an aeration system to enhance homogeneity. The contents of this dosing tank can be pumped to any, or all, of the Amiad filter, the sonic disintegrator and the ultra-violet unit. Sampling points are available before and after the pump and after each treatment method.

This filter can be used with a number of different sized screens and the project has available to it 20, 50 and 80 micron screens. To date only the 80 micron screen has been used. The sonic disintegrator is

driven by a variable frequency drive that allows the speed of the machine to be varied to optimise effects. The ultra-violet unit operates at 254 nanometres. All components are designed to be able to be operated at greater than the design capacity of 3 litres per second.

Test protocols

The pilot plant has been operational for two weeks and protocols are presently being refined. Our initial objective is to manage variabilities in sampling the 10,000 litre tank and at the sampling points with no treatment of the water occurs. A sampling regime is being developed that will determine with 95% confidence that the variability in the numbers of organisms counted is less than 5%.

We have chosen to use *Artemia* for initial testing. The *Artemia* Testing System protocol (Voigt, 1999) suggests the use of different life stages of *Artemia* as a surrogate for pelagic and benthic cysts as well as numerous planktonic organisms. While it is clear that *Artemia* cannot be used as surrogates for smaller organisms – due to its size – its availability and ease of culture makes it attractive, at least for the early stages of testing.

It will be necessary to repeat the testing for variability for each class of organism tested. These will include larvae of bivalves, fish, echinoderms, algae and free-swimming phytoplankton. Dinoflagellate cysts will also be used.

Post-treatment and control samples will be stored under temperature controlled, dark conditions to simulate hold-up in ballast tanks. Sub-samples will be taken immediately and after suitable periods of dark storage (e.g. 24 hourly for 5 days).

Results

Biological testing of the ballast water pilot plant

The pilot plant is comprised of two distinct parts, firstly the shipping container with built-in treatment options (filters, sonic disintegrator, UV) and sample outlet points and secondly, the external system of storage and culture tanks and sampling outlet points (see appendix A). The experimental system is designed to enable the inoculation of a known density of mono-specific culture in the 10,000 litre culture tank which is then pumped through the pilot plant with selected treatments activated. Samples are collected to determine changes in population density and the viability of organisms at key locations in the system (i.e. pre and post-treatment). At a later stage, several smaller culture tanks (2-500 litre) will be placed in the container to examine longer-term effects on surviving organisms.

The location of sampling points is an important aspect of the process of biological testing and experimentation of the efficacy of the system. At present there are 7 sampling points in the whole system (Table 1). The diameter of these sampling points varies, as some were built into the steel piping system prior to arrival and testing, and the diameter of others is governed by the diameter of the attachment location. If necessary, sampling points will be changed so that they are identical. An explanation of the location and role of each sampling point is given in Table 1.

Table 1. *Sampling points throughout the external and internal pilot plant system. 'Internal' refers to within the pilot plant container and 'external' is outside.*

Sampling point	Location	Sample method	Information derived
Point 1	External – Samples collected in the 10,000 litre culture tank	25mm suction hose at 5 locations and three depth strata	Accurate estimate of initial stocking density of culture
Point 2	External – PVC tap (50mm outlet) with valve at outlet pipe just after 10,000 litre tank and prior to inlet pump	Collect 10 litre sample (allows full-flow flushing) and take one 250 ml sample from each bucketful	Estimate of organism density exiting tank and entering pump
Point 3	External – PVC tap (25 mm outlet) just after pump and before filtration unit	Collect 10 litre sample (allows full-flow flushing) and take one 250 ml sample from each bucketful	Estimate of organism density after pumping and prior to treatment.
Point 4	Internal – 6 mm steel tap outlet on pipe just before sonic disintegrator	Collect 10 litre sample in bucket and take one 250 ml sample from each bucketful	Estimate of organism density in piping just before sonic disintegrator and after filtration
Point 5	Internal – 20 mm steel tap outlet on pipe just after sonic disintegrator	Collect 10 litre sample in bucket and take one 250 ml sample from each bucketful	Estimate of organism density in piping just after sonic disintegrator
Point 6	Internal – 20 mm steel tap outlet on pipe just before exiting pilot plant after UV	Collect 10 litre sample in bucket and take one 250 ml sample from each bucketful	Estimate of organism density in piping just after all treatments
Point 7	External – 50mm pvc valve tap outside of pilot plant	Flush pipe then collect 10 litre sample in bucket and take one 250 ml sample from each bucketful	Full-flow sample after all treatments

Experiment 1 (18/6/03 and 25/6/03)
Number and volume of subsamples required to estimate Artemia density in the 10,000 litre culture tank

To examine the effect of treatments, knowledge of pre-treatment and post-treatment density of organisms is necessary. Further, it is important to understand the variability of subsamples and be able to state the accuracy of any density estimate based on subsamples. We have chosen the 95% confidence interval as a statistical measure of accuracy. We undertook a preliminary assessment of subsampling variability in order to determine the required number of samples to obtain a predetermined accuracy. Initially it was thought that we would aim for 95% confidence that the density estimate was within 5% of the actual density.

A series of 15 replicated 1 litre samples (30 total) were collected at 15 different locations within the 10,000 litre culture tank on 18/6/03. The locations were chosen to include all obvious factors that may cause aggregation. These were:

- 3 depth strata from top to bottom,
- above and between aeration lines, and
- sunny versus shaded parts of the tank (since *Artemia* are photophyllic).

The 1 litre samples were collected with a 25mm suction hose and then concentrated to 250 ml by removing water using a small suction hose within a container fitted with 20 micron mesh (to prevent *Artemia* removal).

Concentrating samples proved time consuming. Subsequently, 10 × 250 ml samples were collected at 10 locations in the same tank on 25/6/03 to examine the possibility of taking smaller-volume samples.

The results of the above experiments were used to determine the number and volume of samples required to obtain a 'starting density' estimate with a pre-specified degree of accuracy. Both experiments used cultures of newly hatched *Artemia* nauplii (24 hrs post incubation). Samples were sorted fresh in a Bogorov tray using a stereo microscope.

The results of analysis on the first set of samples are shown in Table 2. The small confidence limits (mean = 86 +/- 5.8), show that 30 samples enabled a relatively accurate estimation of density. Further analysis showed that 53 × 1 litre samples would be needed to be 95% confident of obtaining a density estimate within 5% of the actual mean density in the tank.

Table 2. *Statistical analysis of samples taken at 15 locations in the 10,000 litre tank on 18/6/03.*

Number of samples	30
Mean density (# per litre)	85.8
Standard error of mean	2.54
95% Confidence interval	5.81

To examine the possibility of collecting smaller samples; a second set of 250 ml samples were collected on 25/6/03 and an analysis of the variance was undertaken. Results are shown in Table 3. It was calculated that 145 × 250ml samples would be needed to get within 5% of the actual mean. These results suggest that 250 ml samples may not be viable.

Table 3. *Analysis of 10 X 250 ml samples collected in the 10,000 litre tank.*

Number of samples	10
Mean density (# per litre)	74.4
Standard error of mean	7.13
95% Confidence interval	16.14

Experiment 2 Analysis of mixing by aeration in 10000 litre culture tank

As yet a statistical analysis of variability in sample density with location (ANOVA on 30 samples – 18/6/03) has not been undertaken but visual inspection of the data suggests that there were no obvious points of aggregation and that density estimates in samples were generally similar with random variation.

Experiment 3 Analysis of variation between different sampling points after the 10,000 litre tank ('control samples') and effect of the intake pump on Artemia*.*

Samples were collected at 4 post-culture tank sampling points to make a preliminary comparison of these and further to examine if passage through the pump was effecting *Artemia* densities. Table 4 shows that the pump appears to have reduced *Artemia* density by more than half the tank density. Further, while there were no dead nauplii in tank samples, there were high proportions of dead nauplii in most samples taken after the pump. Thus it is evident that the pump may be reducing densities and killing nauplii. This will require further investigation to quantify. The densities at the three post-pump locations are comparable to the pre-treatment point. There is a suggestion of some variation between points which again will require further sampling and analysis, particularly with regard to the unexpected apparent increase in numbers as the organisms progress through the system.

Table 4. *Densities of* Artemia *in 250 ml samples collected at 4 sampling points with no treatments operational.*

	Tank	S2 (just after pump)	S3 (just before sonic disintegrator)	S6 (external to system)
	80	24	44	12
	60	24	28	36
	56	24	32	28
	76	20	28	44
	68	12	20	28
	112	28	28	40
	64	36	12	16
	60	4	32	40
	52	4	16	44
	116	8	20	16
Mean	74.4	18.4	26	30.4

Experiment - 3 Treatment effects

Tables 5, 6 and 7 summarise the preliminary experiments on treatment effects. Due to the short time available and the need for further analysis to determine sampling requirements, these results are of a preliminary nature having not been done with a systematically established sampling protocol.

Filtration rates with the 80-micron screen are between 92 and 96 % (Table 6). It is likely, given the size of nauplii (300 by 150 microns), that some *Artemia* in the post filter samples may have been caught in the system prior to filter activation since sample point 6 was not flushed prior to sampling. All post sonic disintegrator samples contained no *Artemia* (alive or dead) (Table 7). While the sample numbers were low this is an encouraging result.

Table 5. *Preliminary experiments to determine treatment effects.*

Date	Treatment	Post–treatment number of samples
18/6/03	Filter – 80 micron	5
24/6/03	Sonic disintegrator	4
24/6/03	Filter – 80 micron	10
25/6/03	sonic disintegrator	10

Table 6. *Experiment with 80-micron filter screen – mean densities at sample points are given. Number of samples shown in brackets.*

Date	Tank	Pre-filter densities	Post-filter at sample Pt. 6 *	% filtration
18/6/03		85.8 (Tank density)	3 (5)	96.5
24/6/03*	74.4 (10)	25.9 (30)**	2 (10) (all nauplii)	92.3
			1.2 (10) (alive only)	95.4

* On 24/6/03, post filter samples at point 6 were collected while the filter was on; pre-filter samples (pts. 1, 3 & 6) were taken in a run with no treatment operational just beforehand. Therefore these can only be used to infer the likely system densities before the filter.

** Mean pre-filtration densities from sample points 1, 3 and 6.

Table 7. *Experiments with sonic disintegrator – mean densities at sample points are given. Number of samples shown in brackets.*

	Tank	Sample pt. 1	Sample Pt. 3	Sample Pt. 4
24/6/03*	74.4 (10)	18.4 (10)	26 (10)	0 (4)
25/6/03	52.8 (10)		5.3 (10)**	0 (10)

* Sonic disintegrator samples at point 4 were collected a few hours after the other samples were taken with sonic disintegrator off. Thus these can only be used to infer the likely system densities before the sonic disintegrator.

** Unusually low pre-treatment densities – filter may have been accidentally left on filtering a component (not all due to plumbing design) of the throughput water.

Utility of the technologies used

There has been much reporting of the difficulties associated with the flow rates required for vessels to treat ballast water. Often the stress has been on the relatively small number of large vessels (e.g. Cape Class) with ballast loading rates of 3000 tonnes per hour or more. It is important to weigh this against the average bulk carrier dead weight tonnage being 35,750 tonnes and the average DWT of tankers being 38,000 tonnes (Anon, 2002). This indicates that there are a very large number of vessels that will have loading rates that are more of the order of 500 tonnes per hour.

While filtration and/or ultra-violet treatment at the higher loading rates is possible, albeit difficult, there is a significant proportion of the world fleet that will be much more easily catered for using this kind of technology. As has been pointed out by Oemcke (1999 (2)), that small ships will release much less ballast water than large vessels and, therefore, a given kill rate will only need to be proportionally smaller to achieve approximately the same level of risk reduction. Furthermore, as suggested by Hilliard (2001), there is evidence that discharge frequency is at least as important as volume. Thus there would be great advantages in risk reduction by incorporating treatment measures in the large number of smaller ships.

The two established technologies being tested, filtration and ultra-violet light, have existing facilities that can treat upwards of 1000 tonnes of water per hour. In the case of Amiad filtration, this can be achieved through a single large filtration. However, this throughput would almost certainly require several ultra-violet units running in parallel. The scaling up of the sonic disintegrator is being carried out as a related research project within the School of Engineering at James Cook University.

Inspection of ships' pump and engine rooms do not indicate that there will be major issues with space requirements.

Conclusions and recommendations

While it is too early to form conclusions regarding the efficacy of the pilot plant, the results to date indicate that with further development the technologies are capable of effectively removing organisms from ballast water as it is being loaded aboard ship.

Acknowledgments

This project is being supported by:

Environment Australia, Ports Corporation of Queensland, Townsville, Mackay and Gladstone Port Authorities, Amiad Australia, CRC Reef Research Centre, URS Australia, the Great Barrier Reef Research Foundation and Pasminco.

The researchers gratefully acknowledge this support.

References

Anon, 2002. Lloyds Register – Fairplay, 2002. See http://www.lrfairplay.com/.

Hilliard, R. 2001. Determining Practical Evaluation and Approval Guidelines and Criteria for "First Generation" Ballast Water Treatment Systems: Some Issues on their Derivation, Application and Development. *1st International Ballast Water Treatment R&D Symposium, IMO London 26-27 March 2001: Symposium Proceedings*. GloBallast Monograph Series No 5. IMO London.

Oemcke, D. 1999 (1). *The Treatment of Ships' Ballast Water*. EcoPorts Monograph No 18, Ports Corporation of Queensland, Brisbane.

Oemcke, D. & Hillman, S. 2001. Ultra-Violet Treatment of Ships' Ballast Water – Research to Reality. *Proceedings of the First International Conference on Ballast Water Management, Singapore*.

Oemcke, D. 1999 (2). Comparing ballast water treatments on a cost-benefit basis: the balance of needs. *The Ballast Water Problem- Where to from here? Proceedings of a workshop held 5-6 May 1999, Brisbane Australia*. EcoPorts Monograph Series No 19. Ports Corporation of Queensland, Brisbane.

Voigt, M. 1999. *Artemia* Testing System Protocols, developed by dr.voigt-consulting, Germany. See www.dr.voigt-consulting.se/atseng.

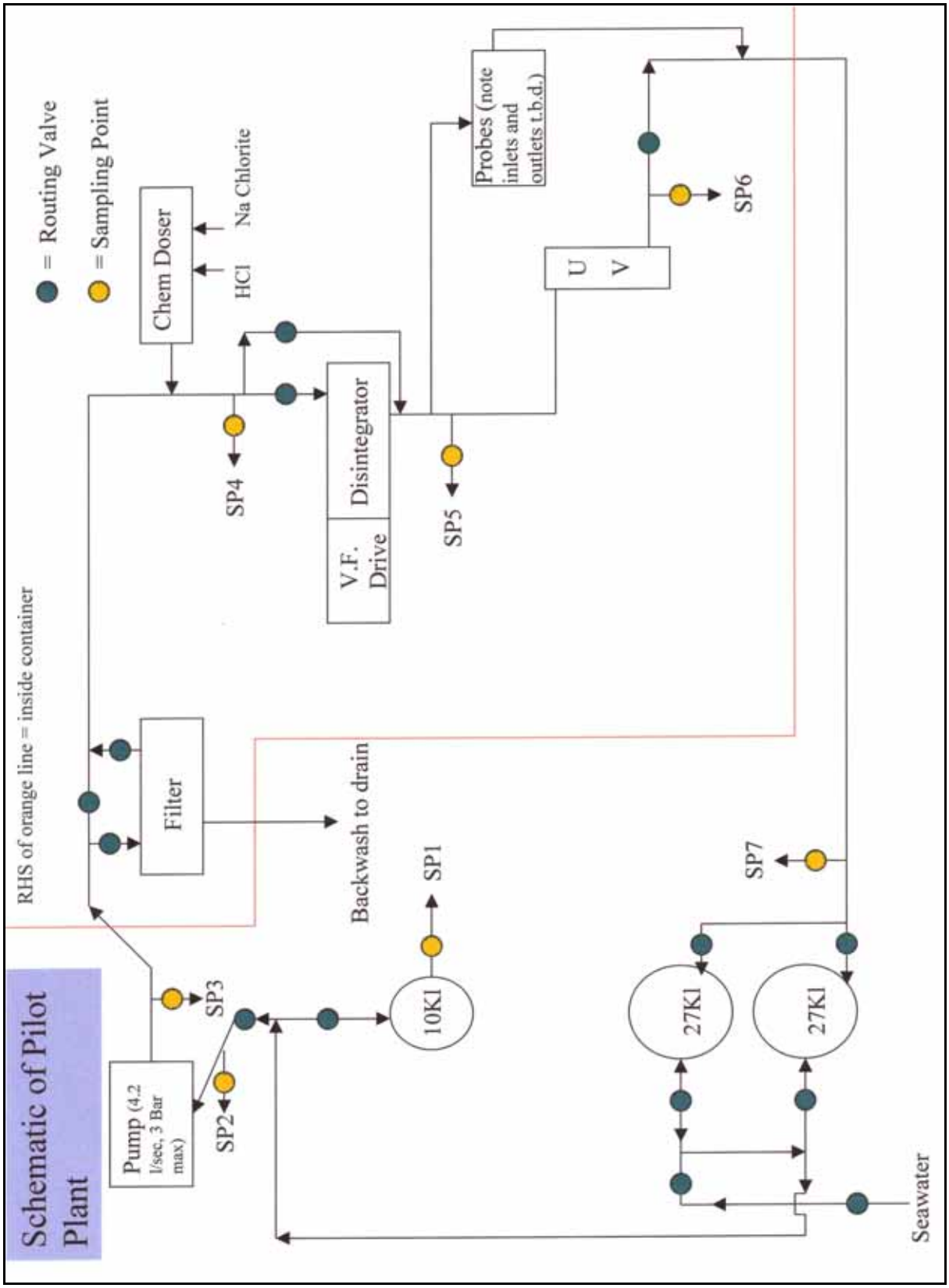


Figure 1. *Schematic of pilot plant.*

Ballast water treatment R&D in the Netherlands: Ballast water treatment on-board of ships & evaluation of market potential and R&D requirements

C.C. ten Hallers-Tjabbes[1], J. Boon[1], M.J. Veldhuis[1], J.L. Brouwer[2] & J. Rvan Niekerk[2]

[1]*Royal Netherlands Institute for Sea Research (NIOZ)*
The Netherlands
cato@nioz.nl

[2]*Royal Haskoning, Shipping HSE services*
The Netherlands
leo.brouwer@royalhaskoning.com

Summary

In this paper, we give an overview of the future needs for ballast water treatment systems on board of the worlds' shipping fleet. In our view, such systems should consist of a two-stage design, involving a primary particle exclusion step followed by a secondary step, that kills the remaining living organisms. An important prerequisite of the treatment is that the receiving ecosystem should not be damaged by discharged ballast water. Therefore the use of (toxic) chemicals for this purpose appears a risky way to go. Assessment of the adequacy of treatment systems requires a reliable evaluation process.

The minimum size of organisms that should be removed from the seawater during primary treatment should be in the order of 10 µm. A larger diameter for particles to be removed will result in an incomplete removal of silt and clay particles and will allow for formation of a substantial sediment layer that acts as a seafloor offering shelter for living organisms in the ballast tanks. A secondary treatment step should kill the remaining organisms after primary treatment. These mainly involve part of the algal species responsible for harmful algal blooms, bacteria and viruses.

The performance of ballast water treatment equipment should in the future be monitored in an automated way. Flow-cytometry offers good potential to achieve this goal, since it can be fully automated, and discriminate between living and dead cells.

A future global market potential has been estimated based on a relevant world fleet for ballast water management requirements of some 33,000 vessels (larger than 1,000 tonnes dwt) and a model general cargo vessel of 12,000 tonnes dwt with a ballasting capacity in the range of 600 – 1,000 m^3/h. This showed an annual market potential ranging from USD 225 million to USD 350 million for the period between adoption and ratification of the international convention. After ratification of the international convention this annual market potential is expected to increase to a range from USD 700 million to USD 1,100 million.

Introduction

Ballast water has been subject to the development of (inter)national legislation and the problem has been studied for many years, in particular with an aim to minimise the risk of introduction of alien organisms in marine ecosystems through the transfer of organisms through ballast water.

One of the preliminary results is the "draft international convention for the control and management of ships' ballast water and sediments", which is expected to be adopted by IMO in 2004.

Recent studies performed by Royal Haskoning looked into the possibilities and constraints of ballast water treatment on-board of ships and the global market potential for this equipment. The most relevant studies are *Application of ballast water treatment techniques on Dutch vessels (2001), Global market analysis of ballast water treatment technology (2001)* and *Ballast water treatment; full scale tests, strategies and techniques (2002, in co-operation with Royal Netherlands Institute for Sea Research - NIOZ).* This is intended to lead to full-scale tests of treatment equipment on-board of ships, which is currently in development by NIOZ and Royal Haskoning.

Ballast water: the problem

The use of (sea) water as ballast for the stability and trim of the vessel and to submerge the propeller is a necessity on one hand, but poses a risk of the movement of non-indigenous marine organisms between ecosystems on the other hand. This is considered today to be one of the most important threats to the stability of local ecosystems, and thereby biodiversity.

The size of organisms and sediment particles is a key factor and serves as a classification basis in ballast water management, as the efficacy of ballast water treatment depends on the potential to remove particles, including those of a smaller size. This capacity in turn is related to the techniques that should be applied to analyse (or test) for the presence of such tiny organisms. The natural range of organisms is very variable, and as an example the size classes of pelagic organisms are given in figure 1, indicating a wide range of size classes from < 1 μm until > 1000 μm.

Besides marine organisms, ballast water also contains sediment (sand and clay). Sediment in itself is not a problem in the sense as described above, although it reduces the maximum cargo weight to be loaded. But a stable sediment layer in a ballast tank provides a 'sea-bottom' and thereby a stable hideout place for organisms and a hothouse for growth and increase of numbers until the ballast tank are emptied. Many organisms experience an emptying ballast water tank as a low-tide situation, to which they respond by hiding in the sediment, only to emerge again at the next flood, i.e. when the ballast tanks are filled again.

The size range of sediment plays an important role; clay particles are generally smaller than 2 μm and sand particles are in general larger than 50 μm. Sediment can also build up in a ballast water tank by decaying organisms that were killed or damaged at intake or died during the voyage. The resulting detritus is often minute in size and by its nature can increase the coherence of the tank sediment. Depending on the location of intake of ballast water, sediment can be easy or very difficult to remove. Several NW European ports have sediment that is mainly in the range of 10 – 50 μm (i.e. the silt fraction); such conditions are also common in estuaries and deltas in flat coastal areas elsewhere the world.

IMO requirements for ballast water management

The current draft international convention for the control and management of ships' ballast water and sediments (MEPC 49) gives, amongst others, guidelines for ballast water treatment and for efficacy of treatment by indicating what needs to be absent in treated ballast water that is considered safe to discharge. This includes a measure for the level of organisms that should not be present in treated ballast water, standards for ballast water management and the review of standards.

Ballast water that is considered safe to be discharged should minimise the risk of harm to the environment, human health, property and resources; the standards that are being developed for the purpose of the convention reflect such quality.

Standards for ballast water quality under development aim to determine a cut-off size class for different classes of organisms, together with a concentration level that should not be exceeded. According to the currently proposed levels, ballast water should meet the following performance

standard: zooplankton greater than 10 µm in size should not exceed 25 viable individuals per litre and phytoplankton greater than 10 µm in size shall be less than 200 viable cells per litre. These values are reflecting the current state of understanding and are likely to be further developed and refined alongside further developments in treatment and testing research. Of even more importance than minimum numbers is the viability of the remaining cells. In other words can those alien introductions form new populations in the area of the port of destination. A proper treatment method should in the end focus on a reduction of viable organisms, and treatment performance should be evaluated accordingly.

It is proposed to review the standards before the effective date in order to determine the availability of appropriate technologies; thereby enabling optimum performance and innovation.

Ballast water management systems should be safe in terms of the ship and its crew, environmentally acceptable (i.e. not causing more or greater environmental impacts than it solves), practicable (i.e. compatible with ships' design and operations), cost effective (i.e. economical) and biological effective in terms of removing, or otherwise rendering inactive harmful aquatic organisms and pathogens in ballast water.

Ballast water treatment options and restrictions

In theory ballast water can be treated on-board of the ship or in a land-based facility. This paper will focus on on-board treatment only.

The treatment of ballast water can be performed upon intake or discharge of ballast water, and during the voyage. Each option has its own advantages and disadvantages and the choice in favour of an option is also dependent on the type/size of the marine organisms and sediment and the treatment equipment to be used.

Treatment upon intake of ballast water has the advantage to prevent organisms and sediment to enter the ballast tanks in the first place, but the required equipment will be relatively large. It has also been proven, since a hundred percent prevention and/or killing is not possible, that some organisms even at a low initial concentration are able to increase in numbers during the voyage, while others will die and decay in the sediment. This indicates that treatment upon intake only will not be sufficient.

Treatment upon discharge prevents organisms to enter the threatened marine environment, but this option also requires a relatively large equipment. A disadvantage of this option is that the removed and/or killed organisms and sediment will either built up in the ballast tanks or have to be given off as waste in the respective ports.

Treatment during the voyage requires fairly small equipment, because of the time available for treatment. On the other hand there is no guarantee that all ballast water (including organisms and sediment) will be treated during circulation over the ballast tanks, mainly because organisms and sediment have a tendency to settle during the voyage. Also the removed and/or killed organisms and sediment will either built up in the ballast tanks or will produce additional waste.

This all indicates that treatment at one moment is not sufficient. As the required equipment for treatment during intake and discharge are of similar capacity, this seems to be the combination that has the most potential.

The ship itself also gives a set of restrictions to the treatment equipment because of its design characteristics and operating circumstances, which might prevent well-proven land-based equipment to be installed on-board a ship without modifications.

The restrictions due to the ships' design are related mainly to the available space and specific ballast water piping configuration on-board the ship. The main operating constraints relate to the changing

atmospheric conditions during the voyages, the highly corrosive atmosphere at sea and the limited availability of crewmembers to operate the treatment equipment.

Ballast water treatment equipment

The treatment of ballast water aims at reducing the risk of viable organisms entering the marine environment at destination and can include both removal of marine organisms and sediment and killing of organisms.

Based on the characteristics/sizes of organisms and sediment and the potential of treatment equipment, it is not likely that one type of equipment will cure the problem sufficiently. This will result in the necessity of a combination of techniques to cure the problem to the maximum extent possible, as will be explained below. The effectiveness of each technique will not be discussed.

Techniques to remove organisms and sediment from seawater include filtration, separation, (hydro) cyclonation and centrifugation. Such techniques are all based on physical properties, like particle size and specific gravity. The smaller the particles and the smaller the differences in specific gravity, the more difficult it becomes to remove the particles from the water. Very small particles (< appr. 10 μm) will be quite hard to remove; such conditions are likely to be found in many locations where ballast water is loaded, which is often in ports. Also some organisms consist mainly of water and consequently have almost the same specific gravity as water, which will decrease the efficiency of especially hydrocyclonation and centrifugation

Since the application of the above mentioned primary techniques cannot be expected to result in ballast water of the required quality, secondary techniques that kill the organisms are necessary. Examples that have been applied in ballast water treatment are UV-irradiation, heat treatment, chemical treatment, ultrasonic treatment, and biological treatment. For all these techniques, organisms to be killed should be in actual contact with the active ingredient of the treatment. Without primary - treatment, this will be hardly possible as high concentrations of suspended sediment will be present and organisms can then easily “hide”, from the mortal secondary treatment.

The above justifies the statement that a combination of primary and secondary treatment techniques will be required. Sediment and larger organisms should be removed as much as possible, to allow for a high efficiency of the secondary treatment to kill the remaining organisms. The latter will mainly be of a size below 10 um, and involve (cysts of) algae that contributes to harmful algal blooms, bacteria, and viruses.

Promising combinations of techniques include filtration and hydrocyclones as primary treatment, followed by UV-irradiation as secondary treatment. Other combinations are also explored although investigations are currently in an earlier phase.

A well-designed ballast water treatment system will contain more than just the equipment to remove and kill the organisms and sediment. Although the system will be type-approved and as such will not require proof of effectiveness by analysis of samples on each journey, a testing system will be required for random checks in harbours or for monitoring the equipment by the crew during the voyage. As the system is type approved prior to use by a proper evaluation method, this system requires an independent, automated control and register device that will prove the proper use of the system. For such evaluation system both the sampling and analysis techniques should be robust, reliable and reproducible and described in a consistent manner and for personnel that should (routinely) perform the evaluation. Both sampling of treated ballast water and analysis of the sampled matter should be developed such that they can be applied on a routine basis, by authorities and management personnel. Elaborate sampling from ballast water tanks or from discharged ballast water by a range of sampling equipment and analysis of the sampled material by biological specialists are important steps on the way to evaluate the problem and the quality of ballast water; to meet the requirements of a full-proofed type test and routine evaluation system, further development is needed.

For the measurement techniques required for evaluation of the treatment product, a purpose-oriented adaptation of flow-cytometry is promising for the realisation of an automated measurement of ranges of particle sizes and forms present in ballast water before and directly after treatment, and upon ballast water discharge at the end of a journey. For this purpose, automated equipment should be developed, which allows monitoring of the performance of the installed ballast water treatment system and which can also be used by the responsible authorities. The more elaborate, research-oriented forms can also discriminate between life and dead particles.

Ballast water treatment equipment: market potential

A study (Royal Haskoning, 2001) was performed to estimate the market potential for ballast water treatment equipment. This study used a three-step approach:

- **Step 1**: defining the relevant part of the world fleet
- **Step 2**: determine the "qualified available market"
- **Step 3**: predict the future market behaviour

This study made use of the data of the world fleet, but based its qualitative analysis on information from Dutch ship owners.

Step 1: defining the relevant part of the world fleet

In 2001 some 91,000 vessels were registered with Lloyds. Part of the registered vessel types does not use seawater as ballast, or return always to the same port. Examples of such vessels are tugs, lighthouse vessels, fishing vessels etc. After excluding these vessels a number of appr. 47,000 vessels remains. Besides the type of vessel, also the area of operation will determine whether a vessel will need to comply to ballast water regulations. As a measure to determine whether a vessel makes long voyages (i.e. international or intercontinental trade) the vessel size was used. Most of the world fleet is actually quite small (see figure 2). In the study it was concluded that all vessels under 1000 tonnes dead-weight probably have regional modes of operation. Excluding also these category of vessels yields an estimate of about 33,000 vessels that will in some way face regulations on ballast water management.

Step 2: determine the "qualified available market"

It was assumed that after the adoption of the international convention (expected in 2004) the main driving force for installing treatment equipment, during the first 5 years, would be unilateral legislation based on this convention. Ship owners with sufficient awareness and financial means were selected to be the short-term market (the first 5 years); this was based on the 52 high-income countries. The ship owner can either consider retrofitting or phasing out the vessel .

The age-distribution of the world fleet is important to determine the expected amount of new buildings in the future, and the number of vessels on which retrofit will be likely. Based on expert opinions, an age of 10 years (dependent on trades, vessel types, ship owner) was deemed the maximum age on which a vessel may still be considered for retrofitting ballast water treatment equipment.

These analyses resulted in an estimate of appr. 675 vessels to be retrofitted and appr. 450 to be newly built as replacement for old ships per annum for the short-term market.

Step 3: predict the future market behaviour

After ratification of the convention (expected in 2009?), many more ship owners will be obliged to either retrofit existing vessels or phase out and replace the vessel. The analysis resulted in an estimate of appr. 2,400 vessels to be retrofitted and appr. 1,050 to be newly built per annum for the mid-term

market (after 5 years until all existing vessels have been retrofitted). In the long-term the market will mainly consist of new-builds only.

Potential market prediction

Based on the analysis of the Lloyds' register, the modal vessel is probably a general cargo vessel of 12,000 tonnes dead-weight. According to a survey for the Royal Netherlands Association of Ship Owners (KVNR), this coincides with approximately 4000 tonnes ballast capacity, and a ballasting capacity of 600-1,000 m^3/h.

Data from suppliers of treatment equipment, provided cost estimates of USD 200,000 (lower estimate of 600 m^3/h) until USD 310,000 (higher estimate of 1,000 m^3/h) per vessel for the modal vessel.

For the short-term period (2004 – 2009) the annual turnover is estimated to be in the range of USD 225 million to 350 million. After ratification of the convention the potential annual turnover will increase and is estimated to be in the range of USD 700 million to 1,100 million. The long-term annual turnover is estimated to be in the range of USD 200 million to 325 million.

These estimates are, of course, subject to a number of uncertainties and constraints. Firstly, the actual adoption and ratification of the convention is still uncertain and this will be the main determining factor. Secondly, the appropriate treatment technologies are under development and so far it is not clear which technologies can and will be used in the future. A last, but not least, aspect is the market penetration of the equipment suppliers, which will require a thorough marketing strategy.

Full scale ballast water treatment on-board testing

Before on-board test on commercial ships can be performed, land-based and controlled sea borne (pilot) tests in a research environment (preferably a research vessel) are required to prevent major setbacks .

The test program, which is being developed by the NIOZ and Royal Haskoning in co-operation with ship owners and equipment suppliers, includes three main parts, which are (1) a land-based pilot test close to NIOZ, (2) a controlled pilot test on the NIOZ research vessel and (3) a full-scale test on-board of a commercial vessel.

This test program will investigate different treatment options and will simultaneously develop protocols for sampling and analysis. The sampling technique will also require modifications to the currently available sampling systems, which will be part of the project.

It is also envisaged as being adequate to cover all seasons of a year, so as to meet the variations in presence and absence of the relevant organisms over the year.

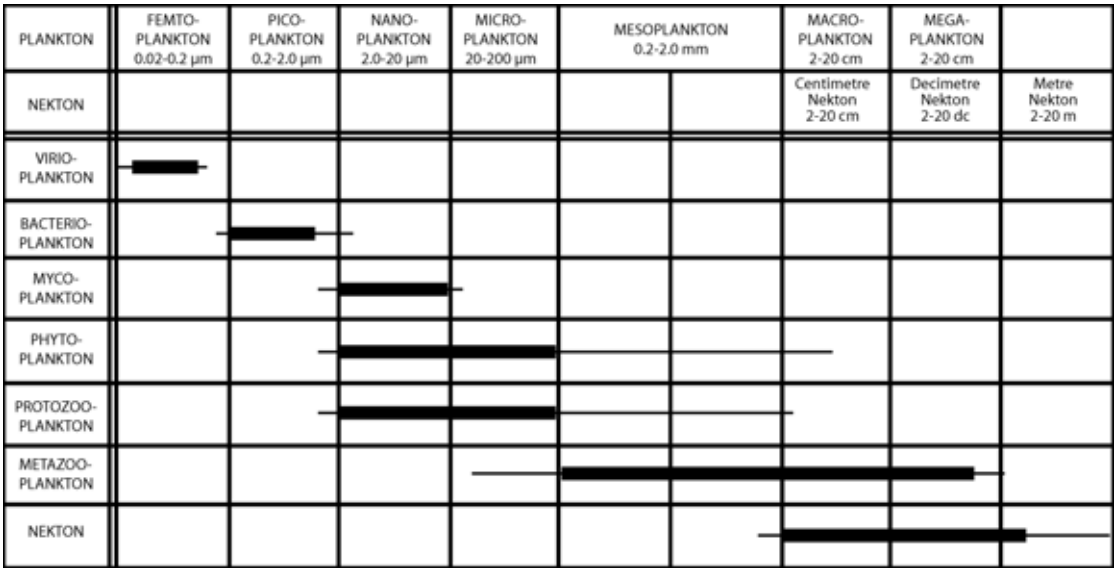


Figure 1: *Size classes of Pelagic organisms.*

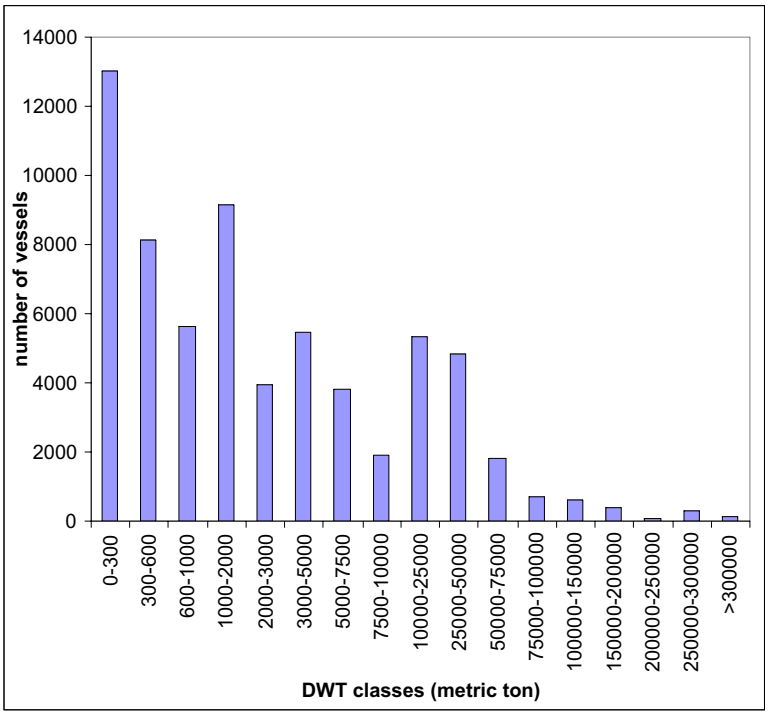


Figure 2. *Distribution of dead-weight in the world fleet.*

Ballast water treatment - management and research in Washington State

S. S. Smith

Washington Department of Fish and Wildlife, USA
smithsss@dfw.wa.gov

Abstract

Washington State has established a ballast water treatment discharge standard and an interim approval process for technology evaluation. This process is intended to further the development of promising treatment systems while international and national standards are being established. The Washington State interim approval process will be described along with ballast data that identified high-risk vessels. Planned and completed research on various treatment methods will be reviewed. Treatment systems currently under consideration include filtration and UV light, SeaKleen, ozonation, chlorine dioxide, filtration and mixed oxidant process, and the use of treated wastewater for ballast. A cooperative ballast water treatment research and development project was developed to promote the installation and testing of ballast treatment systems. Vessel operators, regulators, technology vendors, ports and governments are sharing the risk and cost associated with on-board testing. The more we install and test technologies, the faster they will improve, and the sooner we will solve the problem of ballast related invasive species introductions.

Treatment options

Treatment options currently being considered for interim approval:

- Hyde Marine – Filtration and UV Light
- Garnett - Sea Kleen
- EcoChlor - Chlorine Dioxide
- NuTecho3 - Ozone
- Marine Environmental Partners – Mixed oxidant process

Other treatment systems will be considered for approval as they become available.

Aims and objectives

Washington Department of Fish and Wildlife is striving to improve our capacity to protect Washington's waters from aquatic invasive species. The development and implementation of practical, effective and environmentally sound ballast water treatment systems is key to achieving this goal. Promising treatment systems must be installed on vessels and tested for operational, biological, and environmental performance. Each installation yields new information that leads to improvements in future performance. More installations will increase production, which leads to lower prices. Improved and cheaper technologies will not just happen; they must be allowed to evolve through use.

Installing experimental technology is risky. What if it's not approved for use? What if it's impractical? What if it just doesn't work? Programs should be developed that allow for the risk to be shared, thus minimizing the impact to any one group. Vessel operators, regulators, technology vendors, ports and governments should share the risk to promote more installations. The more we install technologies, the faster they will improve, and the sooner we will solve the problem of ballast related introductions. The Washington state ballast management program is designed to identify high-

risk vessels that need treatment, and provide incentives for vessel operators to install technologies for evaluation in our interim approval process.

Research methods

Testing protocols are currently under development. They will be designed to evaluate each treatment system's capacity to achieve our percent removal standards, which are 95% removal of zooplankton and 99% removal of phytoplankton and microorganisms.

Results

Washington State has taken the following steps to further the implementation of ballast treatment.

- Implemented a mandatory ballast water reporting program that can identify high risk vessels that need ballast treatment.
- Established a standard for the discharge of treated ballast.
- Created an interim approval process for ballast treatment technologies.
- Mandated treatment after July of 2004, if exchange cannot be conducted.
- Created a cooperative ballast water treatment research and development project to fund the installation and testing of on-board treatment systems.
- Established the Ballast Water Work Group made up of representatives from the maritime industry, environmental organizations, and agencies to further the implementation of ballast treatment.

Conclusions

Cooperative ballast water treatment research and development projects should be developed around the world to promote the installation and testing of ballast treatment systems. Vessel operators, regulators, technology vendors, ports and governments should share the risk and cost associated with on-board testing. The more we install and test technologies, the faster they will improve, and the sooner we will solve the problem of ballast related invasive species introductions.

Corrosion effects of ballast water treatment methods

E. Dragsund, B. O. Johannessen, A. B. Andersen & J. O. Nøklebye

Det Norske Veritas
Norway
egil.dragsund@dnv.com

Abstract

This paper outlines the main mechanisms and factors affecting corrosion rates in ballast tanks and associated piping. Further, the paper discusses the main ballast water treatment techniques proposed with emphasis on their potential effects in relation to corrosion. The paper is based on laboratory studies and desktop evaluations of ballast water treatment methods carried out by DNV over a period of time. These treatment methods comprise a range of solutions and operating principles and may in many cases involve a combination of several technologies, in which case the effect of the individual components has been assessed. A more detailed assessment for ozone treatment is provided as case example for the purpose of illustrating corrosion testing methodologies.

Background

During the last years ballast water treatment methods have been subjected to extensive investigations driven by future regulations and anticipated future requirements for the limitation of transfer of marine organisms. Some of these methods are now commercially available while others are still at the development stage. Studies of such technologies have had prioritised focus on the ability to eliminate various classes of marine organisms. However, the operational applicability of the solutions involves other aspects, of which the potential for increased ballast water tank corrosion is a main concern. For the maritime industry, corrosion and corrosion protection is a considerable cost element in the operation of a vessel. Consequently, any method which significantly accelerates corrosion or can reduce the efficiency of presently applied protective corrosion measures are likely to be discarded even if the ballast water treatment performance is good.

Corrosion mechanisms in ballast tanks

Electrolytic corrosion

In relation to ballast tanks, main corrosion mechanism is that of electrolytic corrosion (general corrosion). For steel submerged in sea water, the accessibility of oxygen to the surfaces is the main controlling factor for the corrosion rate. The increase in present levels of oxygen (oxygen surface exposure), will act as a corrosion rate catalyst. Corrosion rates will also increase with increase in temperatures. An often referred to example illustrating this effect is the double hulled tanker carrying heated liquids compared to that carrying liquids of a lower (or ambient) temperature. The surfaces facing the heated tanks will experience the higher rate of corrosion.

However, interrelationship between the various factors and conditions must always be considered, e.g. oxygen content of the seawater will decrease with increasing temperature and thus have a possible decelerating effect.

Surface protecting coatings will always have imperfections causing local corrosion with the potential of spreading if not repaired.

As a first approximation it can be stated that the corrosion rate for different low alloy steel grades in submerged, static condition is approximately the same, independent of minor alloying elements.

However, for long term exposures the development of rust deposits and their protective effect and reduction of direct oxygen flux to the steel surface is a critical factor. Present knowledge on corrosion for various seawater type exposures is not sufficiently understood to accurately predict the development of rust deposits as function of either the steel grade or the environmental impact.

The corrosivity of sea water as regards general corrosion on steel, increases with increasing:

- temperature
- oxygen content
- water velocity
- content of corrosive compounds (e.g. H_2S, CO_2, H_2O_2)
- velocity of eroding particles

Bacterial corrosion

In stagnant ballast water containing organic material (including oil), microbes may thrive. High corrosion rates are caused by chemical processes initiated by bacterial and/or fungi activity, and often proceeds in two or three stages:

1. During initial microbial proliferation dissolved oxygen in water is used up by microbial and chemical degradation of organic matter. Already at this stage, mildly acidic organic chemicals are produced by the microbial oxidation processes which may accelerate ongoing electrolytic corrosion. The zone near the microbial growth becomes oxygen deficient and anodic.
2. In some cases, conditions are such that a second stage occurs, where one or a few specialist species of anaerobic bacteria take over the scene, feeding on the acidic chemicals. The best known are the Sulphate Reducing Bacteria (SRB) which reduce SO_4^{2-} to S^{2-}. Hydrogen sulphide gas is also an end product of the SRB activity and promotes corrosion.
3. Strong acids such as sulphuric acid can be produced from sulphides when oxygen becomes available again. This will further accelerate the corrosion rate.

Bacterial corrosion is found most frequently underneath sludge or dirt settling out from the water on bottom plating and other up-facing, horizontal surfaces. Water properties affecting bacterial corrosion include:

- Low oxygen level (anaerobic)
- Hydrocarbons or other pollutants (carbon sources) nourishing bacteria
- Temperature (20 – 40°C)
- Sulphates (in sea water sulphates are always present in excess quantities)

Typical corrosion levels in ballast tanks

DNV (1993) presented ballast tank corrosion rates compiled from available sources and from DNV's ship surveys. It should be noted that reported corrosion rates in literature may be either for one side or for both sides of the plate. All rates reported in the following refer to one side.

Corrosion rates vary between different parts of the ballast tank:

- Corrosion rates of bare steel fully submerged in sea water (i.e. the lower part of the ballast tank) are usually 100 – 200 µm/year.
- In the splash zone (mid section of the ballast tank) corrosion rates can be 200 – 400 µm/year.
- Highest corrosion rates (350 - 400 µm/year) were found in the upper 2 meter of Side Plating. This was explained by the combined effect of increased average temperature due to sun

heating, abundant oxygen supply, splashing of sea water, and cyclic temperature changes leading to cyclic condensation (wet and dry).

However, the variation in the reported rates is large leading to a "normal" range roughly indicated as 200 ± 200 μm/year, and in extreme environments (such as high temperature and bacterial corrosion underneath sediment) corrosion rates may be several millimetres per year. The variation depends on a number of factors e.g. (DNV, 1996):

- A layer of built up corrosion products (rust) on a steel surface will have a protective (coating) effect by limiting the access of oxygen to the steel, thus lowering the corrosion rate.
- A layer of corrosion products may render parts of the surface cathodic in relation to other, anodic, parts of the surface lacking such layer experiencing increased corrosion rate.
- Surfaces exposed to vibrations and/or high stress levels may have increased corrosion rates with time, due to the thickness reduction of steel plates causing reinforced vibrations and stress levels.
- Macro-elements or large aeration cells caused by variations in oxygen concentration, e.g. at different depth levels in ballast tanks and over or under sediments, may create anodic parts experiencing accelerated corrosion and other parts cathodic, non-corroding.
- Areas with locally degraded coating may become anodic compared with intact coating, resulting in pitting corrosion.

Corrosion protection in ballast tanks

The SOLAS Amendment *Corrosion prevention of seawater ballast tanks* gives direction to include corrosion protection of ballast tanks in oil tankers and bulk carriers within the scope of classification. A good coating applied on a well prepared surface at the newbuilding stage is the most effective means of avoiding corrosion. Coatings will have varying useful lives in ballast tanks, from a few months to more than 25 years, depending largely on steel surface and edge preparation and application conditions. An important contributing factor to coating degradation is the increasing brittleness and loss of flexibility with time, causing cracking and disbonding at structural hotspots, typically in deckhead structures.

Some of the proposed ballast water treatment systems may accelerate this degradation. This is in particular cyclic high temperature (heat treatment) causing loss of low molecular weight components of the coating, and oxidation (treatment by oxidants) of the coating constituents which further contribute to gradual loss of flexibility and may lead to disbonding.

Ballast water treatment technologies and their expected effects on corrosion

This chapter summarises assessments of potential corrosion effects of various presently known ballast water treatment methods. The assessment focuses on the treatment categories.

A range of ballast water treatment methods have been developed or are subjected to research and development. Ballast water treatment systems may involve a single method or a combination of several principles. The methods may have an instantaneous biological effect or require a prolonged time for exposure of organisms to achieve the desired effect.

The methods have for convenience been grouped by their general operating principle according to three main classes:

Mechanical methods

Methods by which organisms are physically removed, completely or partially, at the ballast water loading stage resulting in reduced organic material in the ballast tanks. This may provide conditions that are less favourable for bacterial growth and thereby reducing the oxygen consumption in ballast water. As a result, this class of methods may lead to higher oxygen levels in ballast water which is favourable to general corrosion. The effect is not believed to be dramatic.

A higher oxygen level combined with reduced organic material presence, may reduce bacterial corrosion.

Examples: filters, hydrocyclones, separators. The method does not necessarily imply neutralisation of organisms.

Physical methods

Methods by which organisms are rendered harmless (neutralised) by a physical method but remain in the ballast water to sediment, degrade and/or be offloaded. Typically the methods work by physically damaging the structure or tissue of the organisms by rapid stress variations on a scale comparable to the dimensions of the organisms. The methods vary in required exposure time for the desired effect to be achieved. Examples are ultrasound, pressure fluctuations, aggressive mechanical methods, temperature treatment (heat), UV, nitrogen/air supersaturation and cavitation.

Ultrasound/Cavitation/Aggressive mechanical methods

Physical disruption of organisms will release easily degradable organic material resulting in a gradually reduced oxygen level. General corrosion rates may therefore be reduced. Due to the same effect these methods may provide conditions that promote bacterial corrosion.

Heat

Generally increased temperatures lead to higher corrosion rates. However, as a secondary effect, high temperatures will lead to reduced oxygen level which may lead to lower general corrosion rates. Organisms killed by treatment may be basis for bacterial decomposition. Reduced oxygen level and increased carbon sources may lead to bacterial corrosion.

The real effects on corrosion rates related to heat treatment are not clear and should therefore be investigated.

Chemical methods

This class includes any method by which aquatic organisms are neutralised by addition of any active chemical substance. The class may be further subdivided into group of methods. Examples are:

Oxidants

Organisms are neutralised by addition of an oxidant or any other substance that will form oxidants in reaction with the sea water. Examples: ozone, hypochlorite, chlorine, hydrogenperoxide, hydroxyl radicals and several combinations called multioxidants.

Increased oxidant level in the sea water will normally lead to an increase in the corrosion intensity that may range from mild to severe. The corrosion effect may be reduced with time as oxidant is consumed by the organic material oxidising process. On the other hand immediate corrosion may be severe at the location of oxidant introduction. Treatment by ozonation leads to higher oxygen and oxidant level. The build up of rust deposits and their protective effect by reducing the oxygen flux to the steel surface may substantially change corrosion rates, in particular in short term tests of corrosion.

Organic macromolecules easily available as nutrient for bacteria will be oxidized thereby reducing an important source for bacteria growth. These methods are therefore believed to have a positive effect on bacterial corrosion.

Biocides

Organisms are neutralised by addition of a biocide or any substance that will form a biocide in reaction with sea water. Examples: acrolein, formaldehyde, copper sulphate and varying brands of microbiocides.

Unless containing oxidising substances, biocides are not likely to have any effect on general corrosion levels. However, the organic content in the ballast tanks will not be reduced and effects on environmental conditions affecting corrosion will therefore be similar to physical methods.

De-oxygenation

Nutrients or other chemicals are added into the ballast water leading to anaerobic conditions in the ballast tank. This will neutralise most animals and algae, but not anaerobic bacteria and spores/cysts.

Reduced oxygen content will lead to lower corrosion rates. Bacterial corrosion may, however, increase. If water contains normal oxygen levels for surface water when pumped into ballast tanks, this may lead to high pitting corrosion by oxidizing sulphides to sulphuric acids.

Table 2 summarises expected corrosion effects for some of the discussed treatment methods.

***Table 2**. Potential effects of some treatment methods on corrosion in ballast tanks. For details see text. ↑ = Increased level, / = Unchanged level, ↓ = Reduced level. Expected corrosion rate: + = higher, - lower, / = Unchanged. ? = not clear.*

Treatment	Effect on selected environmental conditions				Expected effect on corrosion rate		
	Temperature	Oxygen level	Oxidant level	Organic carbon	General corrosion	Bacterial corrosion	Total effect
Mechanical	/	↑	↓*	↓	(+)	-	(+)?
Ultrasound	/	↓	↑*	/	-	+	?
Heat treatment	↑	↓	/	/	(+)?	(+)	(+)
Supersaturation nitrogen	/	↓	/	/	-	(+)	-
De-oxygenation	/	↓↓	/?	/	-	(+)	- ?
Ozone	/	↑↑	↑↑	↓	++	-	++
Hypochlorite	/	↑ ?	↑↑	↓	+	-	+

* = increased CO_2 level.

Conclusion - testing of corrosion effects

Corrosion effects are only occasionally included in tests carried out on ballast water treatment systems. If included, methods used are most frequently measurements of linear polarisation resistance or redox-potential. As illustrated in the case example below, the testing of corrosive effects of ozonation, such measurements can only be indicative and seldom conclusive. Long term tests using standard coupons should be carried out if significant corrosion effects are feared or likely.

When tests of corrosive effects are carried out in the laboratory, it is important to simulate a real ballast situation as exact as possible. Corrosion rates in ballast tanks vary between different levels in the tank. Highest corrosion rates are experienced in the upper segment of the tank. Temperature, abundance of oxygen supply and splashing of sea water is important factors impacting the corrosion rates. The tanks should therefore be stirred or moved during the experiment.

The build up of rust deposits and their protective effect by reducing the oxygen flux to the steel surface may substantially change corrosion rates, in particular in short term (1 – 3 months) tests of corrosion. It is important to keep in mind that a stable "steady state" corrosion rate will not be achieved before an exposure period of about 6 months.

Furthermore, the water used in experiments often has relatively low organic content and the set-up seldom includes tank sediments.

The corrosion rates as such are therefore not directly comparable to actual corrosion rates found on ships in service. This implies that it is the relative differences between the results from the experiments that are of the greatest interest.

A case example – testing of corrosion effects of ozone treatment

A feasibility study of ozone treatment of ballast water was carried out including both biological efficiency and corrosivity measurements. Similar to several other oxidants, ozone reacts with seawater and produces a number of corrosive compounds (e.g. several forms of bromine and chlorine). These corrosive compounds were found to decay after a period from some hours to more than one week following treatment. The decay rate is a function of ballast water characteristics (presence of organic compounds, metal ions and organisms). In polluted water the decay rate will be higher compared to clean water.

The corrosivity study included two phases:

- Short term; determination of corrosion rates based on linear polarisation resistance (Rp) immediately after treatment. The platinum wire was also used as an electrode for measuring the redox-potential.
- Long term; this phase was designed to reflect typical ballasting scenarios over a three month time period and was based on the long term exposure of bare steel and coated coupons. Weight loss of the bare steel coupons were used as measure for corrosion while visual observations and coating disbonding were used for the coated coupons. The coupons were exposed by repeatedly emptying the ballast tanks and refilling with ozonated seawater.

Short term test

1. The corrosion of carbon steel in an ozone-injected system was found to be about 500% higher than the corrosion rate of steel in normal oxygen rich seawater. The free oxidant level at the electrode position was 0.85 ppm or higher in all tests.

2. This initial corrosivity did not change due to the presence of the algae or other types of organic matter.

In Figure 1, the electrode to the right was exposed to ozone treated water in one test compared to untreated electrode.

In real ballast water scenarios, the oxidant concentration will decay after hours to days depending on water quality. To give an estimate of a maximum level of corrosion based on the Rp measurements, the following approach was adopted:

- Extensive inspection and surveys done by DNV have established that the average general corrosion rate of carbon steel in ballast tanks are around 0.1 to 0.2 mm/year (for single side of a tank).
- This represents the Rp results of no ozone in the test. As an approximation, this measured corrosion rate is assumed to represents the "base-line corrosion" equivalent to an in-service corrosion at about 0.1 to 0.2 mm/year. Based on this assumption, the corrosion rates for the

other exposure conditions can be calculated from the "base-line corrosion". This implies that the corrosion rate of steel will increase to 0.5 to 1 mm/year (for the single side of a tank) provided the presence of chlorine at a level of 0.85 to 5 ppm.

- The rates of corrosion estimated above assume the presence of a constant level of chlorine over a period of one year. This will not be the case in a ballast tank in a vessel in normal service. Oxidant decay will incur immediately following ozonation (ballasting). The established elevated levels of oxidants can be expected to last from some hours up to 2-3 days. This will dramatically change the corrosion picture. Annual corrosion effects due to ballast water ozonation will depend upon the ballasting pattern (no. of ballast voyages/ quality of ballast water).

This approach for estimating maximum corrosion rates, is only a first estimate. Only long term testing can establish accurate corrosion rates for a given ballast scenario.

Long term test

The tests were designed to simulate three sailing schedules/scenarios, which resulted in the following scenarios:

1. Ballasting once per week, i.e. 3.5 days full, 3.5 days empty, totally 12 fillings.
2. Ballasting every second week, i.e. 7 days full, 7 days empty, totally 6 fillings
3. Ballasting once per month, i.e. 14 days full, 14 days empty, totally 3 fillings

Corrosion was monitored using steel coupons mounted at three different levels in the test tanks. The tanks were filled to a level of approximately 80% of the tank height, always leaving the upper steel coupons out of water. Similarly the tanks were emptied to about 20% always leaving the bottom row of steel samples permanently in the water phase. For each of the three scenarios, a reference test with untreated water was carried out.

The steel coupons had three different surface qualities:

1. Bare steel (grit blasted)
2. Primed with 15 µm zinc silicate and coated with 2 layers of modified epoxy (totally 300 µm) - intact
3. Primed with 15 µm zinc silicate and coated with 2 layers of modified epoxy (totally 300 µm) - scribed

An average corrosion rate was calculated for the total area of the plates based on the weightloss of each sample. This provided a "one side corrosion rate". It should be noted that this average corrosion rate does not provide information on local corrosive attacks.

1. Corrosion rates did not achieve a steady state during the testing period. The decline in corrosion rates that was observed in each individual tank over the project period, was caused by increased quantities (thickness) of corrosion products forming a protective layer covering the metal surface.
2. In the lower segment of the tank (permanently submersed in water) testing showed increased corrosion rate as a result of ozonation. This is assumed to be due to the increased level of oxygen and corrosive compounds. Normal corrosion in this part of ballast tanks, which is a minor part of the total tank area, is 100 – 200 µm/year indicating an increase if ozonated to 200 – 400 µm/year. The absence of sediments may have contributed to this increase.
3. In the mid-section (air and water) testing demonstrated a lower corrosion rate in the ozonated tanks than in the untreated tanks. This is assumed to be due to the initial corrosive product resulting from ozone treatment being denser, less permeable to air and hence more protective. In a ballast tank this protective layer will probably peel off after some time due to ship

movement and wave induced loads on the ballast tank side plating. This, however, will also be the case for uncoated tanks exposed to untreated ballast water. It may therefore be assumed that ozonation will not represent an addition to normal corrosion rates (200 – 400 μm/year) in the mid- section of ballast tanks.

4. In the top segment (air only), very limited corrosion was found and the testing did not show a significant difference in corrosion rates between the treated and untreated tanks. The test results for this segment is, however, assumed to have limited relevance for ballast tanks as condensation and splashing normally will occur, wetting also the upper part of the tanks. The highest corrosion rates (approximately 400 μm/year) in ships ballast tanks are observed in this segment. This has been explained by the combined effect of increased average temperature due to sun heating, abundant oxygen supply, splashing of sea water, and cyclic temperature changes leading to cyclic condensation of water and drying. These factors will not be affected by ozonation and it is therefore assumed that the corrosion rates will be unchanged after treatment.
5. Ozonation clearly affected the bonds between the topcoat and primer close to coating defects. In total more than 80% of the coated plates from the mid- and lower level in ozonated tanks showed disbonding of coating, compared to 0% from the untreated tanks. The oxidising properties of the ozonated seawater may have affected the properties of the primer at the topcoat interface leading to a reduced bonding between the primer and the coating.

Figure 2 shows coated coupons with scribed surface showing disbonding of coating after ozone treatment.

References

Askheim, E., Nakken, O & Haugland, B.K. 2000. *New class rules for protective coating*. Presentation at the 8th ICMES/SNAME, May 22-23, 2000.

Beech, I., Campbell, S., Mills, G. & Walsh, F. 1996. Engineering problems caused by microbial corrosion and their prevention. *Corrosion Management*, June/July 1996.

Brown, B.E. & Duquette, D.J. 1994, A review of the effects of dissolved ozone on the corrosion behaviour of metals and alloys. *Corrosion* 94. Paper no. 486.

Campbell, S.A., Scannell, R.A. & Walsh, F.C. 1988. Microbially-assisted pitting corrosion of ships hull plate. *UK Corrosion* 88, Brighton 3-5 October 1988, pp. 137-157.

Cleeland, J.H. 1995. Corrosion risks in ships' ballast tanks and the IMO pathogen guidelines. *Engineering Failure Analysis*, 2 (1) pp. 79-84.

DNV, 1993. *Corrosion wastage rates and corrosion additions in ships ballast tanks*. DNV Report 93-0117.

DNV, 1996. *Corrosion protection of ships*. Guidelines no. 8. July 1996.

DNV, 1999a. *PLUS and COAT notations. Fatigue and corrosion prevention*. DNV brochure.

DNV, 1999b. *Corrosion prevention of tanks and holds*. Classification notes, No. 33.1. July 1999.

DNV, 1999c. *Bacterial corrosion in ballast tanks. Problem and solution*. DNV Brochure 1999.

DNV, 2000. *Ballast water treatment by ozonation*. DNV Report no. 2000-3229.

Korbin G. (Ed.) *Microbiologically influenced corrosion*. Nace International, 1993.

Figure 1. *Electrode to the right was exposed to ozone treated water in one test compared to untreated electrode.*

Figure 2. *Coated coupons with scribed surface showing disbonding of coating after ozone treatment.*

Session 5:
Test Protocols and Verification Procedures

A proposed frame-work for approving ballast water treatment technologies

D. Mountfort, T. Dodgshun & M. Taylor

Cawthron Institute
New Zealand
douglas.mountfort@cawthron.org.nz

Introduction, aims and objectives

Recent progress by the Marine Environmental Protection Committee (MEPC) toward achieving an interim standard for ballast water treatment (eg the draft report on ballast water management [MEPC 48/WP.1.5]), represents an advance in quality assurance beyond the current protocols for ballast water management, which are essentially restricted to mid-ocean ballast water exchange (http://globallast.imo.org). With the pending implementation of a ballast water treatment standard in 2003, it is necessary to develop systems under which the performance of a new treatment technology can be measured. In this regard we consider it important to also introduce the following:

1. A framework to evaluate the performance of new treatment technologies;
2. A certification system leading to the ultimate approval of a technology;
3. An effective management system for performance review and certification.

In this paper we outline how these objectives might be achieved and describe the operation and management of the proposed performance evaluation system. Our proposed framework is formulated on the experience of our team and our collaborators, the Centre for Research on Introduced Marine Pests (CRIMP), in developing a systems-based approach for risk assessment for marine pests in Australasia (eg Hayes and Hewitt, 1998) and builds on Cawthron's expertise in the validation and approval of new methods for marine pest management (e.g. harmful algal blooms and the Asian kelp, *Undaria pinnatifida*). It also builds on our experience in developing new methods for ballast water treatment (Mountfort *et al*., 1999 a,b; Mountfort *et al.,* submitted) and in working with the shipping industry in ballast water management since 1995 testing the efficacy of ballast water exchange and shipboard treatment systems (Taylor and Bruce, 1999: Mountfort *et al.,* 1999c; Mountfort *et al*., 2003). More recently we have initiated new international partnerships evaluating the efficacy of biocides and ozonation.

We provide a rationale for the proposed framework and describe how ongoing developments in the refinement of international standards for sampling and treatment of ballast water would be accommodated. The framework aims to provide a pathway for the approval and implementation of new treatment systems so that the process will have a minimum impact on the shipping industry.

Advancement of the performance evaluation system for new treatment technologies

The "moving target" of global protocols and standards

Any new framework should be flexible enough to accommodate both the present "state-of-the-art" standards for both ballast water treatment and sampling, and future developments in these areas. For example, future standards might include the use of representative indicator taxa for the certification of a particular ballast water treatment system.

The proposed ballast water treatment approval framework

Currently there are a number of agencies involved in the formulation of approval methods for ballast water treatment. These include Det Norske Veritas (DNV) who, in co-operation with the Norwegian Institute for Water Research (NIVA), are developing standard methodologies for evaluating the biological effectiveness of a given treatment (http://projects.dnv.com/). Also, the work of Taylor and Rigby (2001) emphasises the need to consider design aspects of ballast water treatment systems during shipboard operations. Such initiatives are timely in the context of developing an internationally accepted approval system. In our proposal, which stems from our earlier considerations on future strategies for ballast water treatment (Mountfort, 2000), the following points are considered:

1. The need to minimise the intrusion on ships' operations in the early phase of treatment assessment;
2. The need to minimise costly shipboard installation of inefficient or inappropriate units that have not undergone an appropriate preliminary testing regime;
3. The need to recognise that the criteria for assessing the performance of a shipboard system may differ from those required for pre-shipboard testing;
4. The need to minimise scientifically indefensible commercial bias;
5. The need to obtain a performance and provisional compatibility assessment before installation on any ship.

Consequently, we are advancing a three tier framework for the approval of ballast water treatment systems. The essential components of the framework are:

Tier I Testing of a promising treatment in an IMO approved testing facility;

Tier II Pending tier I approval, shipboard assessment of the performance of the treatment or treatment facility;

Tier III Ongoing performance review of the technology after it has been certified for shipboard use.

The criteria for approval (Tiers I and II above) would be based on standards and protocols ratified into IMO convention by the Marine and Environmental Protection Committee (MEPC) and would include:

1. Performance of the treatment system measured against the IMO approved ballast water treatment standard and using an approved international standard for ballast water sampling;
2. Assessment of the environmental impacts from discharged treated ballast;
3. An assessment of compatibility with candidate ships including factors such as:
   - Ship type
   - Ship design including ballast tank configuration
   - Ship's operations
   - Ship safety
4. An economic appraisal of the treatment, especially in relation to point 3 above.

Treatment systems proposed by a vendor would be assessed and scored under each criteria. Thus for example, assessments conducted in regard to point 2 might score filtration more highly than for biocide treatment. Importantly, the framework recognises that the ballast water standards and protocols, as set out by the IMO convention, are likely to change over time with new treatment technologies and member-state priorities. Figure 1 shows how the proposed system would accommodate such changes over time. As an example of how this might operate, the interim standard may require that a IMO approved testing facility (Tier I) tests to a standard based on a complete kill or removal of organisms greater than 100 microns in size. However in the longer term, the testing facility might be required to test to a different standard, possibly one in which the maximum size of

the test organisms is reduced, or one in which a universally applied set of indicator taxa is used to assess performance.

We anticipate that the criteria used for assessing the performance of the technology in a shipboard situation (Tier II) would be similar to those for the treatment facility (Tier I) except greater emphasis would be placed on criteria 3 and 4.

In Figure 2 we show diagrammatically how the tiered system of treatment approvals might work in practice. Implicit in the scheme would be the overseeing of the testing for Tiers I and II, and performance review (Tier III) by an independent IMO approved expert (or experts). The make-up of the team might be different for each of the three Tiers. For example, the team for Tier 1 testing might be limited to an IMO approved scientist. In Tier II testing might include an IMO approved scientist, a ship's engineer and could include consultation with a wider group including an economist.

We contend that once installed, any newly certified treatment technology should be periodically subjected to a performance review (Tier III) by IMO approved experts. We suggest that performance reviews should be carried out on all ships equipped with treatment systems for the first 5 years after implementation of the interim ballast water treatment standard, and that at least one inspection is carried out on all units installed during this period. The rationale for this is that (i) the interim standard will apply for approximately this period, and (ii) the number of ships equipped with ballast water treatment systems will be relatively few compared to those carrying out ballast water exchange. Over the longer time period, the system of performance review may need to be revised according to the number of ships with treatment systems onboard and the development and implementation of new treatment standards and protocols.

Among the criteria that we believe should be considered for assessments during performance monitoring are:

1. comparison of performance against that at the time of certification (see criteria for Tiers I and II);
2. inspection for deterioration of plant;
3. where appropriate, inspection of ships log to determine use of plant.

Should the treatment continue to meet the standards under which it was initially granted, then its certification should be extended.

How the framework would be implemented

The framework would essentially operate on a report and recommendation basis for each Tier. Because of the anticipated ongoing improvements to ballast water standards and protocols, it would be necessary to consider the timing and duration of approvals and certification. Thus, in the case of a technology that has been approved under Tier I, testing in a shipboard situation should be completed within a period of time that is consistent with current standards and protocols.

Similarly, approval for shipboard installation should be valid for a minimum period (*e.g.* 5 years). Extension of the approval would be subject to performance review on the basis of the criteria for which the technology was originally approved. On the other hand new treatment technologies entering the system would have to meet the requirements of any new standards and protocols. We believe our framework allows for reasonable life-times for treatment systems once installed, but at the same time is flexible enough to meet the requirements of standards and protocols set by international convention. The framework also minimises the need to replace newly-installed treatment equipment (eg by retro-fitting) in order to meet a new standard.

Additional considerations

In addition to the criteria set out for assessing the performance of new treatment systems (Tiers I and II above), some countries may elect to have stricter standards for the management of ballast water discharge. These might be applied, for example, after a risk-based assessment of specific ships or shipping pathways. We believe, therefore, that the framework finally adopted will need to be sufficiently robust to accommodate such variations.

Conclusions and recommendations

To date there has been very little progress in the development of an effective framework for the approval of ballast treatment technologies. With the interim standard for ballast treatment technologies being included in the pending IMO convention for ballast management, a need has arisen for a framework under which approvals for new treatment systems can be granted. This would ensure that ballast water treatment facilities are able to meet the standards and protocols set by international convention. We have outlined how this could be achieved by proposing a three tier framework of performance testing and review. The framework would:

1. Minimize the impacts on existing ships' operations resulting from the installation and trial of treatment systems that are either inappropriate or have not met the required standard;
2. Minimize the environmental impact that may be caused by an inappropriate treatment or one that has not met the required standards;
3. Minimize and structural damage and safety concerns resulting from a treatment that has not been subjected to performance assessment and review
4. Remove scientifically indefensible commercial bias in the advancement of new treatment technologies;
5. Provide an internationally recognized framework for approval of ballast treatment systems;
6. Maximize the efficiency with which new treatment technologies can be certified for shipboard use;
7. Protect the vendor from liabilities that may arise from adverse structural, health or environmental impacts.

Key future considerations for implementation of the framework include:

1. Refinement of the criteria for certification;
2. The composition of the IMO approved teams who would oversee and report on performance testing and review;
3. Certification period and frequency of performance review.

Acknowledgements

We express our appreciation to the shipping industry particularly in providing access to vessels for ballast management investigations. We express also our thanks to the New Zealand Ministry of Fisheries (MFish) for their support in preparing this paper, and in particular to Elizabeth Jones and Dr Chad Hewitt. We also thank members of the Biotoxin Monitoring Team at Cawthron for providing valuable information in regard to the granting of approvals for new methods in phytoplankton toxin analysis. We also thank the New Zealand Foundation for Research, Science and Technology for supporting our work on ballast water management since 1996.

References

Hayes, K.R. & Hewitt, C.L. 1998. *Risk assessment framework for ballast water introductions*. Technical Report No 14, Center for Research on Introduced Pests, pp 1-75.

http://projects.dnv.com.

http://globallast.imo.org.

MEPC ANNEX. 48/WP.1.5. 2002. Draft international convention for the control and management of ship's ballast water and sediments. 31 p.

Mountfort, D.O., Hay, C., Dodgshun, T., Buchanan, S. & Gibbs, W. 1999a. Oxygen deprivation as a treatment for ships' ballast: laboratory studies and evaluation. *J. Mar. Environ Engg*. 5: 175-192.

Mountfort, D.O., Hay, C., Taylor, M., Buchanan, S. and Gibbs, W. 1999b. Heat treatment of ships' ballast water: development and application of a model based on laboratory studies. *J. Mar. Environ Engg*. 5: pp. 193-206.

Mountfort, D.O., Dodgshun, T., Gibbs, W. & McCallin, B. 1999c. Towards a feasible heat treatment system for ships' ballast water. Proceedings of AAPMA meeting, Brisbane, May 5-6, pp. 125-126.

Mountfort, D.O. 2000. Ballast water treatment-the future. In "Developing a strategy for Marine Biosecurity in New Zealand" Proc 1st National Workshop on Marine Biosecurity, Nelson, pp. 19-21.

Mountfort, D.O., Parker, N. & Oemcke, D. Effect of UV irradiation on viability of micro-scale and resistant forms of marine micro-organisms: implications for the treatment of ships' ballast water (Submitted *J. Mar. Environ Engg*).

Mountfort, D.O., Dodgshun, T. & Taylor, M. 2003. Ballast water treatment by heat: New Zealand laboratory and shipboard trials. In Raaymakers (ed) *1st International Ballast Water Treatment R&D Symposium, IMO London 26-27 March 2001: Symposium Proceedings*. GloBallast Monograph Series No 5. IMO London. pp. 45-50.

Taylor, A.H. (1996). *Design considerations for ballast water control and treatment*. IMAS. Paper 10: pp. 23-29.

Taylor, M., & Bruce, E. 1999. *Mid ocean ballast water exchange: Shipboard trials of methods for verifying efficiency*. Cawthron Report No. 524.

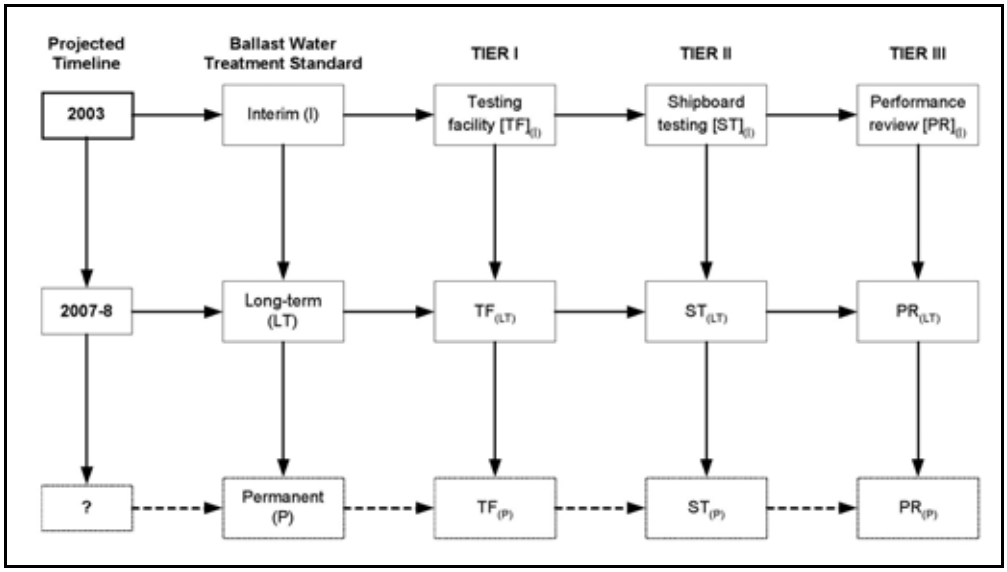


Figure 1. *Response of the tiered system for ballast water treatment approval to perceived changes in the ballast treatment standard over time.*

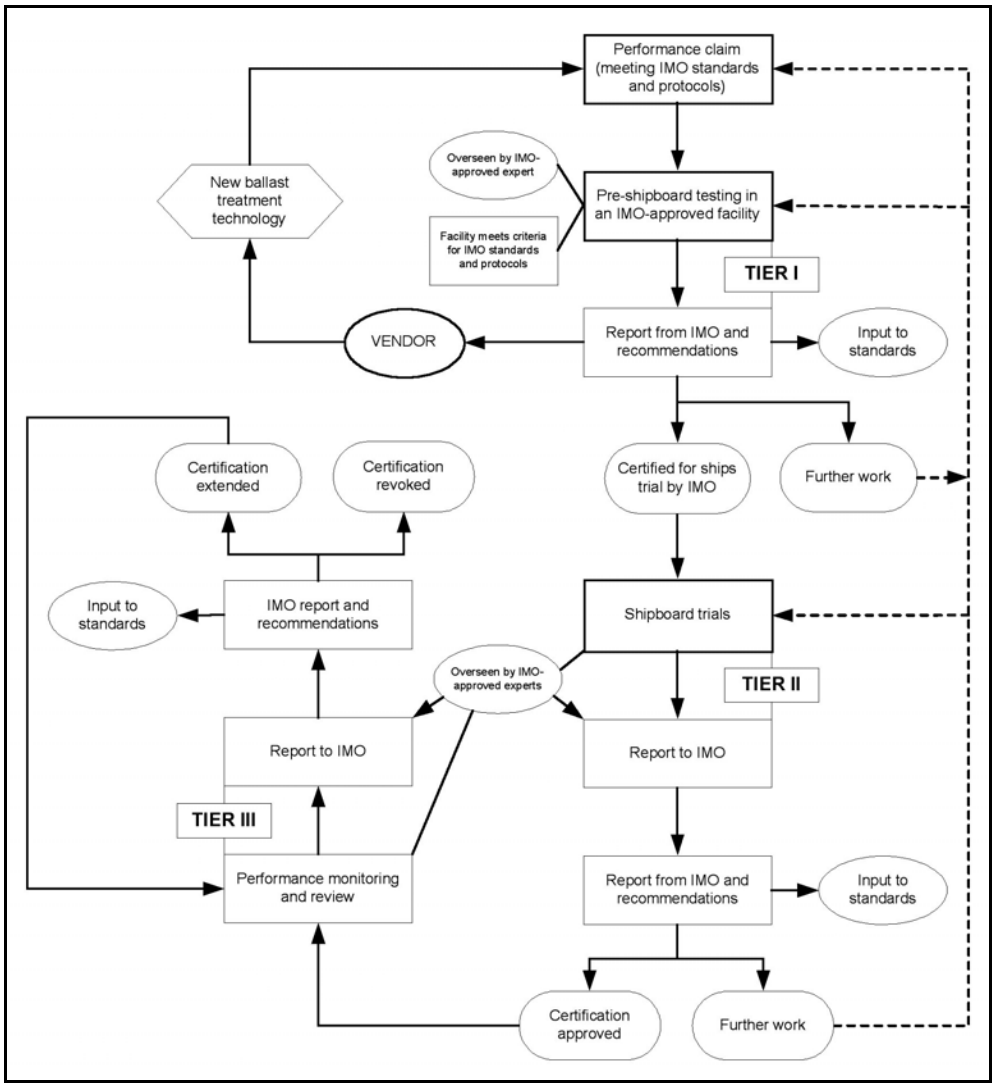


Figure 2. *Scheme for the approval of new treatment technologies.*

Ballast Water Treatment Verification Protocol - DNV

A. B. Andersen, B. O. Johannessen & E. Dragsund

Det Norske Veritas
Norway
aage.bjorn.andersen@dnv.com

Introduction

The ballast water treatment challenge has inspired numerous owners of technologies of a wide range of associated applications resulting in a significant volume of development projects parallel to the development of *the International Convention for the Control and Management of Ships' Ballast Water and Sediments* (the Convention). Main focus has been that of treatment efficiency and a number of different assessment approaches have emerged. DNV have also assessed various proposed treatment concepts.

Evident need for a uniform reference for performance assessments resulted in the development of the DNV "Model Group Concept" which was presented to the *Marine Environmental Protection Committee* (MEPC) at its 46th session. (MEPC 46/3/8). This methodology introduced an approach for setting standards and allowed performance comparisons between different ballast water treatment concepts with respect to treatment efficiency to be undertaken.

Experience from the application of this methodology to actual concept assessments including laboratory work and inputs from the iterative processes related to the ongoing development within MEPC of the Convention, have formed the basis for the development of a protocol covering a wider range of issues requiring consideration in light of the issuance of compliance documentation. The DNV protocol will cover:

- *Application and Feasibility.*
- *Occupational Safety and Health (OSH).*
- *Treatment Efficiency.*

The protocol and its appendices are under development and will be available following the adoption of the Convention.

Aims and objectives

DNV have established the project; *Ballast Water Treatment Technologies – Standards for Certification* for the purpose of developing a protocol or standards for certification for the approval of onboard installations of ballast water treatment systems. These standards will form procedures and rules that will be developed in coordination with the *Guidelines for Type Approval of Ballast Water Treatment Systems* currently being drafted by IMO. The standards will provide as an *Operational Performance and Testing Programme* that may be adopted by any Party to the convention.

Research methods, test protocols and experimental design proposed

The development of standards for certification is a process representing a methodical approach itself that requires the definition of:

- Principles
- Acceptance criteria

- Required information

In order to assess compliance and thus issue an approval document, the considered treatment system must meet the requirements of the standard which includes the following four areas:

1. Provision of satisfactory documentation: *Compliance to the standard of certification*.
2. Occupational safety and health norms: *Safety margins with respect to risks-levels (ship, its crew, etc.)*.
3. Demonstrate sustained performance to meet any applicable IMO conventions: *Ballast Water Performance Standard.*
4. Demonstrate no present unwanted effects: *Environmental, other.*

The conformity assessment process may be illustrated by step 1, 2 and 3 as illustrated in figure 1. The starting and ending points represented by Phase I and Phase II respectively, relates to:

I *Idea and investigation:* This represents the motivation of the owner of the treatment technology or system.

II *Certification:* The issuance of compliance documentation following a successful conformity assessment process by an Administration (or an appointed party).

Steps 1, 2 and 3 represent the procedures of the actual protocol. The process of identifying content, criteria and assessment procedures in relation to the areas covered by the standard have rested upon actual system assessments. These have included the following:

General review (relates to step 1, figure 1):

Technology considerations (feasibility assessments) focussing on occupational safety and health, potential shipboard impacts, possible constraints in relation to operations (practicality, long term effects, etc.), treatment sequence and performance characteristics.

The general review has rested upon available literature and in-house knowledge and experience. Initial small scale laboratory tests have also been performed to improve the understanding of methodologies and interrelations when applied together in a system.

Laboratory studies (relates to step 2, figure 1):

For the purpose of evaluating treatment performance and thus to provide recommendations on aspects related to treatment performance reliability, potential scaling effects and particulars of the treatment concept requiring attention (treatment sequence, occupational safety and health aspects, energy consumption, residual products, etc.), meso-scale laboratory set-ups have been established and testing performed.

The driving principle when sizing the laboratory treatment system has been that of simulating the actual full scale process by dimensioning with emphasis on treatment speed. Thus, the speed of flow throughout the system including piping to ballast tanks (holding time) has been included.

Conditions in ballast tanks have been simulated (darkness, limited ventilation) over time. However, our work has not included motions and vibrations as will be an integrated factor in a full scale application and may impact aspects associated to the operations of some technologies.

In cases where the general review has identified particular aspects of concern, these have been encountered for in the laboratory testing, e.g. corrosion/ coating impacts.

Treatment performance has been undertaken by applying the principles of the Model Group Concept:

Model Group Concept:

The diversified presence of organisms in an ecosystem can be organised and represented by defining groups of organisms – model groups. The model groups are exposed to the treatment process of the system under consideration and efficiency may then be measured. The concept is similar to that of eco-toxicological testing (*in reverse*).

Selection criteria for species for each model group and further, the number of model groups required will reflect the applicability of the method. When the concept is applied for the purpose of assessing ballast water treatment system performance, the selection criteria must mirror the global perspective.

*Full scale verification (*relates to step 3, figure 1*):*

Based on output from the above procedures, full scale verification procedures for the treatment systems tested have been identified. These have included:

- System performance (operational verification)
- Treatment performance (sampling under varying conditions)
- Effects (atmospheres, residuals, etc.)

The above approach has been applied to mechanical, physical as well as chemical treatment systems. Based on experiences and findings, the frames of a protocol or a standard for certification has been developed.

Results

The draft Ballast Water Treatment Verification Protocol outlines the DNV process for the approval of ballast water treatment systems to be installed onboard DNV classed vessels.

The protocol, as illustrated in figure 2, consists of three sections:

- Protocol infrastructure: *Introduction, Definitions, Conformity Assessment Procedures*
- Criteria: *Regulations*
- Tools: *Appendices*

The protocol will be reviewed in accordance to any revisions associated to the development of the Convention.

Protocol infrastructure

The three introductory chapters (see figure 2) explain the area of application of the protocol and how it is applied when used for compliance assessments.

For practical purposes, the protocol has established a number of definitions. Some examples are listed below:

Ballast Water Treatment Systems

Applies to the collection of all components that make up a complete, operating ballast water treatment arrangement, from ballast water intake to discharge.

Ballast Water Treatment Systems Components

Applies to any of the various components that make up the complete ballast water treatment system (e.g. filtering unit, primary treatment unit, piping, pumps, control units, etc.).

Ballast Water Treatment Units

Applies to the component of the ballast water treatment system specifically designed to remove or render harmless (extinguish) organisms. A ballast water system may be composed of one or several ballast water treatment units.

Active substance

Applies to any substance added to, or produced by the ballast water treatment unit, with the purpose to remove marine organisms or render such organisms harmless.

Active physical process

Applies to any physical process utilised by the ballast water treatment unit, with the purpose to remove marine organisms or render such organisms harmless.

The procedural mechanisms of the protocol are also explained

1) *Approval of scaled down system*
   a. *performance testing*
   b. *safety, functionality, quality, documentation*
   c. *unwanted effects*
2) *Desktop scaling of test results*
3) *Approval of large scale arrangement*

Criteria

System compliance criteria are formulated as regulations. The areas considered are listed in figure 2 and follows the methodology represented by the conformity assessment processes.

System performance testing

The performance references include all relevant Regulations of the Convention with emphasis on Regulations E-2 and E-3.

The system performance must be demonstrated through either:

1. Testing of the installed full scale system or
2. Laboratory testing of the full scale system or
3. Testing of a scaled version of the system

Performance testing is subject to the procedure described in Appendix A in the draft DNV protocol (see figure 2).

For scaled testing, the performance of the full scale system must be established through documented and scientifically approved methods. A guideline for scaling of test results is also provided (Appendix B, Guidelines for scaling of performance test data (currently under development). Furthermore, if the system incorporates two ore more dissimilar ballast water treatment units, the overall performance estimate must be based on individual testing of all units. The estimated performance of the scaled-up version of the system must take into effect any interaction between the two independent systems.

Safety, functionality, quality and documentation

These aspects are all interrelated. Requirements to these are based on relevant applicable existing standards and norms (e.g. ISO standards, EU Directives (Directive on Marine Equipment), ILO requirements, DNV rules, etc.).

Unwanted effects

This relates changing characteristics of the ballast water as a consequence of the treatment. Unwanted effects are those affecting:

- Ballast water tanks and/or associated systems including pumps, piping, valves, etc.
- The environment following the discharge of treated ballast water

The standards for certification refer to recognised standards and norms in relation to both of these items.

Standard for performance testing of ballast water treatment units

This represents the methodology to be applied for collecting quantitative performance data for ballast water treatment units under controlled test conditions. A ballast water treatment unit is defined as the component of a ballast water treatment system that kills, removes or renders marine organisms in ballast water.

General

A ballast water treatment system may be composed of a combination of several ballast water treatment units. The standard may be applied to establish performance data for the combined unit, as well as for individual units. The boundaries of the tested unit or combination of units, for which test result will apply, must be clearly defined by the party responsible for testing.

The method is designed to provide performance data for a range of operating conditions for the treatment unit, including the required performance data to demonstrate compliance/ non-compliance with relevant IMO Regulations.

Scaling

The testing methodology may be applied to ballast water treatment units of any size. The test results however, apply only directly to the unit tested or to identical units. Care should be taken upon extrapolating test results to differently scaled units. Any such scaling should follow scientifically acknowledged scaling laws and should be carried out according to directions set forth in the Appendix B accompanying the protocol.

In order to form basis for estimation of a full scale ballast water treatment system (after extrapolation), the scaling difference should comply with some limits. At this stage in the process, the following recommendations have been considered:

- Not to exceed 1: 1000 by volumetric capacity.
- Test arrangement must have a minimum water flow of 1 m^3/ h.

Note that these restrictions are preliminary and under further assessment.

It is recommended that basic studies of ballast water cleaning principles are carried out at bench-scale prior to testing according to the DNV Protocol. Recommendations for such studies are given in the Appendix C - Guideline for small scale evaluations of ballast water treatment techniques, also currently under development.

Generalised description of test set-up and methodology

Testing of ballast water treatment units according to the protocol involves three general steps:

1. Preparing simulated ballast water with predefined properties and content of marine organisms.
2. Treatment of simulated ballast water by a flow-through ballast water treatment unit, operated according to its specifications and operating principles.

3. Sampling, monitoring and analysis of treated ballast water for determination of treatment performance as a function of test variables and time.

The standard is applicable to any test arrangement and facility that allows control and monitoring of the test conditions and test parameters. Figure 3 shows two alternative general test arrangements.

Test facility requirements

To perform testing, certain requirements to the facility undertaking the tests have been identified. These are:

1. Uninterrupted access to the needed quantity of fresh and salt water with the desired physical/chemical properties for the entire duration of the testing procedures.
2. Provide means for preparation of simulated ballast water with the desired uniformity in composition and concentration of marine organisms.
3. Functional provisions for the treatment unit to be tested including pumping capacity and piping/hosing arrangements appropriately dimensioned.
4. Tanks and containers with sufficient holding capacity for the test water (before pumping) and for prolonged storage of water for monitoring after pumping
5. Provide a physical environment (temperature, light, air quality) that is not in conflict with storage of live marine organisms (organisms must not die due to the physical environment).
6. Provide (or have access to) laboratory facilities suitable for storage and analysis of water samples for registration of presence of marine organisms
7. Provide all necessary means for correct operation of the ballast water treatment units according to its specifications.
8. Provide all necessary instrumentation for control and monitoring of all operational parameters during testing, (e.g. fluid flow rate, pressure, turbulence level etc).

If tests are undertaken statically, i.e. conditions do not include vibrations and motions, the likeliness of this not affecting the performance of the system must be substantiated.

Testing according to this standard will establish quantitative performance data for the unit as a function of the following parameters:

- Content and concentration of various marine organisms.
- Salt water/ fresh water.
- Content of additional organic material.
- Time for exposure and/or storage.
- Main operating parameters of ballast water treatment unit (such as concentration of active substance, intensity of active physical process; see definitions).

Composition/ concentration of marine organisms

The Ballast Water Performance Standard, as identified in the current draft convention under Regulation E-2, identifies absolute quantifiable levels of aquatic organisms in ballast water for discharge distinguishing between zooplankton, phytoplankton and indicator microbes. Table 1 presents test conditions with reference to required concentrations.

Table 1. *Test organisms and concentrations.*

Organism class	*Concentration*	*Treatment performance requirement**
Bacteria (I.E)		200 cfu/ ml
Bacteria (E.C)		500 cfu/ ml
Phytoplankton	≥200.000 cpl	1,000 cpl
Zooplankton	≥500 cpl	25 cpl

* This will be changed in accordance with future regulation requirements

The selection of test organisms has been based on a criteria weighting model proposed by DNV, see Table 2.

Table 2. *DNV Criteria for selection of model group organisms.*

Prior.	*Weight*	*Criteria*
1	1	The selected species must be easy to cultivate and handle.
2	1	Each organism should represent a typical ballast water organism, i.e. have one or more pelagic life stages which will represent the test stadium.
3	1	The cultivation conditions for each species must be described in detail. The method for assessing the test results (viability) for each species must be clearly and unambiguously described. Selective detection methods should be available for each species.
4	1	The species of the model group must be robust compared to the majority of ballast water organisms implying high tolerance to physical and chemical stress, i.e. salinity, temperature, oxygen demand.
5	2	The species must be non-pathogenic (human and animal). Test should not lead to risk of spreading pathogen organisms.
6	2	The species must be well described and specified with respect to species and strain.
7	3	One species per model group should be readily available for testing irrespective of the geographical localisation of the test laboratory.
8	3	The species should preferably have a fairly worldwide distribution. The organisms must be readily available from culture collection.

Testing shall establish performance data for treatment of water containing the classes of marine organisms (model groups) defined in Table 3.

Table 3. *Alternative model groups.*

No	*Model group*	*Representative species for testing/ certification purposes*	*Lifestages in test set-up*
1	Bacteria	*Bacillus* sp.	Spores
2	Virus	None at present	-
3	Phytoplankton	*Dunaliella salinas*	Vegetative stages
		Diatoms (*Skeletonema costatum*,	
		Dinoflagellates	Vegetative stages Cysts
4	Zooplankton	*Artemia salina*	Larvae
5	Macroorganisms	Red algae (*Heterosiphonia japonica*)	Fragments

Simulated ballast water

The test procedure has to encounter for the large variations in ballast water characteristics. The following variables have been included (se summary in Table 4):

Salinity: Tests includes both fresh and salt water (typical for coastal surface water).

Temperature: The temperature under which the tests shall take place must reflect the natural temperature range of the organisms used and for coastal water.

O_2 - saturation: The level of dissolved oxygen shall reflect normal variations.

pH: Must differentiate between fresh- and salt water.

Turbidity: Turbidity varies over a range depending on local conditions and season and is dependent upon the level of suspended material. Tests for both *clear* and *dirty* water shall be included.

Organic content: Tests for clean and polluted (eutrophic) harbour water shall be included.

Table 4. *Simulated ballast water test variables.*

Property	***Salt water***	***Fresh water***
Salinity	> 32 PSU	< 0.5 PSU
Temperature	5-20°C	5-20°C
0_2 saturation	80-120%	80-120%
pH	7-9	6-8
Turbidity	Clear water, ≤ 2 FNU Dirty water, ≥ 10 FNU	Clear water, ≤ 2 FNU Dirty water, ≥ 10 FNU
Dissolved Organic Content	1($^+$/- 0.5) - 5 ($^+$/- 1) mg C/ litre	1($^+$/- 0.5) - 5 ($^+$/- 1) mg C/ litre

Test concentrations of organisms

For testing, the organisms in Table 3 shall be added to the water in concentrations specified (see Table 1).

Methods for adding marine organisms

The introduction of marine organisms to the treatment process should apply one of the following alternatives:

1. By use of a simulated ballast water holding tank (by stirring) from where the water is pumped to the ballast water treatment unit:
2. By an introduction chamber at the pumping line downstream of the pump (by pressurised injection to overcome the pump pressure).
3. In the sampling tanks after water has passed through the treatment unit.

Alternative 1 shall be the preferred injection point unless any conditions preclude this. Effects of pumping and eventual other physical "treatment" that is not a part of the system must be investigated.

Alternative 2 may be applied if the mechanical action of the pump or any non-essential component upstream of the ballast water treatment unit is considered to influence (increase) rate of mortality of test organisms; and these components are not essential and/or integral parts of the ballast water treatment principle.

Alternative 3 may be applied if the ballast water treatment method acts by generation or addition of active substances, and it is evident (or proven) that the immediate effect in the ballast water treatment unit is of negligible importance.

The uniformity of the simulated ballast water should be demonstrated by sample analyses.

Sampling and analysis

The following water samples should be collected for analysis of:

1. Water properties before and after treatment.
2. Content of organisms prior to treatment.
3. Content of surviving organisms at regular intervals during a minimum period of 2 days (under consideration).

4. Time development of content of active substances in storage over a period one day to one week depending on characteristics of the substance.

Analysis and methods

Analysis of water samples shall establish content of viable marine organisms as a function of time following treatment. Analysis methods are currently being assessed, but should include re-growth of bacteria and microalgae.

Performance parameters

Actual details regarding final performance requirements of ballast water discharge are not available until the convention has been amended. Thus, parameters to be considered will decided following the completion of the ongoing work within IMO.

Recommended testing procedures

Some testing procedures have been assessed. The protocol includes recommendations regarding:

- Preparations prior to testing.
- Testing period.
- After testing.

These are detailed into identified sequential tasks, the aim being to ensure that all tests are uniformly undertaken and thus comparable and at the same time in accordance to protocol procedures.

Quality control

The protocol includes quality control procedures which specify minimum requirements with respect to:

- Number of samples
- Repetitions
- Test duration
- Test volumes
- General (ambient) conditions

This is vital in order to ensure reliability and to gain acceptance and recognition.

Measurements and reporting

This section of the protocol summarises measurements that must be reported and include:

- Water properties
  - Including the parameters listed in table 4.
- Environmental parameters (ambient conditions; air temperature, humidity, barometric pressure, etc.)
- Operating parameters
- Performance parameters
- Any calculated parameters

Validity of certificate

A manual for maintenance, calibration and training should follow the treatment system and needs to be assessed in the evaluation.

The validity of the certificate will be time restricted in compliance with requirements in the Convention but will also reflect the characteristics of the system in question. Regular tests on board shall be conducted to document that performance of equipment are in compliance with requirements. Such control should include overboard discharge control and eventual measurements of concentrations of active substance in ballast water after treatment.

References

DNV, 2003 *Standardised Methodology for testing of Ballast Water Treatment Systems* (Norwegian Research Council).

DNV 2003. *Ballast Water Treatment by Nitrogen Super-saturation*, Technical report no.: 2003-0070.

IMO, 2003. *Draft International Convention for the Control and Management of Ships` Ballast Water and Sediments. MEPC 48*. Note: This is not an approved document and the text of the draft new ballast water convention is still under development, subject to negotiation, and may change substantially.

MARTOB, 2003a. *On board treatment of ballast water (technologies development and application) and application of low-sulphur marine fuel.* Work package 2 completion report. Document Id: DTR-2.9-TNO-12.01.

MARTOB, 2003b. *On board treatment of ballast water (technologies development and application) and application of low-sulphur marine fuel*. Work package 3 completion report. Document Id: DTR-3.11-VTT-03.03.

DNV, 2002 *Multi-oxidant Treatment of Ballast Water*, Technical report no.: 2002-0656.

DNV 2002 *National Regulations on Ballast Water Management* (Norwegian Maritime Directorate).

DNV 2001. *Ballast Water treatment by Ozonation – Biology*, Technical report no.: 2001-0523.

DNV 2001. *Ballast Water treatment by Ozonation – Corrosion*, Technical report no.: 2001-0524.

DNV 2001. *Alternative Ballast Water Treatment Principles and their potential in fulfilling future IMO requirements*, Technical report no.: 2001-1062.

MEPC 47/INF.11. *Harmful Aquatic Organisms in Ballast Water*. Description of the proposed model groups defined under Tier 1. Submitted by Norway.

MEPC 46/3/8. *Harmful Aquatic Organisms in Ballast water*. Proposal for performance criteria of the ballast water treatment standard. Submitted by Norway.

MEPC 47/2/13. *Harmful Aquatic Organisms in Ballast water*. Proposal for performance criteria of the ballast water treatment standard. Submitted by Norway.

IMO, 1997. IMO, 1997 - *Guideline for the control and Management of Ships Ballast Water to Minimise the transfer of Harmful Aquatic Organisms and Pathogen's* (IMO Assembly Resolution A.868.(20).

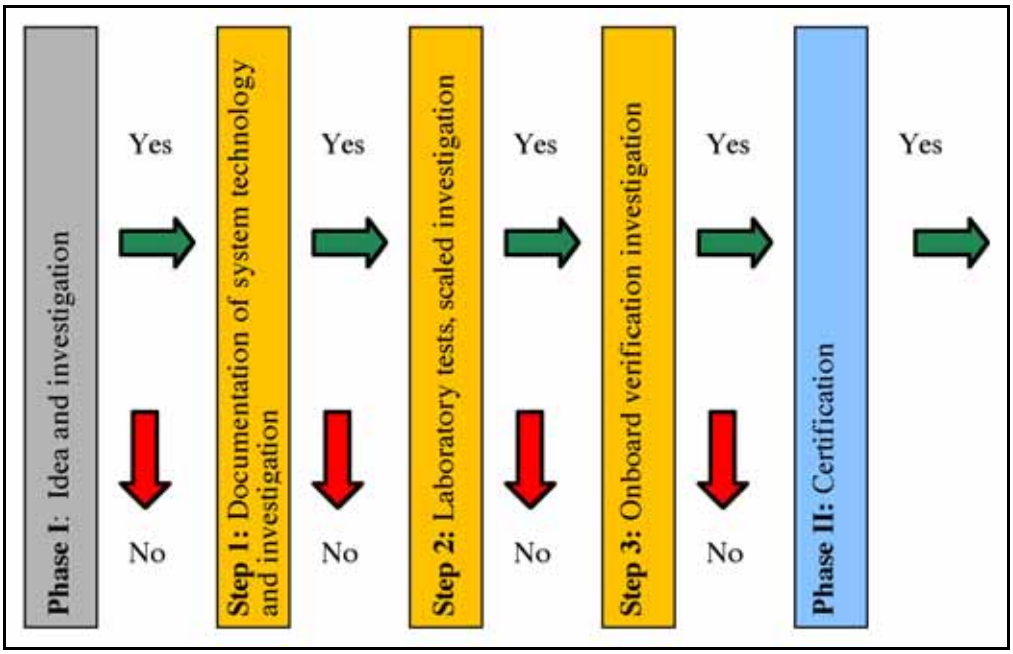


Figure 1. *Steps in the conformity assessment of ballast water treatment systems.*

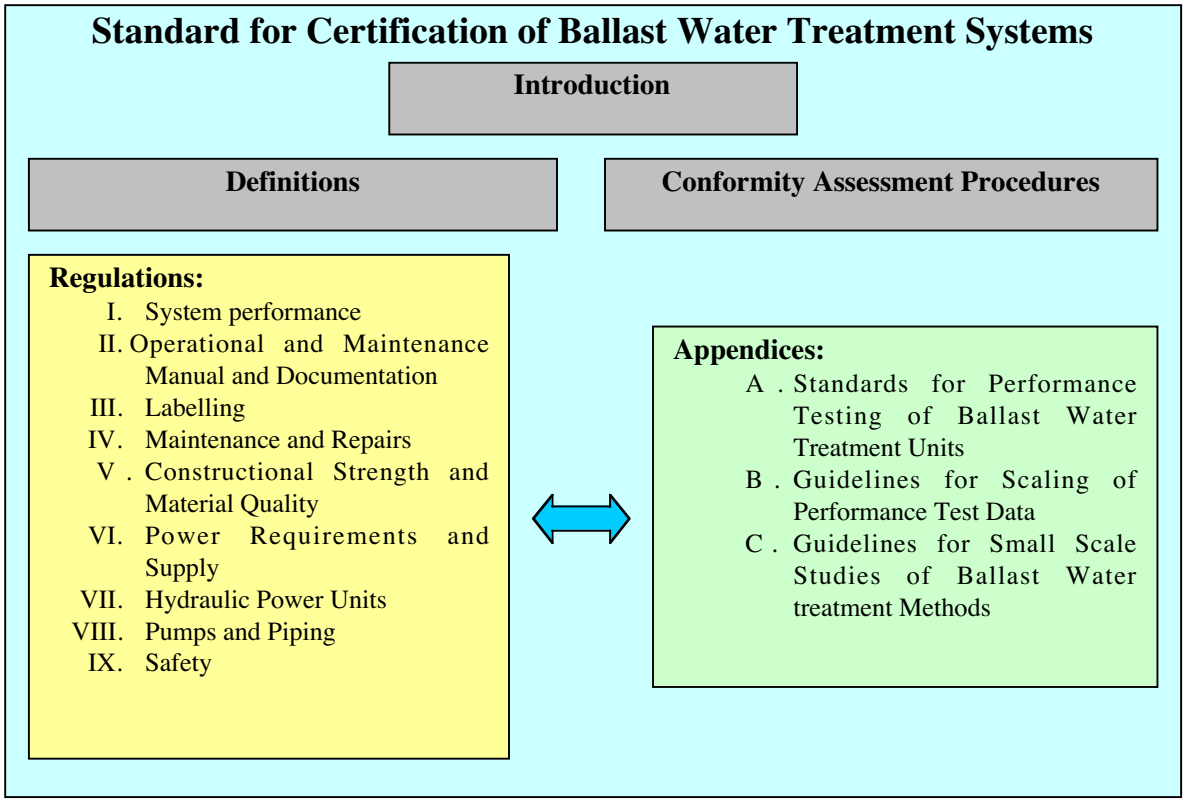
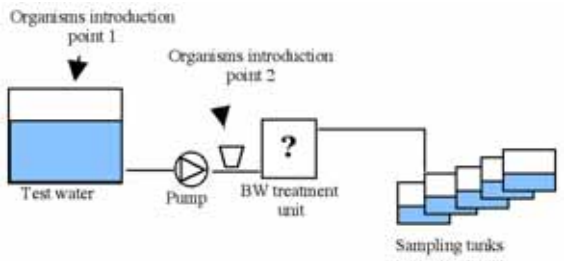
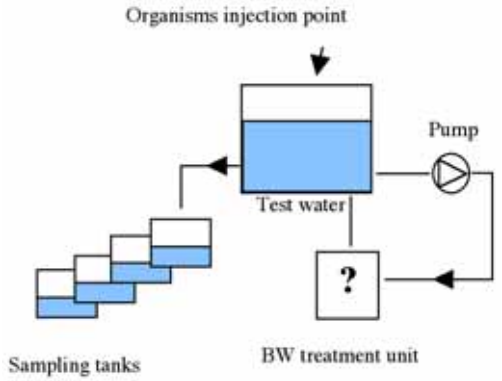


Figure 2. *Standard for certification of ballast water treatment systems.*



Alternative 1 - Loading system (one-pass system)



Alternative 2 - Recirculation system (multiple passes)

Figure 3. *Generalised test arrangement.*

The Artemia Testing System for ballast water treatment options

M. Voigt

dr. voigt-consulting
Germany
m.voigt@drvoigt-consutling.de

Abstract

This paper provides information on a new test system for the evaluation of the efficiency of ballast water treatment options. The test is based on different life-stages of Artemia salina, an organism often used in standard tests. The tests can be carried out at any flow rate and the results give a quick and cost-efficient estimate of the efficiency of the proposed treatment option, avoiding costly and time consuming multiple experiments and minimise the number of necessary field trials. Different treatment options have already been tested at flow rates between 130 m^3/h and 200 m^3/h.

Introduction

It has been demonstrated in numerous studies, that many organisms from different trophic levels can be found in ballast water tanks, ranging from viruses to metazoans as well as algae and various cysts. Any ballast water treatment option has to be able to remove or inactivate all of these different organisms.

The biological efficacy of any ballast water treatment option has to be assed with flow rates representative for ballast water operations The current practice is, to carry out numerous tests, either land-based or onboard of a ship, with the species present in the water at the testing site, or to prime the system with individual test species. All of these approaches are very time consuming, expensive and difficult to standardise. Changes in the species composition at the test site and in the densities of individual species have a negative impact on the statistical analysis of the experimental data.

When surrogate species are used, the test system can be primed with a given number / density of the surrogate organisms and the observed changes in numbers / survival rates are mainly attributed to the treatment.

Results

A new full-scale test has been developed to account for most of the trophic levels and the different physical properties of the organisms frequently found in ships' ballast water. The Artemia Testing System (ATS) involves different larval and development stages of the brine shrimp (*Artemia* salina) as surrogates for a variety of organisms commonly found in ballast water (Table 1). The robust *Artemia* can be produced in any lab with only little effort. Furthermore, they can be easily added to the water prior to the treatment system and are easy to recognise / identify even in samples with high numbers of other taxa and / or high turbidity.

Table 1. *Development stages of* Artemia salina *used in the ATS full-scale tests.*

***Artemia* development stage**	**Trophic level**	**Surrogate for**
Resting stage	inactive cysts	Floating (pelagic cysts) <100 µm
Soaked cysts	inactive cysts	Demersal (benthic) cysts > 100 µm
Developing eggs	floating / demersal eggs	Larval organisms (plankton) 150 µm – 180 µm
Nauplii	larvae (not feeding)	Numerous planktonic organisms > 250 µm

The different physical properties (specific weight, size) and the different behaviour (passive movement with currents and active swimming) make the above development stages ideal surrogates. Furthermore, they show rather low sensitivities to physical and chemical stressors, which makes them a good "worst-case-scenario" for any combination of treatment options as well as for stand-alone treatments.

Because of the rapid development of the cysts and larvae (nauplii), the test results can be obtained 24 hours after the experiment.

So far, the ATS test protocol (see Annex) has been downloaded nearly 400 times from users all over the world (Tab. 2).

Table 2. *Country-codes of servers that have downloaded the PDF-file of the ATS full-scale test protocol.*

Europe	*Over seas*
Norway	
Sweden	USA
Denmark	Canada
Netherlands	Australia
Germany	New Zealand
Lithuania	Saudi-Arabia
UK	Republic of Congo
Austria	
Switzerland	
Italy	
Hungary	

Furthermore, the ATS test protocol has already been applied in several land-based tests with different treatment options.

Conclusions

The ATS is a useful tool for the assessment of the biological efficacy of ballast water treatment options. It can be used as a model for a wide range of organisms with

- different specific gravities
- different sizes and shapes
- different behaviour
- different sensitivities to stress.

The ATS can be used in any location and at any time, independent from seasonal fluctuations of in-situ plankton organisms. The full ATS test protocol is available free of charge in PDF-format in the internet (see Annex).

The ATS poses a low environmental risk from the surrogate species. Only little training is required for the personnel that analysis the samples. High taxonomic skills, as they are essential in most tests

which use in-situ species composition, are not required. As an other advantage, the ATS can be calibrated against more sensitive species, and the results are highly reproducible.

However, any evaluation of the biological efficacy of a ballast water treatment option should not be based only on the results of the ATS. It should be applied in combination with at least one more surrogate organisms that accounts for small (< 50 µm) zooplankton and / or phytoplankton. It has also to be noted, that the ATS should only be applied in test waters that show physical properties within the tolerance of Artemia (e.g. salinity > 12 ppt and water temperature above 15°C, and max. 28°C).

Annex
The ATS© full-scale test protocol

© *dr.voigt-consulting, Germany, e-mail: m.voigt@drvoigt-consulting.de*

Preparation of experiments

The numbers of individuals needed for the tests depend on the capacity of the treatment system. As a role of thumb, one each of the following cultures is needed for every 30 m^3/hour capacity.

Breeding of nauplii

1. Fill a 1-l-bottle with 600 ml of filtered sea water and aerate well.
2. Transfer 1 table spoon of premium grade *Artemia* eggs to the bottle. Incubate in a water bath at 24°C for 24 hours.
3. Decant the hatched nauplii through a sieve (mash 10 µm) and transfer to 10 l to 20 l aquarium filled with sea water (24°C).

Breeding of developing eggs

1. Fill a 1-l-bottle with 600 ml of filtered sea water and aerate well.
2. Transfer 1 table spoon of premium grade *Artemia* eggs to the bottle. Incubate in a water bath at 24°C for 12 hours.
3. Take a sample of the eggs and examine under a stereo microscope at 20 x magnification. If the outer shell of the eggs has opened, the yellowish embryo is clearly visible and the eggs can be used for the experiments. If the embryo is not clearly visible, incubate the eggs for 4 to 6 more hours. Monitor the development closely

Preparation of soaked cysts

1. Fill a 1-l-bottle with 600 ml of filtered sea water.
2. Transfer 2 to 3 table spoons of premium grade *Artemia* eggs to the bottle. Allow the cysts to soak for 2 hours at room temperature

Preparation of resting stages

1. Fill a 1-l-bottle with 600 ml of filtered sea water.
2. Transfer 2 to 3 table spoons of premium grade *Artemia* eggs to the bottle directly prior the beginning of the tests

Preparation of the treatment system

1. Install a by-pass to the first pump of the treatment system in order to prime the system with the cultures of *Artemia* development stages.
2. Identify the capacity (flow rate) of the by-pass and calculate the passage time of the water through the system.
3. Adjust the flow rate of the by-pass to allow min. 5 minutes of test run.
4. Start the treatment system and allow to stabilize for at least 1 hour.

IMPORTANT: re-direct the water flow into tanks with sufficient capacity during the test run to avoid introduction of *Artemia* to the test site

The ATS test procedure

1. Mix the cultures (resting stages, soaked cysts, developing eggs and nauplii) in a bucket or barrel (10 litre volume for every 30 m^3 of capacity of the treatment system). Top up with sea water and aerate well.

2. Transfer a sample of 1 litre to a 200 l barrel (control), top up with sea water and aerate.

3. Prime the system with the prepared cultures through the by-pass of the pump.

4. During the passage of the organisms through the treatment system, take samples of 200l each directly before and after each treatment step (e.g. filtration / separation, disinfection).

5. Mix the water in the 200 l barrels well and take sub-samples (three replicates) of 10 litres each .

6. Put the sub-sample through a sieve (10 µm) and observe under a stereo microscope at magnification of 10 x.

7. Count the numbers for each of the development stages. Record numbers of damaged or dead individuals separately.

8. Observation of test organisms directly after the test run:
   a. The movements of the antenna and legs of the *Artemia* nauplii are monitored under a stereo microscope at 10x magnification. The individual is dead, if no movements of the antenna can be detected.
   b. The resting stages, the soaked cysts and the developing eggs are examined for mechanical damage under a stereo microscope at 10 x magnification.

9. Cover the barrels and leave without aeration for 24 hours.

10. Repeat steps 6 to 9.

11. Calculate the mortality / removal in percent for the nauplii for each step of the treatment.

12. Calculate the removal /damage rate in percent for the resting stages, soaked casts and developing eggs.

If the numbers of developing eggs increases in all three replicates taken after 24 hours in comparison to the samples taken directly after the test run, the treatment was insufficient for the soaked cysts.

If the numbers of the alive nauplii increases in all three replicates taken after 24 hours in comparison to the samples taken directly after the test run, the treatment was insufficient for the developing eggs.

Development of dinoflagellate "cyst-on-demand" protocol, and comparison of particle monitoring techniques for ballast water treatment evaluation

J. T. Matheickal [1], Tay Joo Hwa [1], Chan Mya Tun [1], S. Mylvaganam [1], M. Holmes [2] & L. Loke [1]

[1] *Institute of Environmental Science and Engineering, Singapore*
jtmath@ntu.edu.sg

[2] *Tropical Marine Science Institute, Singapore*

Abstract

There is an urgent need for development of standardized testing and analytical protocols for evaluation of various ballast water treatment technologies. This paper presents the initial results from two separate studies on 1) using particle counts for evaluation of ballast water filtration techniques and 2) development of a "cyst-on-demand" protocol for mass-culturing dinoflagellate cysts. Particle counts, size and distribution analysis can provide reasonably sensitive measurements of particulates in water and as such can be a valuable analytical tool for the evaluation of treatment technologies that "remove" organisms from ballast water. The use of particle counts based on the particle size assumes importance from ballast water quality standards point of view, as there is an increasing consensus on the use of "size" as the basis for ballast water treatment performance standards. In the past, a number of methods have been used to count and size particles in ballast water – each method uses a different counting technique. There is no standard method for performing particle size analysis for ballast water, and each method has its own limitations. One key issue is the reported lack of consistency of such measurements by different instruments in the market as the basic measurement principles vary. Studies were undertaken in our laboratory to test whether different techniques yield the same particle count and size distribution information when applied to ballast water quality monitoring. In this study, two particle counters, based on light obscuration and electrical sensing as the measurement principles are compared. There are many factors that would affect the reliability of such measurements and these include, particle concentrations, size ranges, storage etc. The second part of this paper discusses the initial results of our attempts to mass culture dinoflagellate cysts that could be used as biological surrogates for the evaluation of various secondary treatment technologies. Most of the secondary treatment technologies are based on the inactivation or kill of the organisms that are not removed by a primary treatment process such as filtration. Since using toxic dinoflagellates cysts as a surrogate is difficult due to practical reasons, our research focused on the non-toxic, cyst forming dinoflagellate specie, Scrippsiella sp.**,** *as a surrogate. We have observed that sufficiently large number of dinoflagellate cysts can be produced "on-demand" for lab-scale evaluation of treatment technologies.*

Name of research programme

Singapore Ballast Water Research Programme (SBWRP)

Treatment options being considered

Filtration, Hydrocyclone, UV, Biocides and Photocatalysis

Timeframe of the programme

2002-2005

Overall aims and objectives of the Singapore Programme

- To develop a set of strategies for the control of transfer of non-indigenous species via ballast water for Singapore shipping and port interests.
- To demonstrate ballast water management schemes at suitable scale in order to generate treatment effectiveness, and reliability data, as well as life cycle costs.
- To participate in developing appropriate performance verification protocols for the evaluation and approval of treatment technologies.
- To act as a regional center for coordinating research and development on ballast water management.

As noted above, one of the major objectives of this programme is to develop appropriate verification protocols for ballast water treatment systems. This paper, therefore, discusses the initial results from one such study carried out to evaluate particle counting instruments for ballast water quality monitoring. The paper also discusses the development of a "*cyst-on-demand"* protocol for mass culturing a surrogate organism for ballast water treatment verification.

The main objective of the study reported in this paper, were:

- to evaluate the use of particle counting as a measure of filtration efficiency and to monitor filter failure
- to compare two different particle counting techniques for monitoring seawater quality
- to develop and optimize a culturing protocol for mass-culturing dinoflagellate cysts

Background information on the study

The ongoing research in Singapore, USA, Europe and elsewhere showed the potential for alternate treatment technologies for management of ballast water. However, it has been recognized widely that performance comparison of these technologies has been severely restricted by the lack of standardization in this area. Although, there are a number of on-going pilot-scale and ship-board trials of some of these technologies, the protocols used for evaluation of these systems vary and a reasonable comparison of these test results are, unfortunately, difficult. There is, thus, a need to develop internationally acceptable methodologies for the harmonization of performance testing of "removal" based technologies. One of the pre-requisites to development of these protocols is the identification of suitable water quality parameters or their surrogates and development of reliable measurement tools and protocols to monitor these parameters/ surrogates.

There is an increasing consensus that primary as well as secondary treatment technologies may be required to meet the long-term ballast water performance standards. Broadly, these treatment technologies can be classified as "removal" based technologies and "inactivation/kill" based technologies. Many primary treatment technologies such as filtration, hydrocyclones etc., belong to the former category and the secondary treatment will most likely belong to the later one. The parameters chosen to evaluate technologies therefore should take into account the removal, inactivation and kill effectiveness of treatment technologies. Moreover, the parameters chosen should satisfy the requirements of easy and rapid monitoring needs.

"Size" as a non-biological surrogate measurement

Currently, the scientific basis for establishment of ballast water treatment standards are going through an intense debate both among the scientists and at the IMO. Although there is a general consensus on the primary criteria for acceptance of treatment technologies (safety, environmental friendliness, practicality, cost effectiveness and biological effectiveness), there are two differing views on measuring biological effectiveness of treatment systems 1) a performance standard based on% removal of representative species 2) a water quality standard based on organism size. The former one is based on a perceived risk reduction through % organism reduction and the later one bases its recommendation on the history of past invasions and attempt to identify and group the past invaders as per size.

While it is not attempted here to discuss the pros and cons of these options, it should be noted that the selection of a standard would have significant influence on the way treatment technologies are evaluated and performance assessed. From the previous discussions and looking at the latest draft text of IMO regulations (MEPC-49), it can be clearly seen that "organism size" would play a major role as a surrogate water quality parameter in the long-term as well as short-term definition of ballast water standards. In fact, recent discussions show signs of some convergence between the two schools of thoughts. It is argued that a size based standard can still result in a meaningful reduction of risk, while at the same time "size", as a surrogate measurement, lends itself for easy monitoring. This is supported by the recent literature study by Waite (2002) who suggested a 100 micron size cut-off as a preliminary standard, as this would eliminate most, if not all, of the marine organisms with some past invasion history.

The idea that the material to be removed or inactivated by a shipboard treatment process is larger than a certain size, is an important concept. Moreover, a size based standard can be used to evaluate several treatment technologies, including screening, filtration, and cyclonic separation (Waite, 2002) and if coupled with viability measurement, it can be used for technologies based on killing/inactivation (biocides, heat etc) as well.

Particle size is also an effective surrogate measurement for measuring biological effectiveness of mechanical separation systems (e.g., filtration, hydrocyclone) used in ballast water treatment. Researchers have used particle sizing, counting and size distribution analysis (Parsons and Harkins, 2002) for evaluating performance of screen filters, hydrocyclone and depth filters for ballast water applications.

Particle sizing and counting for filtration evaluation

In the past, a number of methods have been used to count and size particles in seawater – each method uses a different technology, since there is no standard method for performing particle size analysis for ballast water, and each method has its own limitations. One key issue is the reported lack of consistency of counts and sizing by different instruments in the market as the basic measurement principles vary. Also, there are many other factors that would affect the reliability of such measurements and these include, sample concentration procedures, storage, and even different types of concentration standards used for calibration of the instrument. Standardization of particle count/size based measurements and interpretation of data obtained from particle counting are therefore important components of the development of standard protocols for treatment verification.

Dinoflagellate cysts as biological surrogates

Physical separation technologies, including filtration or hydrocyclone methods, may play an important role in the primary treatment for the removal of the larger organisms. For example, a screen filter with mesh size of 50–100 microns could remove the larger planktons. But smaller organisms such as dinoflagellates and plankton, with sizes of 10–30 microns are problematic to remove by physical separation. These smaller organisms may be removed using 20–25 micron filters but such filters are less efficient from an operations point of view (Cangelosi et al., 2001). Although difficult to remove

by physical separation, secondary treatment technologies such as biocides, thermal techniques, electric pulse and pulse plasma techniques, ultraviolet treatment, acoustics systems, magnetic fields, deoxygenation, etc are being considered by many research groups, for inactivating or killing the smaller organisms.

R&D on secondary treatment technologies would benefit considerably if a suitable biological surrogate can be selected for evaluation of various treatment regimes as well as for technology verification purposes. Such a biological surrogate should be representative of target organisms that can be invasive on a global level, should lend itself for mass culturing, should be hardy enough to ensure treatment efficacy and should be non-toxic so that it can be used in pilot-scale and lab-scale studies. One possible class of biological surrogates is the cysts of microalgae, dinoflagellates.

Toxic dinoflagellates have been identified as a major invasive problem worldwide, especially since it can survive long voyages. Blooms of the toxin producing dinoflagellate *Gymnodinium catenatum* were first recorded in Tasmanian waters in late 1985 and may have been introduced by ship ballast water (Hallegraeff et al., 1989). A new toxin producing, benthic dinoflagellate has been isolated from the fringing coral reefs surrounding the Singapore island of *Pulau Hantu* (Holmes, 1998). Dinoflagellate species are globally distributed and many of them are harmful. Toxic blooms have been reported from many countries (Gollach, 1999).

Dinoflagellate vegetative (motile) cells and their cysts often measured between 20 and 40 microns (Anderson *et al*., 1985). Dinoflagellate cysts (hypnozygotes) are often thick walled, highly resistant, non-motile stages that are formed from sexual re-combination. The cysts can often survive in harsh environmental conditions and may be resistant to mild disinfection technologies.

In summary, the following rationale is given to select Dinoflagellate Cysts as a surrogate organism to evaluate the efficiency of the ballast water treatment:

- Dinoflagellate cells and cysts are smaller in size and may escape primary treatment.
- The roles of cysts need more attention as they have thick and special cell walls that are resistant to mild-disinfection that are normally used in other disinfection techniques
- The spread and damage to environment caused by dinoflagellates is of international concern
- The vegetative stage is easy to culture and calcareous cysts of certain species are easy to produce (although not necessary representative of the cysts of harmful species).
- The outcome of minimum test conditions of removal/kill/inactivate technologies can be applied and studied to other organisms including bacteria.

Research methods and protocols

Particle counting for filter evaluation

In order to evaluate the use of particle counting for filtration efficiency, a 30 micron filter was challenged with Arizona Fine Dust (ISO 12103-1 A4) particles suspended in pre-filtered (0.45 micron) water. Arizona Dust was selected due to its wide range of particle size distribution (1-80 microns), its non-coagulating nature and also due to the non-spherical shapes of the particles. A Coulter particle counter (Multisizer III) was used to count the particles before and after filtration. In order to check the usefulness of particle counting for monitoring filter failure, the filter was later on damaged intentionally, by making a pinhole. Filtration experiments were also carried out using actual seawater, containing organisms. Scanning Electron Microscope (SEM) analysis of the particle that passed through the filter was also carried out to study the filtration efficiency. This was performed by filtering a measured aliquot of water sample through a 0.45 micron membrane filter and subsequently air-drying the filter in a laminar hood before SEM analysis.

Comparison of particle counters for ballast water quality analysis

Two different particle counters were compared in this study; 1) light-obscuration based particle counter, that uses both on-line sampling as well as grab-samples. This instrument was size calibrated with latex spheres and set for a flow rate of 100 mL/min by the manufacturer. Software supplied with the instruments allowed the operator to choose the size classes 2) electrical sensing zone (ESZ) instrument using coulter principle which was set to count the particles over a specific period of time at a set flow rate. Three different water samples were used to generate particle counting data 1) actual seawater collected from Sembawang Site in Singapore 2) Arizona Dust suspended in filtered seawater and 3) Dinoflagellate cultures suspended in filtered seawater. Same concentration of particles was used when the instruments were compared.

Dinoflagellate "cysts-on-demand" *protocol development*

A temperature-controlled room with lighted growth tables and height-adjustable table platforms were used to achieve the optimum light intensity required for growth of *Scrippsiella*. A temperature-light cutoff set at 30°C was used to switch off all the culture lights if the temperature in the room significantly exceeded the set temperature of 26°C. A timer controlled all lights on a 12 – 12 hour light: dark cycle photo-period.

Three strains of the known cyst producing and non-toxic dinoflagellates *Scrippsiella sp.* were purchased from USA from Provasoli-Guillard National Center for Culture of Marine Phytoplankton (CCMP 1331 and CCMP 1735) and the University of Texas at Austin culture collection of algae (LB1017). Only CCMP1735 could be induced to routinely produce hypnozygotes. We subsequently found that growth of this strain was faster and the hypnozygotes production better at 26°C than the recommended culture temperature of 20°C. The culture room facilities were adjusted accordingly and the two other strains were discontinued since they could not survive the higher temperature. The counting of cells and cysts was made manually using a Sedgewick- Rafter cell counter and microscope.

The media, f10, were prepared by adding the necessary nutrients to the sterilized seawater. The seawater was 0.2 micron filter-sterilized by the pressure vessel system. Initially, 5ml of soil extract was added per 1 L of media based on the nutrient formulations used by the originating USA culture collection. However, this was discontinued after few months because of frequent fungal contamination. Stock cultures were prepared and transferred to new media every two weeks. All the transfers of cultures were carried out in laminar flow hood to avoid any contamination.

To design and conduct the ballast water treatment experiment efficiently, the growth rate of the *Scrippsiella sp.* was determined. During this study, the morphology of the cells was also studied by using an inverted Olympus IX 70 microscope. The culture was sampled and diluted at known time interval and manually counted using Olympus IX 70 microscope and Sedgewick-Rafter Cell counter to determine the growth rate. Hypnozygotes are the sexual (diploid) stage in the life cycle of dinoflagellates. The strain of Scrippsiella produces hypnozygotes in culture, however, manipulating nutrients conditions can considerably increase the number of cysts. The following protocol was used to determine the patterns of formation of cyst (hypnozygotes) in 250 ml flasks. A 10 ml portion of culture samples were aseptically transferred into a 250 ml flask containing nutrients depleted sterilized seawater as a medium for the formation of cyst. These samples were regularly monitored and counted for cysts after dilution with sterilized seawater. All the flasks were kept in the culture condition of 12:12 hours light: dark photoperiod at 26°C.

Rate of excystment was determined by transferring a 10 ml of culture rich in cyst back to the f10 media. The inoculated samples were kept in the culture condition of 12:12 hours light:dark photoperiod at 26°C and were monitored and counted daily for the formation of cells.

Results and discussion

Particle counting for evaluation of filtration efficiency

It has been well documented that particle counting provides greater sensitivity and increases lead-time in surface water filter performance optimization (Hargesheimer and Lewis, 1995, Bellainy et al., 1993). Particle counters both count and size individual particles as they flow through a sensing zone. They operate by electrical resistance (Coulter), light blockage or light scatter principles. Other instruments, called particle size analyzers, provide information on particle size and particle size distribution, but they do not count. Some will provide an indication of particle numbers by mathematical estimation.

In order to determine if particle counting could be used as a reliable tool for monitoring filtration efficiency, a 30-micron filter was challenged with Arizona Dust Particles suspended in water. Filter integrity monitoring using particle counter was also studied by using a compromised screen. Figure 1 shows the results from these studies. Particle monitoring data are expressed in differential numbers, differential volume and % differential volume. It can be seen that the particle monitoring gave an accurate description of the filtering efficiency for various size ranges of the particles. The filtered water samples showed significantly less number of particles and the same was better expressed when the data was presented in volume fractions.

When a compromised screen was challenged with the test samples, the particle counter responded well and showed a significant increase in number of particles in the filtered samples. Again, when expressed in volume fractions, the particle counter was able to show the sudden peak corresponding to the larger particles that went through the pinhole in the screen. The instrument was sensitive enough to count the small number of particles that went through the compromised screen.

Particle counting was also used to evaluate filtration of seawater using a 30-micron screen. The number of particles in seawater was considerably lower than the Arizona Dust Samples. As shown in Figure 2, Particle counting again proved to be a useful tool for evaluating filter performance. It can however be noted from the particle data that the test filter allowed some particles above 30 microns to pass through. Although this was initially suspected to be the result of a compromised screen, detailed SEM studies showed that these larger size particles were in fact "needle-shaped" organisms with their shortest dimensions being considerably smaller than 30 microns. Figure 3 shows the SEM image of the organisms that had passed through the screen and it can be noted that the diatom skeletonema, one of the common diatoms in Singapore waters, had passed through the 30-micron screen. As the coulter particle counter used in this study measures the volume of particles and subsequently calculate the equivalent spherical diameter, such needle shaped organisms would be shown as larger size particles. These observations are similar to the one reported by Waite et al. (2003).

Comparison of particle counting techniques

Electrical Sensing Zone Technique: This technique was pioneered by the Coulter (USA) Company many years ago for blood cell counts in hospitals, where it is still widely used. Particles are suspended in an electrically conductive fluid (usually saline water with emulsifier) and forced to flow through a small orifice. Conductors are placed in the fluid on either side of the orifice, and the electrical resistivity of the orifice is monitored as particles pass. Each particle produces a sharp "spike" in electrical resistivity as it passes the orifice, and the total area (time x height) under the spike is approximately proportional to the volume of the particle. Each of the spikes is classified according to total area, and a particle count is place in a bin that corresponds to the appropriate particle size. After many thousands of particles have passed the orifice, the bin counts are converted to a particle size distribution, and the distribution is finally adjusted to account for the statistically finite probability of "co-incident" counts.

This technique is suitable for a relatively broad range of sizes (0.5 micron to >300 microns, using different orifice sizes). However, the dynamic size range is limited to about 30 in a single run (from

about 2% of the orifice size to about 60% of the orifice size). Analysis of broader distributions requires pre-separation of samples according to size (for example, via sieves), so that the individual fractions can be run using different orifices.

Light Obscuration Technique: In this method, a laser beam transmits its light through a flow cell to a photo detector and when there is an absence of particles, the light transmitted is received by the detector as an equivalent voltage level corresponding to full voltage intensity. As particles interrupt the laser beam, a shadow equivalent to the particle's size generates a voltage drop that the counting electronics convert into size and count information (Figure 4).

We compared the ESZ zone technique and light obscuration technique by subjecting different seawater samples to two different instruments that use these techniques (Coulter Multisizer III and LaserTech). Our initial experiments included the use of a light scattering type particle counter (Malvern), however its use was discontinued as it was observed that the particle concentration in typical seawater was too low for such measurements and the noise levels were high, masking the actual measurements. Particles and light interact strongly, with lights scattered from refraction, reflection, and diffraction by the particle. Complex equations apply to quantify the change in intensity, and one set of parameters does not apply for all size of particles (Van Gelder et al., 1999). Varying indexes of refraction among the inorganic, organic and biological particles in seawater further complicates the light-scattering response.

The two instruments (based on ESZ and Light Obscuration) were compared by analyzing the same samples using the instruments. Throughout the experiments, large differences in the instrument's counts were seen. Figure 5 shows the results of laboratory counts of three types of samples 1) seawater samples 2) Arizona Dust samples and 3) seawater containing a mixture of dinoflagellates and other organisms. The difference in counts between light obscuration instrument and the ESZ instrument was dramatic and typical of what was observed throughout the research. The light obscuration instrument consistently undercounted particles compared with the ESZ instrument in the smaller size classes and consistently over counted the larger particles.

The variations in counts for the samples can mainly be attributed to the coincidence errors that can happen in light obscuration instruments. This happens when more than one particle passes through the sensor at a time as shown in Figure 6. In the Arizona Fine Dust samples, there is a significant proportion of particles in the less than 5-micron size category. It is possible that several particles were moving through the sensing orifice simultaneously and resulting in several particles detected and counted as one larger particle. The presence of over-concentration errors can be confirmed by reviewing the particle size distribution results shown in Figure 5.

From the data shown, it can also be seen that the differences in counts were also dependant on the samples tested. The difference in counts was maximum (50 times) in the case of 2-10 micron class category of Arizona Dust, possibly due to the largest concentration of particles in these samples. Although the total number of particles in the 2-10 micron range was very similar in the case of seawater samples and samples containing predominantly dinoflagellates, the differences in counts observed was higher (15 times) in the case of dino samples as compared to seawater samples (8 times). This is possibly due to the large difference in refractive index of the calibration particles (latex spheres) used in calibration of the light obscuration instrument and the dinoflagellates. It also shows that appropriate calibration standards need to be selected if light obscuration based instruments are selected for ballast water monitoring. Research in the past had shown that light obscuration instruments have difficulty in counting particles between 2 and 3 microns and this also could have added to the dramatically lesser counts obtained in the light obscuration instrument.

Dynamic size range in light obscuration technique is limited to about 100-200 for a single run. Analysis of broader distributions requires measurement using two different size sensors. Resolution appears to suffer with smaller particles. Non-spherical particles reduce resolution, because the cross section of the particle is evaluated rather than it's volume. The cross-section for a given particle will

depend on both particle shape and orientation as it passes through the detector. A second detector beam perpendicular to the first would allow a better measurement of volume, but to this author's knowledge, only single beam instruments are produced.

It can also be seen that ESZ instrument recorded the events when a large size particle (80 – 100 microns) passed through the aperture, where as the light obscuration instrument did not capture this. This again shows the size limitation of light obscuration instruments as many of them are optimized for the 4-6 micron size ranges. Since the size information is entirely dependent upon the size of the voltage drop, there is a restriction as to how big a particle can be sized since the biggest voltage drop that can be sized is down to zero volts (Figure 7). Particles of around 80-100 microns are usually the highest that can be sized and perhaps represent the extreme range for the instrument used in this study. Bigger particles can be detected, but the optics and electronics have no way of knowing how much bigger than 80-100 microns they are.

Cyst-on-demand protocol

Hypnozygotes are the sexual (diploid) stage in the life cycle of dinoflagellates. The CCMP1735 strain spontaneously produces hypnozygotes in culture, however, manipulating nutrient conditions can considerably increase the number of cysts. Five nutrient treatments for increasing the production of hypnozygotes from the CCMP1735 strain of Scrippsiella sp. were trailed. We developed 2 nutrient protocols (f2 to f10 and f2 to filtered water) to reliably induce hypnozygote-production in 2 litre culture flasks. These protocols rely upon transferring a large biomass of vegetative cells into nutrient-deficient media. Details of this protocol will be published elsewhere.

The CCMP1735 hypnozygotes have an oblong to spherical shape with many, but all, producing calcareous spines (Figure 8). Newly formed cysts are translucent with mature cysts developing a red accumulation body(s). However, the dimensions of newly formed and mature hypnozygotes (with or without spines) are not significantly different (Table 1 and 2, $P > 0.05$).

Table 1. *Longest length (µm) of newly formed hypnozygotes (NFH) and mature hypnozygotes (MH) with (+) and without (-) spines.*

	NFH + spines	MH + spines	NFH - spines	MH - spines
Mean	31.2	32.0	25.2	25.4
Standard deviation	2.66	3.03	1.98	1.92
Minimum	27.5	25.0	22.5	20.0
Maximum	37.5	40.0	30.0	30.0
Sample size	81	81	81	81

Table 2. *Shortest length (µm) of newly formed hypnozygotes (NFH) and mature hypnozygotes (MH) with (+) and without (-) spines.*

	NFH + spines	MH + spines	NFH - spines	MH - spines
Mean	28.9	29.8	23.3	23.3
Standard deviation	2.31	2.77	1.75	1.76
Minimum	25.0	25.0	20.0	20.0
Maximum	35.0	37.5	27.5	27.5
Sample size	81	81	81	81

Development of methods for excystment of hypnozygotes: The excystment of CCMP1735 hypnozygotes were characterized. In 250 ml flask cultures, mature hypnozygotes form after 9-20 days and begin spontaneously excysting after 2-28 days. It was found that mature hypnozygotes could be

stored for more than 1 month in a quiescent state in the dark at 5 to 7°C. Hypnozygotes transferred from cold storage to 24 to 27°C excyst in a time-dependent manner (Fig. 1).

The time to excystment (days) = 0.2 x (days storage at 5 to 7°C) + 0.9 [$P < 0.001$]

The pattern of encystment and excystment was observed and could be used to store mature hypnozygotes for more than one month and predict time-to-excystment to about ± 1 day.

Although mature hypnozygotes could be held in cold storage for longer than one month, the proportion of viable cysts reduces the longer the storage time. There were also indications that the linear relationship between time of storage and time to excystment may not hold for more than 2 months cold storage.

Cyst formation was minimal for the first three days but increased considerably from the 7th day of the inoculation (Figure 9). Excystment of cyst was confirmed by the presence of a motile cell and an empty cyst wall, with or without archeopyle (characteristic excystment pore). Cysts were not excysted after one month of regular weekly observation nor after two months. This indicates that accumulation bodies are necessary for excystment and could be a source of energy for the excystment process. However, when these conditions were met, we observed the excystment pattern as shown in Figure 9.

Conclusions and recommendations

Ballast water standard based on organism size can provide an ideal basis for defining ballast water quality and treatment technology evaluation. Particle counting and sizing is an extremely useful tool for ballast water treatment monitoring and verification. Participle counters, if properly used, can monitor the treatment performance on a continuous basis and offers a sensitive tool for monitoring events such as filter failure. Nevertheless, particle counters themselves and the ability to check their sizing and counting accuracy need improvements. During the research, the variation in counts taken by two different instruments when the same samples of various types was measured was documented. Dramatic variations in counts were present between electrical sensing zone based particle counters and the commonly used light obscuration based counters. The later one dramatically undercounted particles in smaller size classes compared with the research grade ESZ instruments for all types of samples, and there is ample evidence to suggest that the ESZ instrument was most correct. However, light obscuration particle counters can give a cheap and practical solution for online monitoring of ballast water, provided the instrument is calibrated using appropriate calibration standards, right concentration of particles used and correct flow rate is chosen. It may perhaps be required to improve the methods the manufacturers use to set the lowest millivolt calibration value. It is strongly recommended that ballast water monitoring be conducted using an electrical sensing zone based particle counting instrument for any verification purposes.

The second part of the study developed culture protocols for producing hypnozygotes (cysts) of the CCMP1735 strain of dinoflagellate *Scrippsiella Sp*. on demand. It was observed that transferring a large biomass of motile cells to nutrient deficient media induces cyst formation. Once the hypnozygotes mature they begin spontaneously excysting after about 2 days. However, hypnozygotes can be stored in a quiescent state for up to 2 months in the dark at 5 to 7°C, although the proportion of viable cells drops after about 1 month storage. The time to excystment of cold-stored hypnozygotes can be predicted from the time of cold storage. Dinoflagellate, being an invasive species of international concern, can be an ideal surrogate organism for treatment system evaluation. The protocol developed in this study can be used to produce sufficiently large number of dinoflagellate cysts. Detailed protocols for the use of these cysts for evaluating various treatment options are currently under development in our laboratory.

Acknowledgement

The study was supported by the Agency for Science, Technology and Research (A*STAR) and the Maritime and Port Authority of Singapore (MPA).

References

Anderson, D.M., Lively, J.T, Reardon, E.M. & Price C.A. 1985. Sinking Characteristics of Dinoflagellate Cysts. *Lymnol.Ocenogr.* 30: pp. 1000-1009.

Bellaíny, W., Cleasby, J.L., Logsdon, G.S. & Allen,M.J. 1993. Assessing Treatment Plant Performance. *Jour. AWWA*, 85(12): pp. 34-38.

Gollach, S., Minchin, D., Rosenthal H. & Voigt M. (eds.) 1999. *Exotic Across The Ocean, Case Histories on Introduced Species*.

Hallegraeff, G.M., Stanley, S.Q., Bolch, C.J. & Blackburn, S.I. 1989. *Gymnodinium catenatum* blooms and shellfish toxicity in southern Tasmania, Australia. In: Okaichi T, Anderson,D.M, Nemoto,T., (eds) *Red Tides: biology, environmental science toxicology*. Elsvier, Amsterdam, pp. 75-78.

Hargesheimer, E.E. & Lewis, C.M. 1995. *A Practical Guide to On-Line Particle Counting*. Denver, Colo.: American Water Works Association Research Foundation.

Holmes, M.J. 1998. Gambierdiscus Yasumotoi Sp.Nov (Dinophyceae), A Toxic Benthic Dinoflagellate From South Eastern Asia, *Journal of Phycology*. pp. 661-667.

Parsons M.G. & Harkins, R.W. 2002. Full-scale Particle Removal Performance of Three Types of Mechanical Separation Devices for the Primary Treatment of Ballast Water, *Marine Technology*, 39(4): pp. 211-222.

Van Gelder, A.M, Chowdhury, Z.K & Lawler, D.F. (1999) Conscientious Particle Counting, *Jour. AWWA*, 91(12): pp. 64-76.

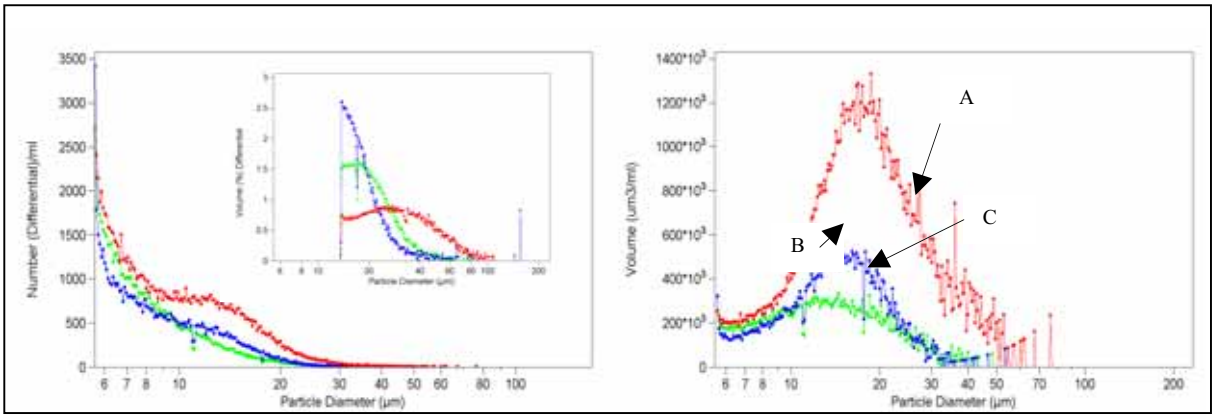


Figure 1. *Particle data for raw and filtered Arizona Dust samples.* ***(A****. ISO Dust solution without filtration* ***B.*** *ISO Dust solution filtered with 30um filter* ***C.*** *ISO Dust solution filtered with a failed filter (30um with a pinhole)).*

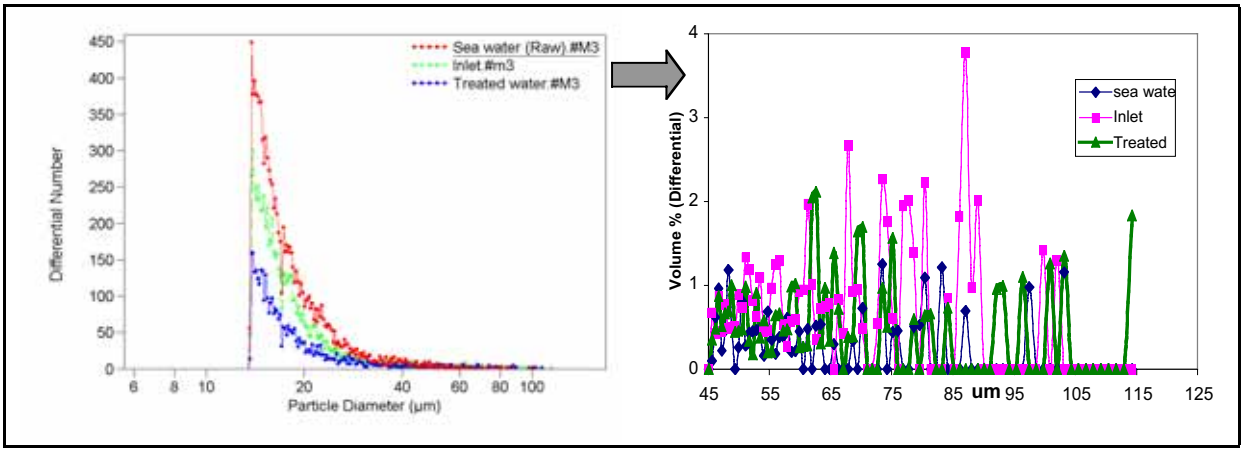


Figure 2. *Particle counts data for raw and filtered Seawater samples.*

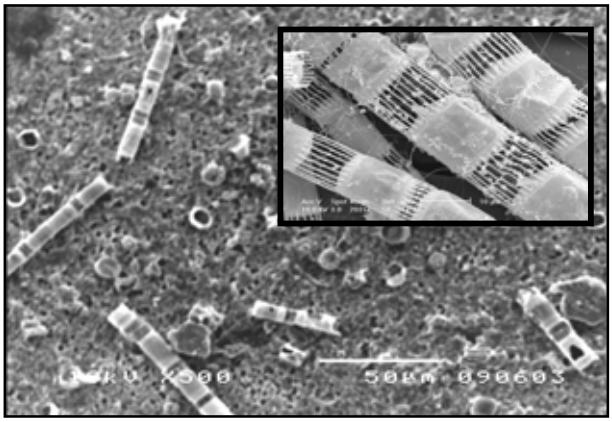


Figure 3. *SEM image of particles passed through 50-micron screen filters.*

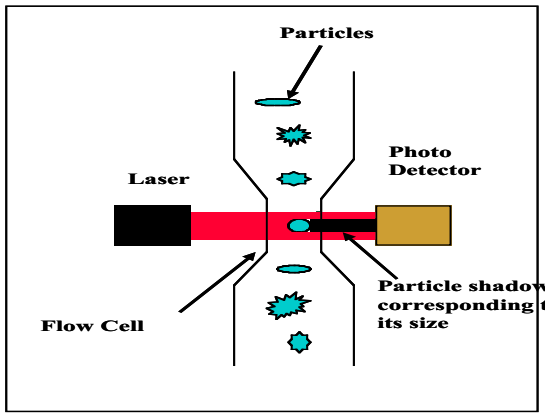


Figure 4. *Light Obscuration Principle.*

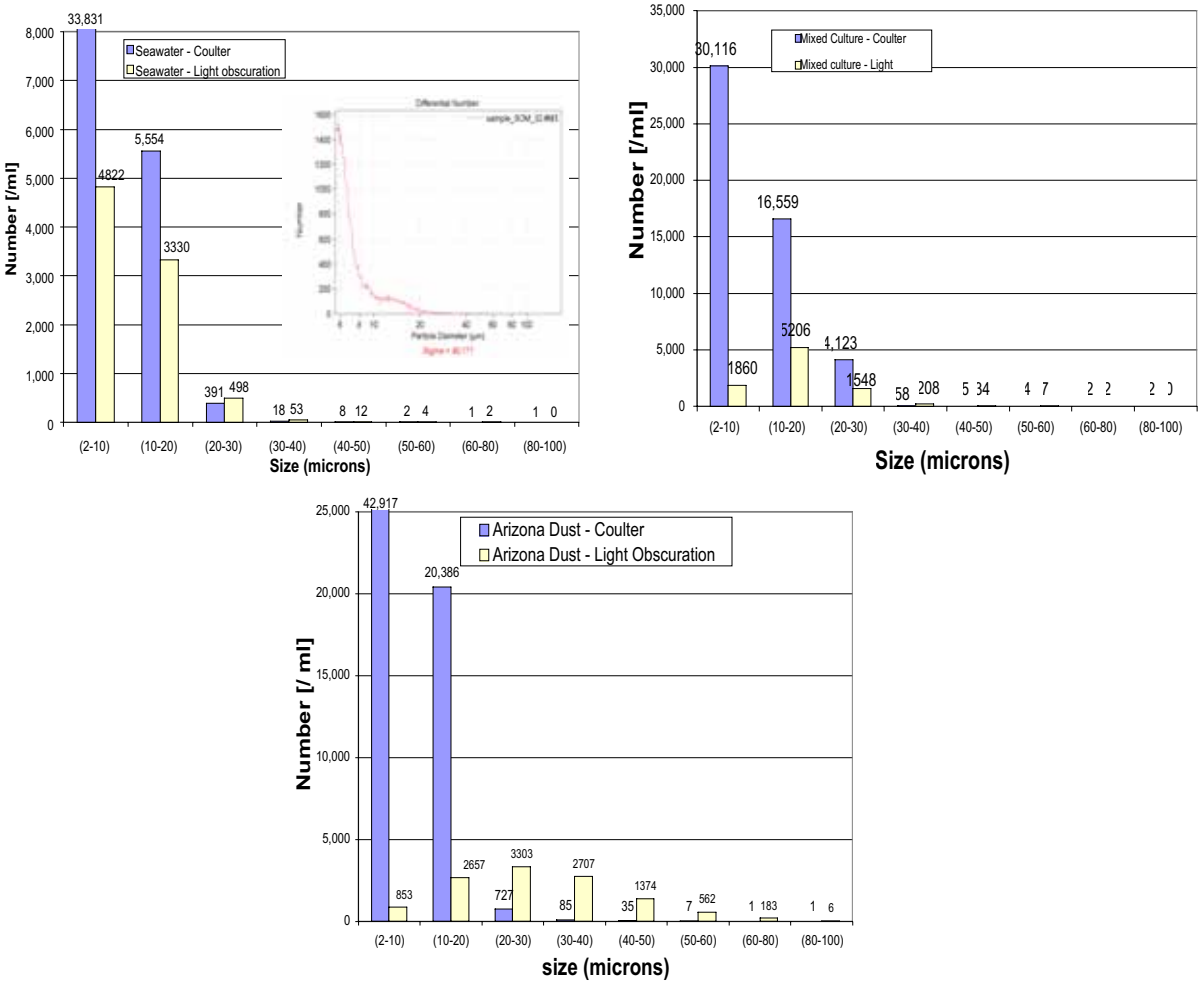


Figure 5. *Comparison of particle counts obtained for different water samples.*

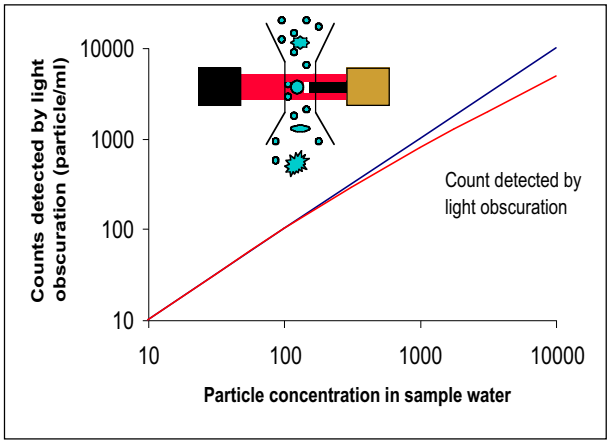


Figure 6. *Coincidence error in light obscuration instruments.*

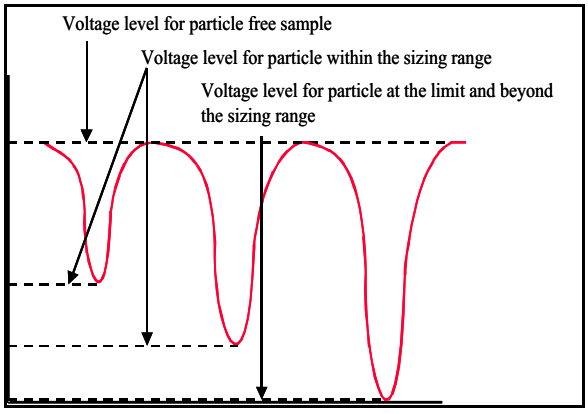


Figure 7. *Diagram explaining particle size range limits of light obscuration instruments.*

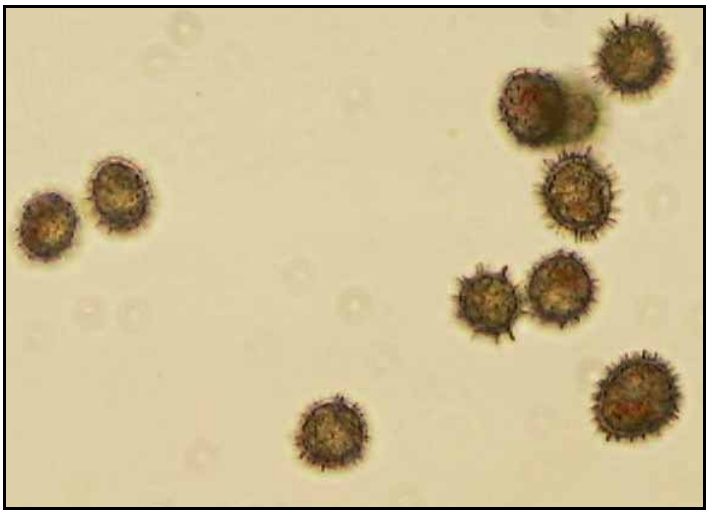


Figure 8. *CCMP1735 hypnozygotes formed using the protocols developed in this study.*

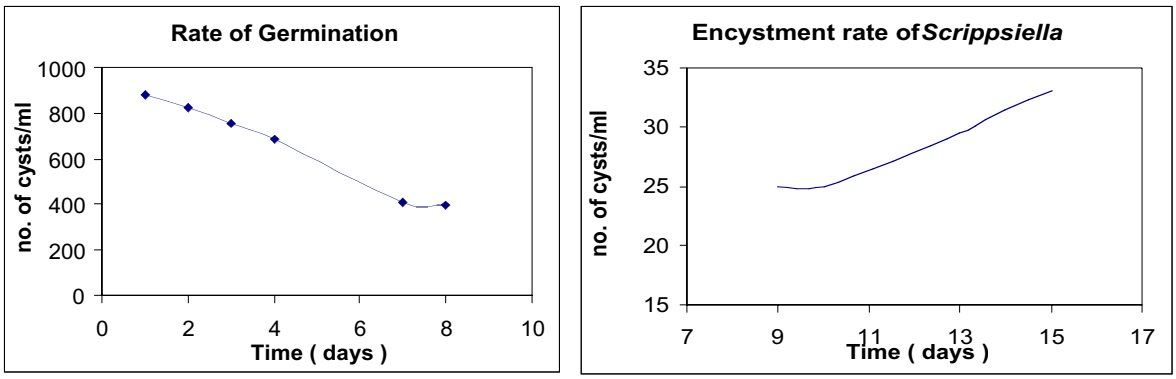


Figure 9. *Excystment and encystment patterns for CCMP1735 hypnozygotes.*

Test procedure for evaluation of ballast water treatment system using copepoda as zooplankton and dinoflagellates as phytoplankton

T. Kikuchi[1], K. Yoshida[1], S. Kino[1] & Y. Fukuyo[2]

[1]*The Japan Association of Marine Safety,*
kikuti@oak.ocn.ne.jp, yoshida@lasc.co.jp,
mti@felco.ne.jp

[2]*Asian Natural Environmental Science Center*
University of Tokyo
ufukuyo@mail.ecc.u-tokyo.ac.jp

Name of project

The project "Research and Development of the Special Pipe System for Ballast Water Treatment" implemented by the Japan Association of Maine Safety with the support of Japan Foundation has two components: 1) improvement the special pipe system to achieve better effectiveness in the termination of zooplankton and phytoplankton, and 2) development of the procedure and standard for evaluation of the effectiveness of the treatment system. This paper describes the second component, and the first one is also explained in another article recorded in the same proceedings.

Treatment options being researched

The test procedure was first designed to evaluate the special pipe system, one of the mechanical treatments. But its concept and the procedure itself can be applied to the analysis of the effectiveness of any other method.

Timeframe of the project

The project commenced in April 1999 and is still on going.

Aims and objectives of the project

The objective of this study is to develop a specific test procedure for evaluation of a ballast water treatment system to terminate and eliminate harmful aquatic organisms in ballast water based on biological and ecological nature of the organisms in coastal waters.

Research methods

In order to establish an appropriate test procedure, it is essential to analyze the biological and ecological features of organisms in port areas where ballast water has been taken. Seasonal change and regional difference of composition and numbers of plankton in Japanese waters were observed using several references such as Nomura and Yoshida (1997). Special attention was paid to high phytoplankton numbers occurring during red tides.

Based on data obtained by the analysis of plankton nature, necessity of selection of test organisms for evaluation of ballast water treatment system was assessed. For the selection, following criteria were considered; 1) the test organisms should be available in a certain amount easily anytime and anywhere to put enough concentration in test water to evaluate the result; 2) the organisms must be found in

both near-shore and off-shore waters easily, as the evaluation experiment includes a test bed test on land and a onboard test in ship; 3) the organisms should be easily differentiated with respect to its survival or fatality with high accuracy for evaluation of effectiveness of treatments. A test procedure and a standard for ballast water treatment were also designed using results of above mentioned analysis.

Ballast water has not only planktonic organisms, but also small benthic ones living in bottom sediment and being re-suspended by water flow, if water is charged at shallow ports. But it is appropriate to use only planktonic organisms at first for the materials of the present study in order to simplify the way of discussion. Introduction of benthic organisms such as mussel and seaweeds may be made not by transport of benthic adult organisms, but by planktonic eggs and larvae, of which numbers are usually larger by more than several thousand times.

Results and Discussion

Phytoplankton and zooplankton community changes in natural environment

Phytoplankton

Tokyo Metropolitan Government monitors red tide occurrence in Tokyo Bay regularly and reports phytoplankton number as one of the parameters observed. In 1999 and 2000, the highest, lowest and average cell numbers were 188,860, 76 and 16,260 cells/ml, respectively, among 312 samples (Tokyo Metropolitan Government 2002). Their methods of sampling and observation were not described in details. But the cell numbers must be based on quantitative analysis of live samples collected by a bucket and kept without using any fixative reagent under a regular compound microscope, as commonly applied for red tide research.

Seasonal fluctuation of plankton number is wide in eutrophic temperate areas such as Tokyo Bay. High nutrient concentration can keep high number of plankton individuals. However, sometimes other environmental parameters disturb the increase of plankton number, and therefore range of individual number becomes wider. Nomura and Yoshida (1997) reported the change of phytoplankton composition and cell numbers of 35 monthly samples collected by a bucket from surface and preserved by formalin at Tokyo Bay during 1991 and 1993. Summary of their results is as follows;

1. 55 species (33 diatoms species, 19 dinoflagellates species and 3 other algal species) were identified,
2. plankton community was composed of diatoms (92%), dinoflagellates (7%) and others (1%),
3. phytoplankton cell number was 7 – 8,607 cells/ml by counting after preservation of specimen under a regular compound microscope
4. plankton composition and cell number sometimes showed big difference from those suspected from the chlorophyll *a* amount analysis and the preliminary observation of live specimen. This means that phytoplankton was sometimes dominated by unfixable species.

Nomura (1998) reviewed historical phytoplankton records in Tokyo Bay between 1907 and 1997 using more than 45 publications and summarized the number of species reported in certain duration. In the whole years occurrence of more than 273 species, of which 78, 66, 59, 187 and 119 species were reported in 1900-1940s, 1950-1960s, 1970s, 1980s and 1990s, respectively, were recorded. The number of species varied depending on environmental condition of the bay and techniques of sampling and observation used for the study.

Red tide is defined as discolored water caused by high concentration of microscopic unicellular organisms. This represents one of the highest concentrations of plankton. Japan Fisheries Agency has been issuing an annual report on red tides that occurred in Seto Inland Sea in western Japan

since 1973. Following is a summary of data collected between 1992 and 2000 (Japan Fisheries Agency 1993-2001).

Total case number of red tides: 1020 cases

Number of causative species: 46

Highest and lowest cell number: 476,700 and 10 cells/ml (a half of cases >5,000 cell/ml)

Longest and shortest duration of a red tide: 276 and 1 day (a half of cases <4 days)

Largest and smallest area size covered by a red tide: 1360 and 0.0005 km^2 (a half of cases <10 km^2)

Zooplankton

Most of research on zooplankton composition analysis used a plankton net, with a mesh size of more than 80 μm, as a sampling tool. Quite few data are useful to analyze the change of individual number of whole zooplankton, i.e. plankton community of all size ranges.

Tokyo Metropolitan Government observes zooplankton number simultaneously at red tide monitoring research in Tokyo Bay regularly and reports the number as one of the parameters observed. In 1999 and 2000, the highest, lowest and average individual numbers of zooplankton were 667,140, 90 and 34,299 ind./l, respectively, among 305 samples (Tokyo Metropolitan Government 2002). The numbers were based on quantitative analysis of live samples collected by a bucket and kept without using any fixative reagent. The large part of community was occupied by unicellular protozooplankton, and large-sized zooplankton such as copepods were usually minor member in individual number.

Shizuoka Prefecture (1999) reported seasonal change of plankton composition at the central part of Sagami Bay, which has good water circulation influenced by Kuroshio Current. Microzooplankton smaller than 22 μm was dominated by unicellular protozoa such as ciliates and appeared several hundred individuals per liter. Zooplankton larger than the size was organized into various groups of animals such as variety of copepods (Maxillopoda), arrow worms (Sagittoidea) and planktonic sea worms (Polychaeta). Among them copepods is common and dominant organism, and individual number is about 100 ind./l.

Discussion

Several ecological characters on plankton community in Japanese coastal waters become clearer from the analysis described above.

1) Phytoplankton species number varies depending on environmental physical, chemical and biological condition.
2) Phytoplankton cell number also varies greatly from 188,860 to 76 with 16,260 cells/ml as an average by observation of live specimens, and 8,607 to 7 cells/ml by preserved specimens in Tokyo Bay. It means that the cell numbers decreased much in preserved samples.
3) In red tides cell number reached as much as 476,700 cells/ml.
4) Zooplankton individual number also varies from 667,140 to 90 ind./l, but average is 34,299 ind./l. Most of the community was occupied by unicellular protozooplankton smaller than 20 μm.
5) Zooplankton larger than 20 μm contains a large variety of organisms, and copepods always appears about 100 ind./l.

Quite wide diversity of plankton, both phyto- and zooplankton, is obvious in terms of organism number and species variety. Phytoplankton cell number differs about 5,000 times, and species number 3 times by sampling times. Zooplankton individual number also varies about 7,000 times. Consequently it is fundamentally necessary to define organism(s) to use as test materials for

evaluation of ballast water treatment system. Result using low plankton concentration is not comparable to those using 7,000 times high concentration.

Biological character influencing to the evaluation

Among phytoplankton, diatoms and dinoflagellates are two major components. Zooplankton has two groups, i.e., small unicellular protozooplankton has ciliates, and larger microzooplankton has copepods as major members. For evaluation of effectiveness of treatment the judgment on the viability of the test organisms is crucial. Change of shape and mobility is indicative character useful for evaluation.

Diatoms and copepods do not change their shape by preservation using chemicals. But almost all ciliates burst and disappear by sudden change of temperature or salinity and also by fixative reagents. Dinoflagellates have both groups. One half has thick cellulose plates on cell surface and they do not change their shape by fixation, but the other half has no plate and change shape or disappear by bursting during fixation.

Differentiation of live or dead is easy in organisms that have mobility. All zooplankton actively move and some phytoplankton such as dinoflagellates also can move by their flagella. But diatoms cannot move because of lack of any organ for movement and therefore mobility cannot be taken as an indicating character to judge viability.

Photosynthetic members of phytoplankton, i.e. diatoms and a half of the dinoflagellates, have color due to photosynthetic pigments. After death of cells, the color disappears gradually, but the color remains sometimes for more than a day. Damaged cells also have less color, but potential of recovery cannot be judged by appearance. Therefore color of organisms, either by organism-specific pigment or stained by chemicals, is not adequate to use for the judgment. Many cells show faint color after treatment and it makes judgment of treatment effectiveness very difficult.

Test organisms cannot be preserved by fixative chemical to observe if they are alive or dead. It means that organisms in samples have potential to grow even after treatment. Unicellular organisms can make cell division often once to several times a day. Diatoms often have short doubling time of several hours. But dinoflagellates can make cell division once a day at maximum. Therefore samples after treatment should be analyzed within a few hours to avoid the change of cell number.

Selection of test organisms

In phytoplankton group, diatoms and dinoflagellates are two major members available everywhere almost always. Judgment of treatment effectiveness using diatoms must be impossible, because they are immobile and do not change their shape. Dinoflagellates (Dinophyceae) have advantage, as they stop moving and about a half of them change shape after death. Therefore Dinophyceae have better indicative feature for a test organisms.

In zooplankton group, protozooplankton smaller than 20 μm are abundant near shore, but rare in off shore waters. Copepods (Maxillopoda) is major member and appears everywhere any time, but other zooplankton such as arrow worms occur at certain time in a year.

Based on criteria described in the Methods and data described in the Section 1 of the Results, the testing organisms could be selected Dinophyceae from phytoplankton and Maxillopoda (Copepoda) from zooplankton. These individuals with 20 μm or more in size may be used for experiments.

Settlement of test procedure

Plankton number varies in very wide range. High concentration numbers are several thousand times larger than low concentration numbers. Results of treatment using high concentration of plankton must be very different from those using low concentration.

The observation of performance and the judgment of effectiveness of the treatment may be conducted in the following steps. Observation of all samples collected should be conducted within one day after the sampling of the water, thus avoiding, as far as practical, the change of conditions of targeted organisms under storage. The environmental parameters of the waters before and after the treatment should be observed, including temperature, salinity and pH.

Step 1: Take seawater samples before and after the treatment with 100 litres or more, i.e. at the points of inlet and outlet of a treatment system. Volume of sample water should be noted for calculation of plankton concentration in each sample.

Step 2: Slowly concentrate phytoplankton and zooplankton in the sample water of known volume by using plankton nets or meshes with pore size of 20 μm. This concentration process should be conducted to observe many testing organisms by speedy observations under a microscope. Concentration should be done slowly to avoid any damages to the plankton through such process.

Step 3: Transfer the concentrated sample seawater into a clean receptacle such as a beaker, and adjust to 500ml or one litre with seawater filtrated through GF/F filters.

Step 4: A certain quantity of the sample water should be taken from the receptacle, and then the cell number of Dinophyceae with exercising of flagella and normal shape, and the individual number of Maxillopoda with normal motion and shape must be counted under a compound microscope and a stereoscope, respectively. The volume of water observed must be noted. This observation and counting should be repeated, until not less than 100 cells of Dinophyceae and 100 individuals of Maxillopoda can be obtained, to ensure high reliability.

Step 5: The phytoplankton and zooplankton counted should be identified at the ranks of genus of species.

Step 6: The results of the counting, i.e., the total number of the normal cells of Dinophyceae and individuals of Maxillopoda, must be recorded together with the total volume of test water observed. Then the total number of normal cells of Dinophyceae and of normal individuals of Maxillopoda per liter of test waters before and after the treatment must be calculated and recorded.

Step 7: To ensure the reliability of the data obtained, the test should be conducted not less than 3 times using same seawater under same environmental condition, and the mean and the deviation values from the results should then be obtainable.

Step 8: By comparing the number of the indicator organisms (Dinophyceae and Maxillopoda) before and after the treatment, the rate of diminution and attenuation may be calculated and the efficiency of the system.

Standard for ballast water treatment approval

According to the analysis of plankton community and its ecological characters, such as wide variation of cell density, described above, following standards for type approval is suggested.

95% of Dinophyceae and Maxillopoda more than 20 μm in size should be removed, rendering harmless, inactivated through the process from inlet to outlet of the system.

The percentage looks small, but it should be thought as the starting point of system development. Higher percentage, i.e. higher efficacy, should be applied after certain period.

Conclusions and Recommendations

As the experiment to evaluate treatment systems will be conducted at various places throughout the world under various circumstances by both test-bed and on-board tests, the procedure of the experiment should be clearly defined with special consideration to the reproductivity and reliability of the result. Use of whole planktonic organisms occurring in the areas of the experiment as test organisms for the evaluation increases difficulty of experiments themselves and evaluation of results of the experiments. As the analysis of plankton composition before and after the experiment is by counting only, live individuals is thought to be essential and inevitable, but it is nearly impossible to conduct it with scientific accuracy. Diatoms, one of the major components of phytoplankton, are immobile and the change of diatom cell color may not occur in a short time, even in case the cells died completely.

The conclusions of the present study are:

1. The potential test organisms for evaluation of ballast water treatment system can be Dinophyceae from phytoplankton and Maxillopoda (Copepoda) from zooplankton. These individuals with 20 μm or more in size can be used for experiments.
2. Evaluation of efficacy should be based on termination rate of the test organisms before and after treatment. Live or dead can be distinguished by shape and mobility of the test organisms.
3. In order to keep reproductivity and accuracy of the evaluation, number of test organisms in test water should be counted no less than three times.
4. Standard for treatment approval is termination rate of test organisms more than 95%. The rate should be set higher along with the development of techniques.

Concerning the cost of experiments, it is difficult to calculate it, because it varies depending on scale of experiments. Quantitative analysis (triplicate observation) of phytoplankton and zooplankton with judgment of live or dead costs 200 US$ per sample.

References

Fisheries Agency 1993. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1992*. Seto Inland Sea Fisheries Coordination Office, 59pp. (in Japanese).

Fisheries Agency 1994. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1993*. Seto Inland Sea Fisheries Coordination Office, 48pp. (in Japanese).

Fisheries Agency 1995. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1994*. Seto Inland Sea Fisheries Coordination Office, 61pp. (in Japanese).

Fisheries Agency 1996. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1995*. Seto Inland Sea Fisheries Coordination Office, 54pp. (in Japanese).

Fisheries Agency 1997. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1996*. Seto Inland Sea Fisheries Coordination Office, 46pp. (in Japanese).

Fisheries Agency 1998. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1997*. Seto Inland Sea Fisheries Coordination Office, 79pp. (in Japanese).

Fisheries Agency 1999. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1998*. Seto Inland Sea Fisheries Coordination Office, 81pp. (in Japanese).

Fisheries Agency 2000. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 1999*. Seto Inland Sea Fisheries Coordination Office, 60pp. (in Japanese).

Fisheries Agency 2001. *Information on the occurrence of red tide in the Seto Inland Sea, Annual Report 2000*. Seto Inland Sea Fisheries Coordination Office, 62pp. (in Japanese).

Nomura H. 1998. Changes in red tide events and phytoplankton community composition in Tokyo Bay from the historical plankton records in a period between 1907 and 1997. *Oceanography in Japan*, 7(3), 159-178 (in Japanese with English abstract).

Nomura, H. & Yoshida, M. 1997. Recent occurrence of phytoplankton in the hyper-eutrophicated inlet, Tokyo Bay, central Japan. *La mer,* 35, 107-121 (in Japanese with English abstract).

Shizuoka Prefecture 1999. *Report of the research on the usability of deep sea water in Suruga Bay*. 110pp. (in Japanese).

Tokyo Metropolitan Government 2002. *Report of red tide monitoring survey in the innermost part of Tokyo Bay in 1999 and 2000.* Tokyo environmental office Administrative Division, 235pp. (in Japanese).

Testing ballast water treatment equipment

A. E. Holdø

Faculty of Engineering and Information Sciences
University of Hertfordshire
UK
a.e.holdo@herts.ac.uk

Introduction, aims and objectives

Ballast water treatment equipment is reaching a critical stage of development. There are at present several methods and types of ballast water treatment equipment available for the ship owner or operator and there are also many considerations in choosing the appropriate type of equipment for a specific ship. Importantly, when selecting equipment there is a need to ensure that the equipment will perform to requirements. Computational Fluid Dynamics (CFD) methods can be used with advantage for the design stage of ballast water treatment equipment together with analytical and scale model tests. However, due to the complex nature of most proposed and current ballast water treatment equipment, it is necessary to carry out near full scale tests in order to ensure that the equipment performs according to specification. Furthermore, there may be a range of tests which needs to be performed. This range of tests may well include biological sample as well as being of a hydrodynamic/thermodynamic nature.

In order to ensure that equipment that is installed onboard ships performs to specification and expectation it is necessary to carry out tests using a purpose made facility. The present paper describes such a facility at the University of Hertfordshire.

The aim of this presentation is to stimulate discussion about the next stage of ballast water treatment, namely the application and installation of equipment onboard ships and how to ensure that this equipment will perform according to plan and expectation.

Research methods, test protocol and experimental design proposed

The focus of most ballast treatment equipment is to separate out or render biological hazards harmless. The dimensions and methods used for ballast water treatment equipment means that to ensure physical similarity between a model and a real installation, a number of dimensionless groups have to be satisfied simultaneously for any given treatment method.

An example is the case of a method based on heat treatment. In this case the equations governing the convective flow within such equipment due to an applied temperature field are the conservation equations; namely conservation of mass, momentum and energy. These equations are given as (Holdø et al, 2000):

Conservation of Mass:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} + \frac{\partial (\rho w)}{\partial z} = 0 \qquad 1.1$$

Conservation of Momentum:

$$\rho\left(\frac{\partial u_i}{\partial t} + u_j u_{i,j} \right) = -p_i + \mu \left[u_{i,j} \right]_j + \rho f_i \qquad 1.2$$

Conservation of Energy:

$$\rho c_p\left(\frac{\partial T}{\partial t}+u_j T_{,j}\right)=\left(kT_{,j}\right)_{,j}+H \qquad 1.3$$

The equations give rise to a number of important dimensionless groups or force ratios for convective flows not including the transport of species. These ratios are:

- The Grashof number; which is the ratio of buoyancy to viscous forces and is given as :

$$Gr=\frac{\rho^2\beta_T\Delta TgL^3}{\mu^2}$$

- The Rayleigh number; which is the ratio of inertial times buoyant forces to the square of viscous forces

$$Ra=\frac{\rho g\beta\Delta TL^3}{\mu\alpha}$$

- The Prandtl number; which is the ratio of mass to thermal diffusivity

$$Pr=\frac{\mu c}{k}$$

- The Reynolds number; which is the ratio of inertia to viscous forces and is given as:

$$Re=\frac{\rho UL}{\mu}$$

In analysing this type of problem it is important to choose the relevant physical and geometrical quantities in order to obtain the correct values for dimensionless parameters. Demonstrated by the above equations and dimensionless groups, it is impossible to satisfy them all when using a scale model of the equipment even for the case where there are no species being transported. This is most readily seen from the fact that some groups include L whilst other groups include L^3.

Similar analysis for physical similarity can be carried out for other type of ballast water treatment equipment. Clearly, different types of dimensionless groups will be appropriate for scaling, however, for a majority of the cases it can be shown that is necessary to use near full scale conditions for ensuring that equipment performs according to specification. For this reason it is essential to have facilities which can test and consequently certify equipment at near full scale conditions and where a variety of methods emulating the biological hazards can be introduced.

Results

In order to satisfy ballast water treatment equipment testing a hydrodynamic based test facility for such purposes has been constructed at the University of Hertfordshire. The facility is based in a building with $150m^2$ free surface area. This floor space sits on top of two tanks (Figure 1) which can be connected to each other using various approaches.

The volume of the tanks are $60m^3$ and $630\ m^3$ which enables a realistic amount of sample water to be passed through ballast water treatment equipment on test. It is important to ensure that a sufficient amount of water is passed through the equipment in order to achieve a realistic statistical basis for analysis. The necessary volume of water may be debatable, but it is also related to the typical flow rates that will be used. The flow rates that are used in present equipment is of the order of hundreds of cubic meters per hour.

The test facility has at present installed pump capacity of 400 m^3/hour. This means that the large tank will give an hour and a half of flushing contaminated water through test equipment, whilst the smaller tank can be used for 10 minutes tests. The tanks can be connected in several ways so that the smaller tank can be used as a mixer tank for preparing several types of water conditions to be tested. This may

well be necessary as in some cases the biological contaminant concentration and conditions may vary significantly. Furthermore, the presence of sand, mud or other particles in the water may well affect the performance of the treatment of the biological hazards. If this is the case then such conditions must also be part of a performance test.

It is clearly also possible to exhaust the water back into any of the tanks and this enables long term performance tests. Such tests may well be of interest when equipment contains filters which needs to be cleaned at various stages of operation. Filters may not be the only part of ballast water equipment that may need the long term tests made possible through exhausting treated water back into either of the two tanks. However, it is clearly necessary to perform such tests for operational reasons.

Calibrated flow rate meters and pressure transducers are available in the laboratory together with other standard hydrodynamic instrumentation. Particle counting and sizing equipment available for quantitative measurements is also available and can be used on a continuous or sampling basis for assessing the specification of inflow water composition as well as equipment performance in terms of, for example , separation efficiency of particles.

In many cases, it may not be sufficient to carry out mechanical based particle tests only and it is likely to be necessary to perform biological tests. Towards this end, the facility is equipped with a variety of sampling port locations as well as locations for introducing the biological contaminant. On such sampling point is shown in Figure 3. The biological contaminant may also be introduced and mixed with water in the smaller of the two tanks.

The laboratory also offers facilities such as heating coils, compressed air (e.g. for back-flush of filters) and thermal probes and measurements.

Initial tests have been carried out on Optimarin a/s ballast water treatment equipment with some success. Figure 4 shows the equipment during installation in the test facility.

The tests demonstrated that the flow rates and modes of operation described can be achieved. During the tests, back flush operations for filters were also performed. Biological sample preparation and testing was also carried out by Dr Voigt using the Artemis method (Voigt&Gollasch, 2000; Voigt&Rosenthal, 2000).

Conclusions and Recommendations

- The present paper demonstrates the physical complexity of a ballast water treatment method and proposes that it is necessary to carry out validation experiments for such equipment.
- A facility for ballast water treatment equipment is demonstrated and presented
- A discussion on the testing protocol for ballast water treatment equipment is recommended

References

Armstrong, G.M., Rose, A. & Holdø, A.E. 1999. An Analysis of Flow-through Ballast Water, Trans. *Inst. Marine Eng*. Vol. 112 pp. 51-65.

Holdø, A.E., Armstrong, G.M. & Rose, A. 2000. An Analysis of Flow-through Ballast Exchange, *ICMES* 2000, Trans. Of 8th Int. Conf on Marine Eng. Systems, Paper A6, New York, May 2000.

Voigt, M., Gollasch, S. 2000. Ballast Water: The Latest Research and Methods of Treatment. *Proceedings of the 3rd Annual Conference "Managing environmental Risk in the Maritime Industry" 25th – 26th October 2000, London, UK*, 10 pp.

Voigt, M. & Rosenthal, H. 2000. Management of Ballast Water in Ports. *Maritime Conferences "Ships Waste – Management and Treatment in Ports and Shipyards", 28 – 30 June 2000, Bremerhaven, Germany*. 10pp.

Figure 1. *Top of water tanks with access hatches.*

Figure 2. *Pumping Facility with total capacity of 400 m^3/hour.*

Figure 3. *Injection sampling point for biological samples.*

Figure 4. *Ballast water equipment of Optimar during installation in the test facility at the University of Hertfordshire.*

Performance verification of ballast water treatment technologies by USEPA/NSF Environmental Technology Verification Program

T. G. Stevens[1], R. M. Frederick, R. A. Everett, J. T. Hurley, C. D. Hunt, & D. C. Tanis

[1]*NSF International*
USA
stevenst@nsf.org

Introduction and objectives

The U.S. Coast Guard (USCG) is tasked in the United States with developing and implementing a program for regulating the discharge of ballast water from ships. The USCG has teamed with the U.S. Environmental Protection Agency (USEPA), through the Environmental Technology Verification (ETV) Program's Water Quality Protection Center (WQPC), to develop testing protocols that will evaluate the effectiveness of technologies to address invasive species present in ballast water. The cooperative effort was initiated in June 2001, and has progressed to the development of a draft protocol for evaluation of technologies.

The EPA ETV program provides credible, independent data on the actual performance of technologies designed to prevent or control degradation of ground and surface waters. Stakeholder input is an important aspect of the ETV Program, and provides direction for development of testing protocols and implementation of the Program. Through technically sound protocols and appropriate QA/QC, testing provides information on the ability of technologies to achieve treatment, and provides information for potential purchasers and regulators regarding operation and maintenance of the technology. The information obtained from testing is made public through publishing of a full verification report and a summary verification statement, both of which are posted for general public access on the EPA web site. NSF International, a not-for-profit, third-party certification organization, is the verification partner working with EPA to implement the WQPC. Further information regarding the ETV Program and the WQPC is available on the EPA web site (www.epa.gov/etv), while information about NSF and their effort in the WQPC is available on the NSF web site (www.nsf.org/etv).

The primary objective of the USCG's involvement in the ETV effort is to develop a mechanism for verifying the performance of ballast water treatment technologies. It is likely that many elements of the protocols will be incorporated into type tests, which will provide the information needed for USCG certification of the technologies. It is also the objective of the effort to coordinate protocol development to meet international approval agency needs.

Proposed experimental design

Information and input on the verification approach and experimental design for verification testing of ballast water treatment technologies was obtained from an initial meeting of a general stakeholder group. The straw experimental approach developed from the stakeholder input was presented to an 18-member technology panel, representing developers and vendors, the shipping industry, regulators and researchers. The tech panel has worked with Battelle, the contractor selected to write the protocol, to develop a draft document that will soon be available for general stakeholder review. In developing the draft document, the tech panel was reminded that the ETV program is not a research project – that only essential, need-to-know issues be addressed in the protocol, and that the cost to complete testing needs to be an important consideration in developing the experimental design.

The following verification factors, or questions to be addressed by the testing protocol, were identified by the stakeholders and provide the foundation for the protocol:

Biological treatment performance – determination of the technology's ability to remove, inactivate or destroy organisms, as measured by removal efficiency (percent) or a threshold (water quality standard); this also addresses the potential for organisms to survive treatment to reproduce (regrowth).

Operation and maintenance – measure of the operator time, effort, and skill required to achieve the performance achieved during the testing.

Reliability – measure of the ability of the technology to perform consistently over a period of time.

Cost factors – determine the amounts of consumables (i.e., chemicals, filter media, power, etc) and labor hours required to achieve the stated level of performance.

Environmental acceptability – evaluation of the compatibility of the treatment technology with the receiving waters, particularly with regard to residuals of treatment chemicals or by products produced by the treatment process.

Safety – evaluation of potential chemical, electrical, mechanical or biological hazards associated with the operation and/or maintenance of the technology.

The tech panel agreed that the protocol should only address prefabricated, commercial-ready systems, and that components of systems not be evaluated separately. While operational data for technologies under actual use conditions was deemed desirable, the tech panel decided that the protocol should initially address land-based testing, and that shipboard verification testing be addressed by a later protocol, as appropriate. This decision was based on:

- Land-based testing is necessary to provide comparable conditions for verifying technology performance, particularly systems that will not need to be scaled up for shipboard use; and,
- Shipboard testing is critical for evaluating technology-engineering performance and for systems requiring scale up to accommodate higher flows.

Addressing the verification factors and taking into account the need to provide a repeatable evaluation protocol, Battelle generated an initial document that was subsequently reviewed by the tech panel. A special working group was also formed to consider the challenges posed by the biological measurements necessary to ensure treatment efficacy and to provide input on the experimental design. The second draft of the protocol, which will be submitted for review by the tech panel, incorporated comments from the tech panel and the working group.

Proposed protocol approach

The test design in the protocol addresses the physical/chemical and biological challenge conditions, duration of testing, replication, reliability, biological effectiveness measures, and core measurements. The protocol further describes test site arrangements to conduct the testing, and includes guidance on methods for analysis of samples and statistical analysis of the test data. As with all ETV protocols, a detailed description of QA/QC procedures is provided to assure the credibility of the acquired data.

The draft challenge conditions, shown in Table 1, allow for verification of technology performance with water conditions that are difficult to treat and representative of the range of conditions found in the natural environment, excluding rare or extreme conditions that might occur.

Table 1. *Water Quality Challenge Matrix*

Water Type	Water Quality Characteristics
Fresh (<1 PSU)	DOC = 8 – 12 mg/L POM = 8 – 12 mg/L MM = 16 – 22 mg/L Sum of POM and MM = 24 – 34 mg/L Temperature: 10 – 25ºC
Marine (~ 33 PSU)	DOC: 8 – 12 mg/L POM: 8 – 12 mg/L MM: 16 – 22 mg/L Sum of POM and MM: 24 – 34 mg/L Temperature: 10 – 25ºC

Where: DOC is dissolved organic content
POM is particulate organic matter
MM is mineral matter

The water available at the testing facility will be amended to achieve the required water quality conditions by adding organic and mineral matter as necessary. The purpose of the testing is to evaluate a technology's ability to remove, destroy or inactivate organisms. Three groups of organisms are included in the test protocol, including bacteria, protists and macroalgae, and zooplankton. Both ambient populations in the water at the test location and surrogate (added) species will be used during the testing to determine treatment efficacy. A list of organisms under consideration is included in Table 2. Additional work, described below, is needed to identify the appropriate surrogates to be included in the test protocol.

Table 2. *List of Potential Surrogate Species*

Functional Group	Fresh Water	Marine Water
Bacteria	Bacillus globigii Bacillus similis Bacillus cereus	Bacillus marinus Bacillus licheniformis Clostridium perfringens Enterococcus spp.
Zooplankton	Daphnia Cladoceran Rotifers	Rotifers/Artemia Oyster larvae Sea urchin larvae
Protist (resting cyst form)	Acanthameoba Peridinium	Dinoflagellates
Phage	No surrogate identified – natural populations will be used	
Macroalgae (fragmentor)	To be determined.	Naturally occurring species, such as Entermorpha spp. or Caulerpa spp.

For tests to be initiated, threshold concentrations of ambient organisms are required at a test location. The thresholds are 10^6 bacteria per liter, 10^2 – 10^3 zooplankton per liter, and 10^5 protists per liter. Surrogate additions will be made in the same concentrations. Surrogates used in the testing will be obtained from commercial suppliers where available, or prepared at the test facility. In either case, an assay will be conducted to evaluate the viability of the surrogates upon receipt at the test site and within 24 hours of a test cycle.

Six biological efficacy tests will be conducted to determine a technology's treatment effectiveness. Three marine and three fresh water tests, using surrogate and ambient species to determine effectiveness, will be completed over the course of the technology evaluation.

Two approaches are possible for evaluation of the reliability of the technology – based on either ballasting cycles (as specified in the technology O&M manual) or minimum treated volume. Under the ballasting cycle approach, a technology will be operated for the number of operational cycles needed to achieve 150 percent of the vendor specified operation and maintenance cycles. For example, if the vendor indicates that their technology can operate for 40 operational cycles (or hours of operation) before requiring O&M, the test would run for 60 cycles (or hours), during which six biological efficacy tests would be completed. In-tank treatment technologies using chemical biocides may be operated without active agent addition during non-biological efficacy cycles to evaluate the electro/mechanical aspects of the technology.

The minimum treated volume approach is based on either the number of ballasting cycles required to achieve treatment of a minimum of 10,000 m^3 of challenge water for in-line treatment technologies (equivalent to approximately 30 hours of operation at 300 m^3/hour), or 1,800 m^3 for in-tank technologies (equivalent to six biological test cycles of 300 m^3 of water). Figures 1, 2 and 3 show test set ups and sampling schemes for evaluation of technologies designed for different ballast operation options.

The sampling locations for each of the testing arrangements are indicated in the figures. Samples will be collected simultaneously during efficacy test runs in three one-m^3 tanks, providing triplicate time-integrated samples at each sample location. Each sample will be sub-sampled for the core parameters, as shown in Table 3. *In situ* sensors will be used, where possible, to monitor water quality and proxy (e.g., chlorophyll, turbidity, etc.) parameters during test runs. Standard analytical methods (USEPA methods, *Standard Methods*, ASTM, etc.) will be used for analysis, where available, or non-standard methods will be used and described in the verification Test Plan. The Test Plan will include detailed information needed to complete the verification evaluation, and will be specifically developed for each technology and testing site.

Table 3. *Core and supplemental parameters*

Parameter	**Sample Location and Approach**		**Measurement Location**
	Challenge Water	Post Treatment	
Core Measurements			
Temperature	*In situ*, Continuous	*In situ*, Continuous	Test facility
Salinity	*In situ*, Continuous	*In situ*, Continuous	Test facility
Total suspended solids	Discrete grab	Discrete grab	Laboratory
Particulate organic matter	Discrete grab	Discrete grab	Laboratory
Dissolved organic matter	*In situ*, Continuous, discrete	*In situ*, Continuous, discrete	Test facility, Laboratory
Dissolved oxygen	*In situ*, Continuous	*In situ*, Continuous	Test facility
Dissolved Nutrients (N, P, Si)	NA	Discrete	Laboratory
Indigenous species	Discrete	Discrete	Laboratory
Surrogate species	Discrete	Discrete	Laboratory
Proxy measures			
Turbidity (represents TSS)	*In situ*, Continuous	*In situ*, Continuous	Test facility
Chlorophyll a (biomass)	*In situ*, Continuous	*In situ*, Continuous	Test facility
ATP (living material)	Discrete grab, Continuous as available	Discrete grab, Continuous as available	Laboratory Test facility

A key part of the biological efficacy testing will involve determination of the viability of organisms remaining in the challenge water after treatment by the technology under evaluation. An enrichment

approach will be used for bacteria and protists. A +/- scoring system will be used, with multiple media and nutrient levels, and light and dark incubations to separate autotrophs. Zooplankton viability will be determined by observation of samples for movement.

Part of the evaluation will also include regrowth of the organisms, which will be determined by holding treated water for up to five days, then measuring abundance and viability. Longer holding times may be used where the technology dictates, and will be indicated in the Test Plan.

Part of the verification evaluation for technologies employing a biocide involves toxicity testing to evaluate the potential impact the technology would have on a receiving water , and to be sure that discharge of the waste from the testing site will have no negative environmental impacts. The toxicity testing will be completed during the start-up phase of testing and will use standard wastewater toxicity tests. Favorable toxicity testing is required prior to initiation of the biological efficacy testing. Subsequently, a technology would have 30 days to take steps to comply with discharge requirements or testing would be terminated until the toxicity issue is resolved.

The data generated during testing will be evaluated to determine the efficacy of the technology. The remaining concentration and percent removal for each naturally occurring or surrogate species will be calculated, and the statistical significance of the data will be evaluated relative to the treatment control using a t-test of treated removal versus control removal.

Research needed for indicator species

Although a significant amount of work has been completed toward developing a testing protocol, identification and selection of species that can be used as surrogates during testing still needs refinement. As mentioned previously, addition of surrogates is important from the standpoint of being able to have a protocol that will generate meaningful data from different testing sites, where ambient species would differ in both abundance and resistance to treatment.

The working group formed to address this issue recommended a comparative study to determine the relative resistance of the proposed surrogates to different treatment methods (not to include filtration) through various life stages. The goal is to understand the relative responses of potential surrogate species, as well as ambient organisms present in the source water. The objective of the study is to significantly reduce the number of surrogates needed to be included in the testing.

The first stage of the comparative study is to screen a number of species and a range of basic treatment processes that could be used for ballast water treatment to determine the most resistant species. A second, more detailed evaluation will be conducted on the resistant species identified in the first round of testing, with the goal of arriving at a minimum number of species that will present the greatest challenge to treatment technologies submitted for verification.

Planning is also proceeding for completing a pilot round of testing to evaluate the procedures included in the protocol. Whether this testing will include surrogate species is unclear, but it will be conducted using ambient species at the selected testing site. Completion of the pilot testing will help to identify changes that need to be made to the protocol to achieve the objective of having a test procedure that will generate meaningful and useful information on the performance of ballast water treatment technologies.

Conclusions

The work completed on the ETV Ballast Water Treatment Technology Protocol has developed an approach that will produce data to assist users, purchasers and regulators in making decisions on the use of technologies. There is still work to be done, as the protocol is still in a draft stage. The document will be reviewed by the Tech Panel during the summer of 2003, and should be available for

general stakeholder review in the fall of 2003. While primarily a U.S. effort to this point, international input into the protocol is welcome, as development of a standardized approach to evaluation of ballast water treatment technologies on a global basis, to the extent possible, would be of great benefit to all parties – technology vendors, ship owners/operators and regulators.

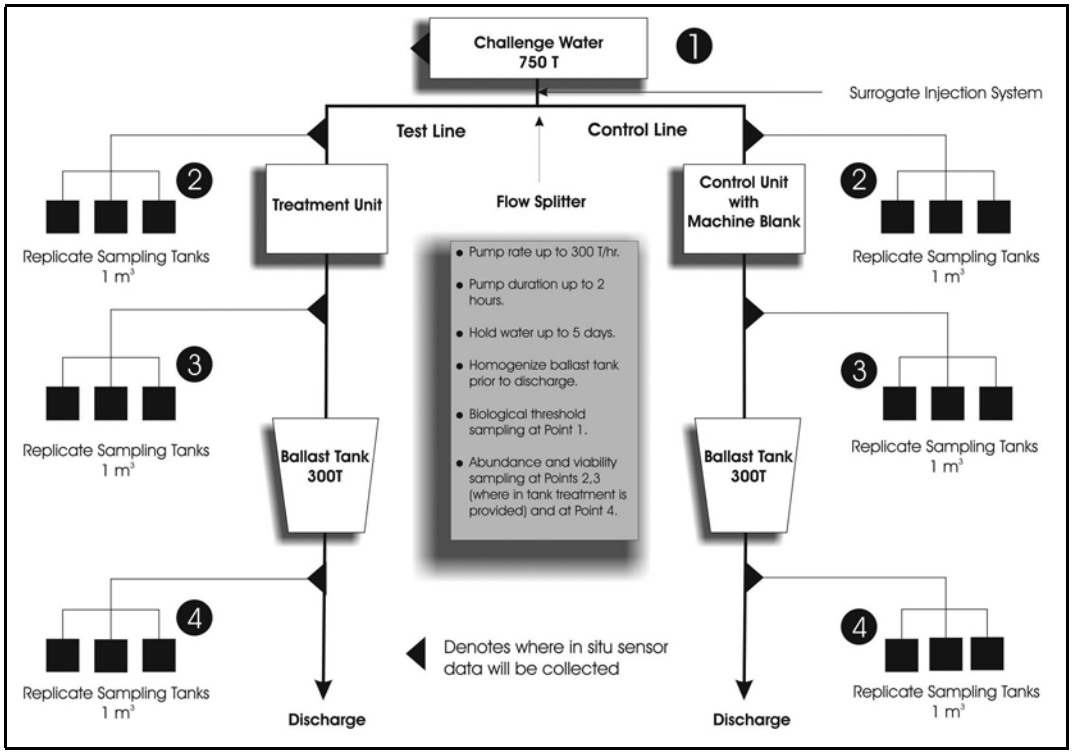


Figure 1. *In-line treatment on uptake or in combination with in-tank treatment.*

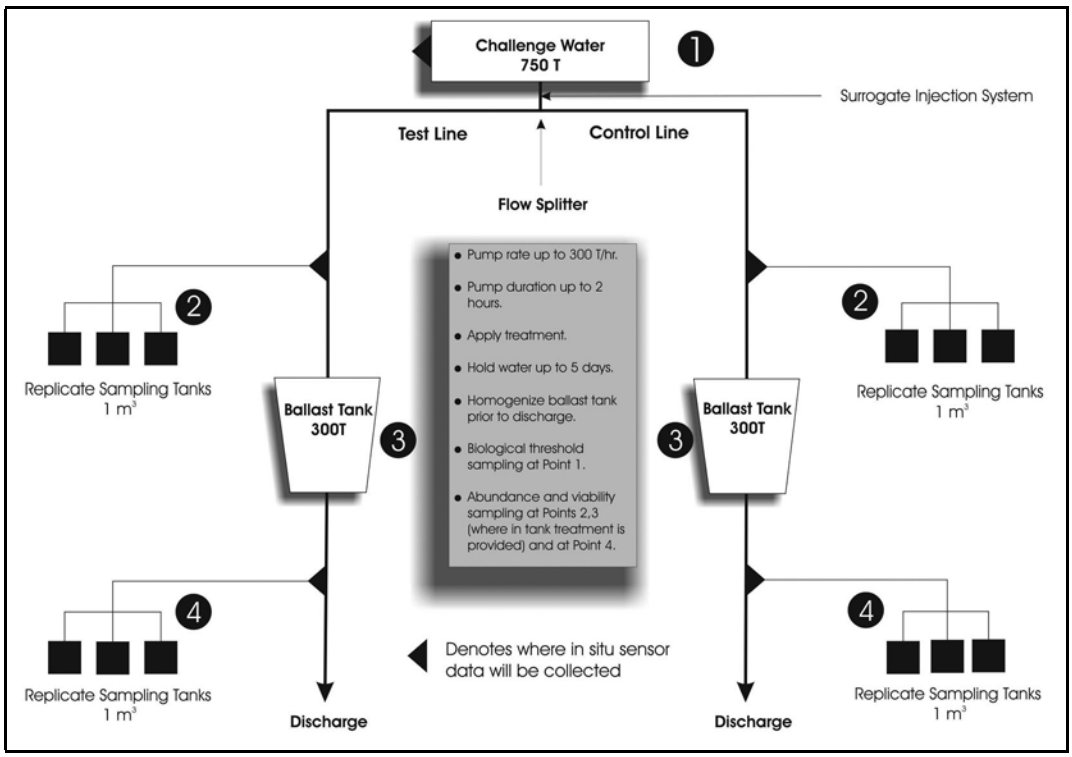


Figure 2. *In-tank treatment.*

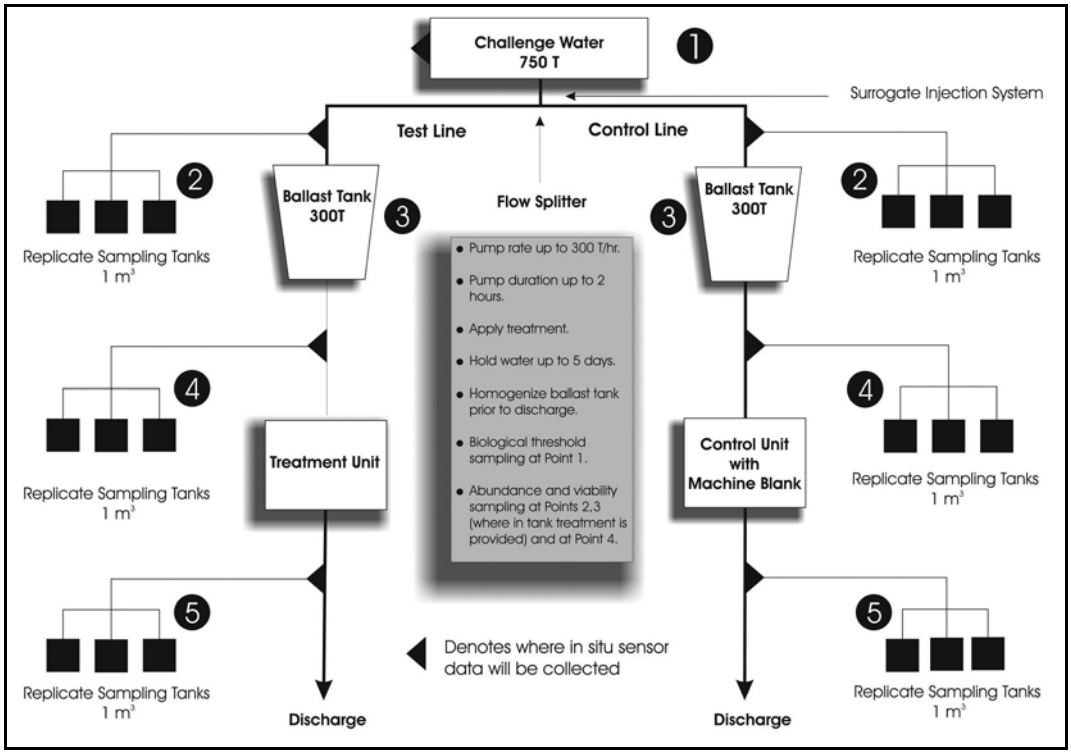


Figure 3. *In-line treatment on discharge or in combination with in-tank treatment.*

Papers submitted
(not presented at the Symposium)

Disclaimer

Papers have been included in these Proceedings largely as submitted, with basic editing and formatting only, and without scientific or technical peer review.

Neither the GloBallast Programme, the International Maritime Organization (IMO), the Institute of Marine Engineering, Science and Technology (IMarEST) nor the symposium sponsors take any responsibility whatsoever for any statements and claims made in these papers, for the quality, accuracy and validity of data presented, or for any other contents of these papers.

Individuals and organisations that make use of any data or other information contained in these papers do so entirely at their own risk.

Inclusion of papers in these proceedings in no way constitutes any form of endorsement whatsoever by IMO, GloBallast, IMarEST or the symposium sponsors.

Design optimisation of a UV system for onboard treatment of ballast water

M. Casey[1], A. Leigh[2] & P. Zhou[1]

[1]*Department of Naval Architecture & Marine Engineering*
Universities of Glasgow and Strathclyde
UK
mcasey@strath.ac.uk
peilin.zhou@na-me.ac.uk.

[2]*Willand U.V. Systems Ltd, UK*
tony.leigh@atgwilland.com.

Treatment option being researched

The current work relates to the design optimisation of a physical ballast water treatment system using ultraviolet (UV) light.

Project timeframe

This work was carried out over a six-month period from October 2002 to April 2003.

Aims and objectives

The harmful environmental effects on the ocean environment as a result of the translocation of foreign or unwanted aquatic bodies via ballast water is well documented. The TREBAWA group is a European consortium that addresses this issue by focusing on the development of a new technically and economically competitive ballast water treatment system to be employed onboard ship. The proposed system consists of a primary (mechanical) pre-treatment phase together with a secondary integrated UV system to prevent microorganisms' transport by disinfection of the ballast water. The current work focuses on the design optimisation of the secondary (UV) system by simulating the flow regimes present in proposed designs by employing Computation Fluid Dynamics or CFD.

CFD enables engineers to gain a valuable insight into the possible weaknesses and strengths of proposed designs. This can reduce the need for costly prototypes and consequently reduce the time from concept to construction. The main objectives of the current work are:

- To produce a practical and efficient prototype UV treatment system to be employed in conjuction with a primary separation system for use onboard ship.
- To carry out design optimisation by taking a wide range of possible UV system geometries and simulating the physical flow characteristics within them using CFD.
- To focus on the most efficient system (or systems) and undertake construction and physical testing of the prototypes under laboratory conditions.
- To undertake sea trials of the chosen prototype system.

This paper provides details of the approaches made to address the first two objectives. At the time of writing construction and testing of the chosen prototype are about to begin. Details of meeting the latter two objectives will be discussed in a later publication.

The UV chamber design must have a geometric form that enables it to be installed onboard together with existing pipe work in straightforward manner with minimal disruption to the operation of the

ship. Design scale-up must be addressed as the treatment system is likely to be employed in a wide range of vessels involving units of differing size. The design must promote ease of use for the onboard personnel and the material costs, fabrication and manufacture must be economically viable. The proposed system must be able to facilitate regular maintenance and monitoring. Examples include cleaning of the UV lamp to avoid foul up, lamp replacement and system shutdown in the event of malfunction. Innovative UV chamber designs are of little use if the pressure loss incurred makes the running costs too prohibitive, therefore pumping power estimates must be made at early stage of the design process.

Research methods

Several previous authors have employed CFD to evaluate UV treatment system performance[1]-[5]. Wright *et al*[1] and Baas[6] have highlighted the usefulness of evaluating different UV system designs using CFD. Both these works involved the development of numerical algorithms to simulate the UV dosage given to particles enabling a comparison to be made of the efficiency of each design. Wright *et al*[1] found that making relatively minor changes to the positions of the inlet and outlet branches resulted in marked improvements to the uniformity of the flow and an increase in the approximated UV dosage. They concluded that the increased pressure drop incurred was acceptable in view of the improvements to the system. Baas[6] found that an original UV chamber design could be improved upon by placing several small UV lamps across the main chamber as opposed to having a single UV lamp running along the chamber.

Employing CFD as a research method enables several areas to be investigated when undertaking design optimisation:

- Highlight areas within the UV chamber geometry where there is the possibility of unfavourable flow regimes. Examples include areas of flow stagnation or areas where the UV lamps are bypassed (so called 'short-circuiting').
- Examine the effect on the predictions by having various UV lamp configurations with varying chamber diameters and varying flow rates.
- Compare predicted pressure drops for each of the proposed designs.
- Obtain predictions for particle tracking and Residual Time Distributions to help estimate the efficiency of the unit to impart a UV dosage to the ballast water.
- Investigate the effects of placing flow devices upstream or downstream of the UV chamber in order to eliminate detrimental secondary flow or back flow elements.

Modeling approach

Model set up

Several commercial software tools have been successfully employed to carry out CFD in UV chamber design including 'CFX'[1] and 'Fluent'[5]. Fluent was adopted for the current work and its effectiveness was assessed in meeting the main objectives. Numerical meshes representing each of the UV chamber geometries were created using Fluent's GAMBIT preprocessor. Unstructured (tetrahedral) elements were employed to model the geometry. These elements were found to model the chamber components more accurately than structured elements. The total number of computational cells making up a mesh typically ranged from 200,000 for straightforward single pipe geometries up to 400,000 for more complicated geometries. All the simulations were run on a Dell GX260 Pentium 4 PC machine and the convergence times varied from 30 minutes to 2 hours depending on the mesh size. The fluid flow properties for each of the simulations involved typical values for sea water at 50F (ρ = 1027.9 kg/m^3 and μ = 0.0014 kg/m-s).

The computations were carried out using the standard set of under-relaxation factors used by Fluent. Similarly, the default values of the first approximation and the standard pressure-velocity coupling solver were used. The convergence criterion adopted for each of the residuals was set to 0.0001 for each simulation. The high velocity gradients and high shear stresses present at the chamber walls were modeled using a standard wall function approach. Ideally a very fine mesh would be employed to model near wall behavior but this was not achievable with the computing power available. For all cases the boundary condition at the chamber inlet was the specified velocity based on the inlet branch diameter and the flow rate. At the chamber outlet the relative pressure was set to zero.

Turbulence modeling

Pipe diameters ranged from 4 inches to 16 inches and flow rates ranged from 30 m^3/hr to 1200 m^3/hr. For the pipe size and flow rate combinations tested this equated to upstream inlet velocities of between 0.5ms^{-1} and 3.0ms^{-1}. The Reynolds number range for the flows investigated lie in the turbulent region and it was therefore necessary to adopt a turbulence model to obtain flow solutions. The more comprehensive Reynolds Stress Model (RSM) and Large Eddy Simulation (LES) models were discounted because of the increased calculation times required considering the number of chamber designs being assessed and the computing power available.

Fluent has a number of (k-ε) based turbulence models available that are the most widely used turbulence models based on work originally developed by Launder and Spalding[7]. For the current work a (k-ε) Realizable model was adopted[8]. It was found that this model gave improved predictions for the swirling flow component due to its anisotropic treatment of turbulence compared to the standard (k-ε) model. This model proved to be more stable compared to the (k-ε) renormalized (RNG) model for a range of simulations. This has been confirmed by Schaler *et al*[9] in modeling similar flows.

Particle tracking and dosage

The standard Discrete Phase Model, or DPM, provided by Fluent was adopted to simulate particle tracking. The Lagrangian model employed firstly involves obtaining the solution of the continuity and momentum transfer equations for the continuous phase then setting the injection conditions (in this case at the UV chamber inlet). The particles are then tracked using visualization or by collecting a data summary of the particle behavior from the inlet to the chamber outlet. Particle movement and particle residence time are critical to the levels of UV dosage the chamber imparts to the ballast water. Particle track predictions assist in determining whether the water is likely to be directed close to the UV lamps to obtain the required dosage. Residence time distributions, or RTD, provide an indication as to whether the particles are in the system long enough to acquire the required dosage.

If the TREBAWA UV system is to achieve a high percentage microorganism kill rate a measurement of the lowest dose per particle should be made. This is calculated from the lowest intensity at any point in the chamber multiplied by the contact time. However, this assumes that the Residual Time Distribution (RTD) has a value of one. That is each particle spends exactly the same time in the chamber as every other particle. In practice this has been a fair assumption and systems have performed well without any performance failures as a consequence of this RTD.

Each RTD data summary provided by Fluent contains statistical data relating to the standard deviation, the mean and the maximum and minimum of the particle residence time. RTD data was recorded for particles that were predicted to escape out of the exit following their introduction at the inlet. Particles that are predicted to become ‘trapped’ in the system and thus show unrealistically long residence times, caused for example by re-circulation, were highlighted in the RTD data summary.

The “time to first trace” is the ratio of the fastest particle (i.e. the shortest time) to the mean time for the particles and was calculated for each chamber design. UV intensity mapping was carried out at Willand U.V. Systems for each of the designs and when combined with the ‘time to first

trace' values was used to develop a system whereby the minimum dose was close to the average dose. A system that falls into this category is most likely to help reduce the problems associated with the logarithmic effect of UV disinfection.

Case comparison

Over 75 UV chamber simulations were carried out for varying UV chamber geometries. Simulations were carried out for designs similar to those that are currently commercially available and for designs that were proposed through collaboration with Willand UV Systems Ltd by drawing on their expertise in UV chamber design. This study involved varying the UV lamp configurations, varying the flow rates, varying the chamber orientations and varying the positions of the inlet and outlet branches.

Design optimisation involving numerical modelling can only carried out by maintaining consistency in the modelling techniques employed. It is for this reason that when obtaining steady state solutions for each of the UV chamber designs the same turbulence model, grid density, fluid properties and convergence criteria were employed. In addition, the same number of particles was released at the inlet boundary condition for each design when employing the Discrete Phase Model. The methods described above were implemented with the aim of focusing on a design or design(s) that consistently gave favorable predictions for a range of flow rates and chamber sizes bearing in mind the unit's intended use on a wide range of vessels.

Results

A selection of the UV chamber designs that were modelled is shown in Figure 1. These geometries were generated using the GAMBIT pre-processor and represent the fluid domain over which the simulations were obtained. The "holes" running through the chambers represent the solid walls of the UV lamps. The diameters of the UV lamps were kept constant throughout at 3.6 cm, as recommended by Willand U.V. Systems. In Figure 1, the designs given in cases 1 through to 10 have inlet and outlet branches in various configurations attached to the main UV chamber. Cases 11 and 12 show 'inline' designs in which the inlet and outlet are the ends of the UV chamber. These two latter examples have UV lamps positioned perpendicular to the primary flow direction.

Flow field predictions

Predictions were obtained of the main flow field parameters, including the velocity components and static pressure values, for each of the proposed UV chamber designs. Each of the designs investigated had a straightforward geometric form but it was clear from the simulations that even minor changes in the geometry caused significant changes in the predicted flow field. Figures 2 to 5 show examples of the predicted flow fields. Only a small selection of the results is presented here graphically due to the large number of simulations carried out. Figure 2 highlights areas of slow flow in a conventional design (case 7). Figure 3 shows the movement of the flow in a vertical chamber around horizontal (and offset) UV lamps. Figure 4 shows the velocity distributions along sections of the UV chamber preceding and following each UV lamp for an inline design (case 11). Finally Figure 5 shows the increase in particle residence time (RTD) as particles move down the chamber with staggered UV lamps perpendicular to the main flow (case12). Static pressure drop predictions between the inlet and outlet for each design are given in Table 1. In general was found that:

- For a given flow rate and single pipe chamber geometry the swirling flow component increases significantly if the inlet and outlet branches are placed on opposite sides and tangential to the UV chamber wall as opposed to them being on the same side (cases 1 and 2). The predicted pressure drop was found to increase by up to 15% due the augmented secondary flow present. This is similar to the findings by Wright *et al*[1].

- Moving the inlet and outlet branches close to the ends of the UV chamber reduced the size of the areas of flow re-circulation in this region (also found by Wright *et al*[1]).

- The flow regime in the main chamber was found to be less favourable with more flow separation and more stagnation if the inlet and outlet branch diameters were markedly smaller than the main chamber diameter.

- Designs that have inlet and outlet branches normal to or in the same direction as the main chamber wall (cases 1 and 5) had little secondary flow present and may well be prone to short circuiting if only one central axial UV lamp is employed.

- The predictions indicated that if there are too many axially positioned UV lamps in the chamber the flow regime becomes too disrupted and a significant pressure drop increase is reported. For example, an 18% increase in pressure drop was predicted when using 6 lamps (case 7) compared to using 2 lamps.

- The predictions indicated that lamps may well need to be off set in order to avoid short circuiting in vertical chambers (case 4).

- The predictions for the twin reactor (case 6) showed a lack of flow uniformity within each chamber and highlighted a number of areas of stagnation.

- The steady state, RTD and UV intensity map calculations indicated that the most favourable predictions were associated with 'inline' designs (cases 11 and 12) when compared to conventional designs (cases 1 and 7).

- 'Inline' designs were all associated with reduced pressure drops (up to 30% lower for a given flow rate and chamber diameter) compared to traditional designs. This is due to the lack of a secondary flow field in the former designs.

Table 1. *Selection of UV chamber pressure drop predictions (8" diameter main chamber)*

Case number	Flow Rate (m^3/hr)	Chamber Length (mm)	Number of UV Lamps	Pressure Drop (mbar)
1	120	1025	1	13.7
2	120	1025	1	16.1
3	120	1025	1	11.1
4	120	500	4	9.8
5	120	1025	1	14.1
6	120	2 x 1025	2	31.2
7	120	1025	1	15.4
8	120	1025	6	22.5
9	120	1025	4	18
10	120	500	4	12.1
11	120	1025	4	7.25
12	120	1025	4	8.3

In the 'inline' designs flow passes all the UV lamps sequentially. This implies that the intensity and dose from each lamp is added to the ballast water thereby avoiding the creation of low treatment zones. In contrast, the UV intensity maps showed that in a conventional unit (e.g. case 9) a poorly performing lamp is likely to cause a low intensity zone, which in turn may cause treatment problems.

The inline type designs not only provided the most favourable predictions but also are likely to be the most favourable in terms of ship installation and monitoring. Installation is made easier if alterations to the existing pipe work are minimised. The inline designs promote this in that separate inlet and outlet pipes are not necessary. In a conventional multi lamp unit the monitor is not truly accurate when measuring multiple lamps, as the water particles may not pass all the lamps. The inline design involves accurate monitoring in that the average UV intensity for the lamps is valid, as each water particle must pass all the lamps. In this way fewer monitors are needed in the inline design compared to a conventional system. In addition, an inline monitor is able to sense multiple lamps without any loss in monitoring performance.

Conclusions and recommendations

CFD has proved to be a useful tool in the design optimisation of a UV disinfection chamber for use onboard ship. The 'Fluent' package has proved to be a robust and easy to use tool for the current study. CFD has enabled the TREBABWA group to evaluate a wide range of UV chamber designs under varying conditions and focus on the most favourable thus avoiding the need to construct numerous physical prototypes. This approach speeds up the design optimisation process and reduces the overall project cost.

Several conclusions were drawn:

- The steady state, RTD and UV intensity map calculations have indicated that the 'inline' designs are likely to be the most favourable for use by the TREBAWA group and represent the most practical and economic solution for a UV chamber design.
- CFD has effectively highlighted possible unfavourable flow conditions within UV chamber designs such as short-circuiting and areas of stagnation.
- CFD has successfully shown the effects on the flow caused by changing the chamber geometry and by changing the lamp configuration.
- The simulations have provided useful comparisons of the pressure drop values between different designs enabling a comparison to be made of the possible running costs of each system.

Future work

CFD methods are of course based inherently on approximation and the true measure of the efficiency of a proposed UV system only really comes about through careful construction and experimentation on physical prototypes. In the short term the research effort is focused on obtaining practical data for measuring the efficiency of the inline UV chamber designs. This will involve testing under laboratory conditions and, if successful, proceed to sea trials in the near future. Work is currently being undertaken on the CFD design optimisation of the primary hydro-clone separation system. Predictions are currently being obtained of the effectiveness of the primary separator system to remove particles within the ballast water prior to entering the UV chamber. In this way the separator system can be designed so that it can be combined effectively with the UV chamber developed in the current study.

References

[1] Wright, N.G and Hargreaves, D.M. February 2001. The use of CFD in the evaluation of UV treatment systems. *Journal of Hydroinformatics Vol. 3, No. 2*. IWA Publishing.

[2] Chiu, K., Lyn, D.A. and Blatchley E.R. January 1999. Integrated UV disinfection model based on particle tracking. *Journal of Environmental Engineering Vol. 125, No 1*. ASCE.

[3] Lyn, D.A., Chiu, K. and Blatchley E.R. January 1999. Numerical modelling of flow and disinfection in UV disinfection channels. *Journal of Environmental Engineering Vol. 125, No 1*. ASCE.

[4] Chiu, K., Lyn A., Savoye P and Blatchley E.R. May 1999. Effect of UV system modifications on disinfection performance. *Journal of Environmental Engineering Vol. 125, No 5*. ASCE.

[5] Lawryshyn Y.A. and Donming L. February 1999. UV reactor resign: It's more than putting a lamp in a pipe. *Water Conditioning and Purification Magazine Vol. 41, No. 2.*

[6] Baas, M.M. June 1996. Latest advances in UV-disinfection: hydrodynamic simulation and relation to practical experiences. *Presented at Aquatech '96, Amsterdam.*

[7] Launder B.E and Spalding D.B. 1974. The numerical computation of turbulent flows. *Comput. Methods Appl. Mech. Engineering Vol 3, 269-289.*

[8] Shih T.-H., Liou W. W., Shabbir A. and Zhu J. 1995. A New *k*- ε Eddy-Viscosity Model for High Reynolds Number Turbulent Flows - Model Development and Validation. *Computers Fluids, 24(3):227-238.*

[9] Scharler R. and Obernberger I. April 2000. Numerical modelling of biomass grate furnaces. *Proceedings of the 5th European Conference on Industrial Furnaces and Boilers, Porto, Portugal.*

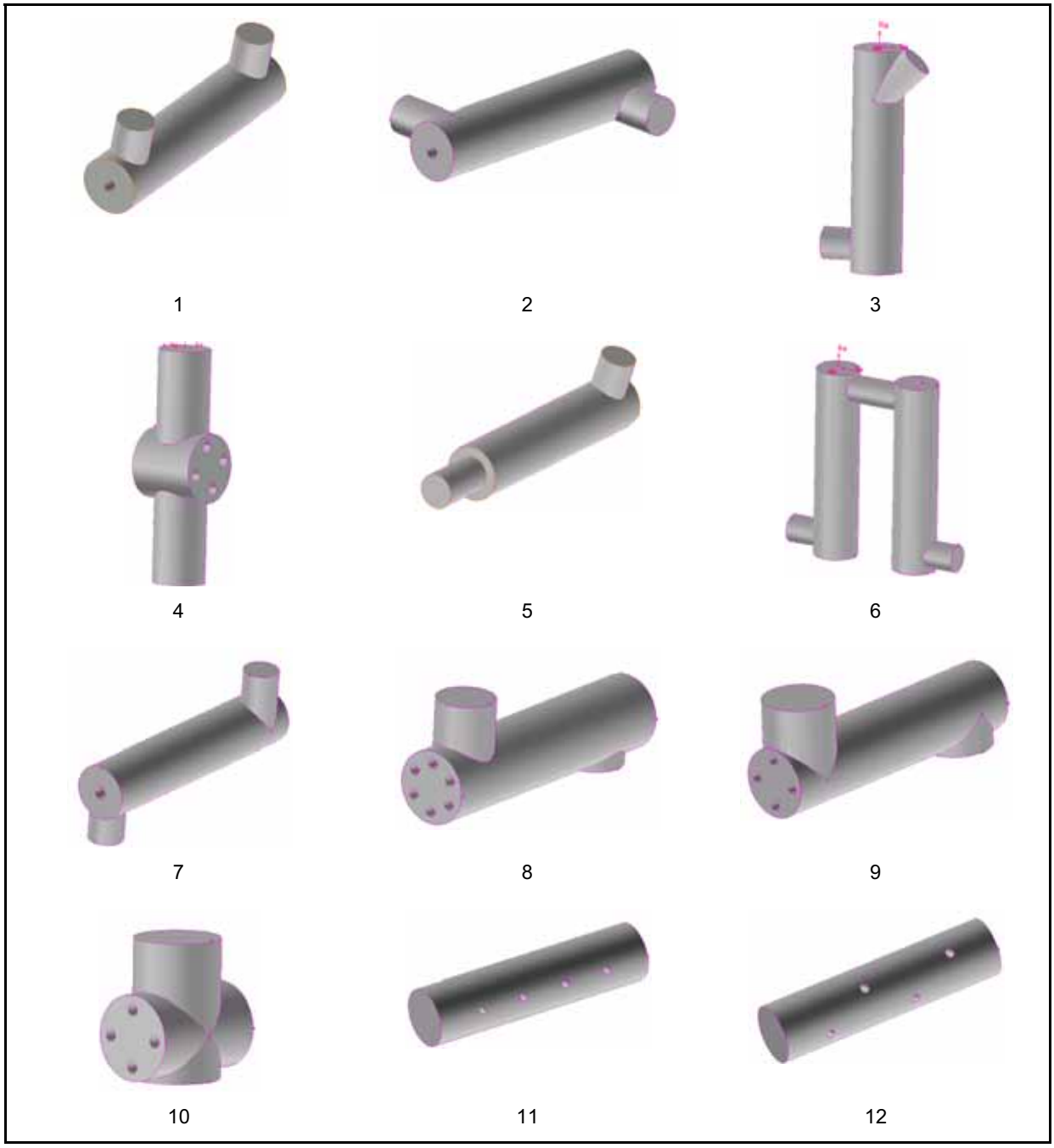


Figure 1. *Selection of UV chamber geometries.*

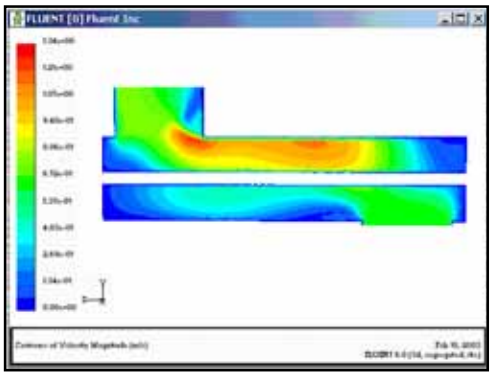


Figure 2. *Velocity Contours (y-z) section - case 7.*

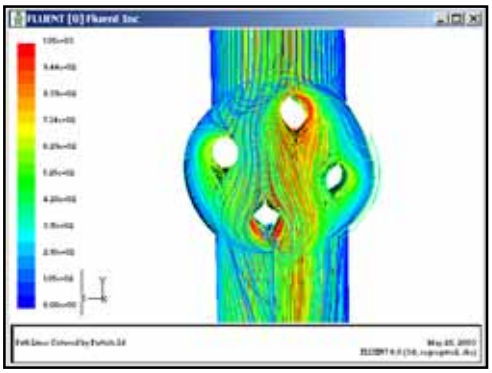


Figure 3. *Pathlines - case 4.*

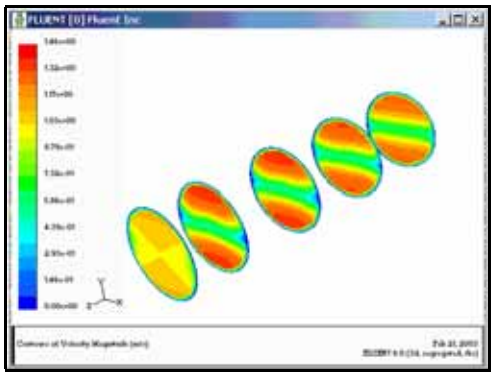


Figure 4. *Velocity Contours (y-x) sections - case 11.*

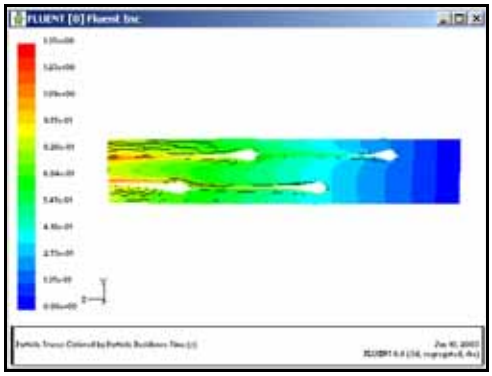


Figure 5. *Particle tracks –residence time - case 7.*

Ship ballast water treatment: the closed-loop option

P. Brodie[1], C. Blatchley[2], M. Balcer[3], Y. Sasson[4], I. Kreisel[5], Y. Kolodni[5], D. Sorek[5], N. Shimron[5], W. Cairns[6] & R. Braun[6]

[1]Balaena Dynamics Ltd,
[2]Purdue University, [3]The University of Wisconsin, [4]The Hebrew University of Jerusalem, [5]Arkal Filtrations Systems, [6]Trojan Technologies Inc
pbrodie@hfx.eastlink.ca

Abstract

A new Ballast Water Treatment (BWT) process option is presented that is potentially advantageous when applied to any number of treatment process configurations, but especially advantageous when used in processes that involve UV-based treatment. The new process option, the use of closed-loop treatment while in transit, is examined for its compatibility with a set of BWT process selection criteria, design options and strategic considerations that are outlined in the paper. The primary advantage of the closed-loop option when used with UV technologies is the ability to accommodate low water qualities in the equipment design without having to size the treatment technology to address the worst case water quality in a single pass. Advantage is taken of the in-transit time to build UV dose to whatever level is specified in the process design. En route treatment also takes advantage of the power availability. The closed-loop option configuration has the flexibility of being used in a single pass process when water quality permits, in a dual pass (ballasting and deballasting) when in-transit growth of organisms is a problem, in the patented closed-loop option while in transit from port to port when the ballast water quality is poor, and is compatible with Ballast Water Exchange (BWE) where it is deemed practicable and safe. The closed-loop process option is also examined for its potential to manage ballast tank sediments.

Introduction

There is a heightened awareness of the economic and health consequences of bioinvasive species that arrive by ballast water and that are increasing at an exponential rate (K. Topfer, UNEP, Ballast Water News 8 (Jan-May) pg 2, 2002). Given the safety and efficacy concerns expressed about Ballast Water Exchange (BWE) on the high seas, there is reason to look at Ballast Water Treatment (BWT). A self-contained BWT process allows independence of seas state/ice pack, etc; independence of ship delays and independence of onshore work disruption. Given a probable 20-25 year phase-out of existing vessels, retrofitting of validated BWT systems becomes an essential consideration in addition to designing BWT systems for new ship outfitting.

The authors of this paper and others collaborators have been developing an optimized ballast water treatment (BWT) process and treatment options that:

- inactivate substantially more than 95% of organisms in a wide range of taxa;
- target resistant aquatic organisms that are not removed by a simple mechanical filtration-UV disinfection process;
- function in a wide variety of water qualities;
- avoid residual toxic problems in discharged water;
- avoid corrosion phenomena in the ballast tank; and
- can be applied to a wide range of ship classes.

Arkal Filtration Systems has issued two pending patents on the BWT process that is named “The Ternary Effect” and presented in detail in another paper in these proceedings.

Figure 1 illustrates the interface of the BWT process and the treatment options that can include single pass, dual pass and multiple pass of the ballast water through the treatment process between the time of ballasting and deballasting. This paper will briefly summarize the process and then expand on the concept of a closed-loop option to enhance process performance.

Figure 2 illustrates the BWT process preferred by the consortium. This patented process employs an enhanced filtration process whereby air, an oxidant (hydrogen peroxide) and a catalyst (MgO) that can promote formation of hydroxyl radicals and can promote coagulation/flocculation are used ahead of the filter to promote aggregation of particles and to facilitate their removal in the filter. The filter of choice is the Spin-Klin disk filter technology of Arkal Filtration (see www.arkal.com and Figure 3). The high surface area and the special structure created by the channels within the discs ensures effective entrapment of particles. The discs are micron grooved, stacked on a spine and compressed by a spring. A number of spines can be stacked together (Figure 4) the disc filters are automatically back flushed. The filtrate with oxidant passes then through a UV system that delivers a target dose of UV for inactivation of the target organisms and for production of target levels of hydroxyl radicals to facilitate disinfection through oxidative mechanisms. The filtered water is then delivered to the ballast tanks where subsequent inactivation will continue due to the combination of oxidant and indigenous or exogenously added catalysts.

Figure 5 illustrates the range of UV technologies that are on the market, with either the industrial or municipal systems in the figure being appropriate for ballast water treatment. Both technologies have cleaning mechanisms. The figure illustrates a very compact UV technology (Trojan UV Swift) designed specifically by Trojan Technologies (see www.trojanuv.com) to fit into tight pipe galleries. These technologies are modular and can be easily handled for installation.

The remainder of this paper will focus not on the specifics of the preferred patented process, but how that process can be interfaced with the different fluid flow patterns shown in Figure 1 for effective ballast water treatment.

Selection Criteria

Numerous processes and technologies have been examined for BWT, but the most successful processes and technologies will meet the following selection criteria:

a) applicable for retrofit and new ship installation

b) able to function in a large variety of water qualities

c) able to address a broad spectrum of organisms (pathogens and non-pathogens)

d) able to address contaminated water previously left in the ballast tank and recovery and growth of organisms in the tank while in transit

e) flexible including compatibility with BWE

f) rugged and reliable

g) cost-effective

BWT processes design options

These can be based on:

a) single pass treatment

b) dual pass treatment (during ballasting and deballasting)

c) multiple pass treatment (using some or all of the available unit operations while in transit between the location of ballasting and the location of deballasting)

d) treatment that is inside the ballast water tanks, external to the tanks, or both

Strategic considerations when designing a BWT process to meet the selection criteria

Retrofitting and new ship installation

This will be simplified when the footprint of the treatment technology can be kept small. A requirement to address the worst possible water quality might require excessive amounts of equipment, but multiple-pass treatment while in transit could augment the treatment given during ballasting and reduce the equipment requirements by allowing lower flow with multiple passes through lesser amounts of BWT equipment to replace a high rate flow through a larger piece of equipment in a single pass during ballasting (or deballasting).

Water quality variation and broad spectrum organism control

Filtration will help narrow the range of particle sizes in the filtrate, and this will both improve water quality for other BWT unit operations such as disinfection and narrow the spectrum of organisms that will have to be addressed. Variation in water quality can also be addressed by multiple pass (closed-loop) treatment while in transit; e.g., repeated passes through UV disinfection units will accumulate UV dose and compensate for poorer water quality that might require large amounts of equipment to deliver the target design UV dose when the water is of poorer quality. In general, the more "exotic" the source of ballast water to the deballasting site, the farther away the source water will have been taken, the longer the transit time between the two sites, and the longer the time available for closed-loop application of the BWT while in transit.

Control of organism recovery and regrowth in transit and prior contamination

It is anticipated that some organisms such as bacteria may reproduce faster than other organisms and that BWT upon ballasting may require additional treatment upon deballasting or while in transit to keep the rapid growers under control. Similarly, previously contaminated water left in the ballast tank would contaminate newly added and treated water unless the residual contamination were also addressed. In-transit BWT keeps the growing populations under control and addresses preballasting contamination in case there is a sudden need for emergency or unscheduled deballasting, and in-transit BWT can, as mentioned above, compensate for poorer water quality that could not be addressed during ballasting or deballasting alone.

Flexibility

Perhaps the greatest need for flexibility is related to the wide variation in water quality that might be encountered. Designing and sizing BWT technologies for the worse case water quality is impractical; however, the ability to address the control of target organisms must not be compromised. Two strategies exist to keep equipment size small while addressing poor water quality when it is encountered. The first is ballast water exchange at sea, although there are certain risks and the procedure is not recommended near island states or continental shelves, constraining BWE for costal shipping. The second is closed-loop recirculation or other forms of extended treatment while in transit

between ports. A flexible process should be able to use either approach interchangeably depending upon circumstances.

Ruggedness and reliability

It is clear that the BWT technologies must withstand the operating conditions to be encountered. When the BWT technologies are modular, then downtime of any component can be addressed by bringing different modules online and/or by extending the treatment in a close-loop treatment option.

Cost effectiveness

Worst case water quality design carries with it unpalatable costs for the amount of equipment able to achieve treatment in a single pass or even in two passes (ballasting and deballasting). Design at the 80^{th} percent water quality or some other standard might enable more cost effective installations with the use of closed-loop or other extended treatment methods being the way to address the remaining 20 percent of water qualities.

Options when selecting the BWT process design:

We have already seen that microbe growth, pre-existing contamination in the ballast tanks, variation in water quality and economics may preclude a single pass process at least under some circumstances. Both extended treatment within the ballast tank and closed-loop recirculation through a treatment process are legitimate methods to downsize equipment but still achieve target performance. ***Ex situ*** treatment; i.e., treatment outside the ballast tank has the advantage of not introducing the treatment into the tank along with any problems that may entail. ***Ex situ*** treatment is compatible with a need for extended treatment of poor ballast water quality only when closed-loop processes are used. Sometimes it may be necessary to carry the treatment to the ballast tank, as for example when not practicing closed-loop recirculation but there is a need to address contaminated water that may be residual from a previous exchange. The greatest flexibility exist when ***ex situ*** treatment outside the ballast tank and ***in situ*** treatment within the tank are creatively combined.

Ballast tank sediment management

Although the primary focus of BWT is control of invasive species and increasingly the control of pathogenic organisms such as ***Vibrio cholerae*** being brought to coastal waters and harbors during deballasting, the sediments that can accumulate in the ballast tanks are also recognized as a problem for which a solution must be found. The sediments are of concern as a potential location where invasive species can lodge, as a location where bioprocesses can promote damage to the ship's structure, and as nuisance accumulations that must periodically be removed.

Closed-loop treatment is examined as a tool to control sedimentation. Filtration during ballasting will contribute to this control process, but particle aggregation and sedimentation while in-transit can still occur. Appropriate positioning of return lines in the closed-loop circuitry will contribute to keeping any particle aggregates in suspension. This would require the reconfiguration of piping to, and between, ballast tanks, specific to individual ship design, to create when in transit, a closed-loop circuit passing through the ***ex situ*** treatment train that would include for example UV for disinfection. Constant speed or variable speed pumps would circulate ballast water, resulting in a series of exposures of organisms and suspended particles to the UV treatment. Each pass allows an increased accumulation of dose towards the target design dose. When a filter is in the recirculation loop, aggregated particles could also be removed. The reduced flow rates of ballast water (to 5-10%) while the ship is in transit, could also permit more effective treatment by mechanical separation to remove sediment and oil residues. The reduced flow rate also places minimal demand on the ship's energy production ability while it is underway. Stagnant regions within ballast tanks can be addressed by retrofitting return piping with an internal manifold; e.g., a rack of nozzles, adjusted to the specific

tank. During at-sea BWE, this same manifold would be used to increase suspension of sediments within ballast tanks and allow discharge of the particles at-sea.

Summary

The closed-loop BWT process option offers the following advantages:

- compact equipment installation
- economic operation by drawing modestly from the ample power of a ship in transit
- operable with existing electrical generating capacity while under way
- capable of continuous operation, but compatible with one or two pass treatment and with BWE when this is practicable and safe
- compatible with a variety of processes composed of different unit operations although the process being developed by the consortium is preferred
- able to address in transit growth and previously contaminated ballast water
- able to address variable water quality without over-design of equipment
- potential for secure monitoring and, ultimately, status transmission on demand
- contributes to ballast tank sediment management.

A Canadian patent has been obtained for the closed-loop process option in BWT, and a worldwide patent application filed.

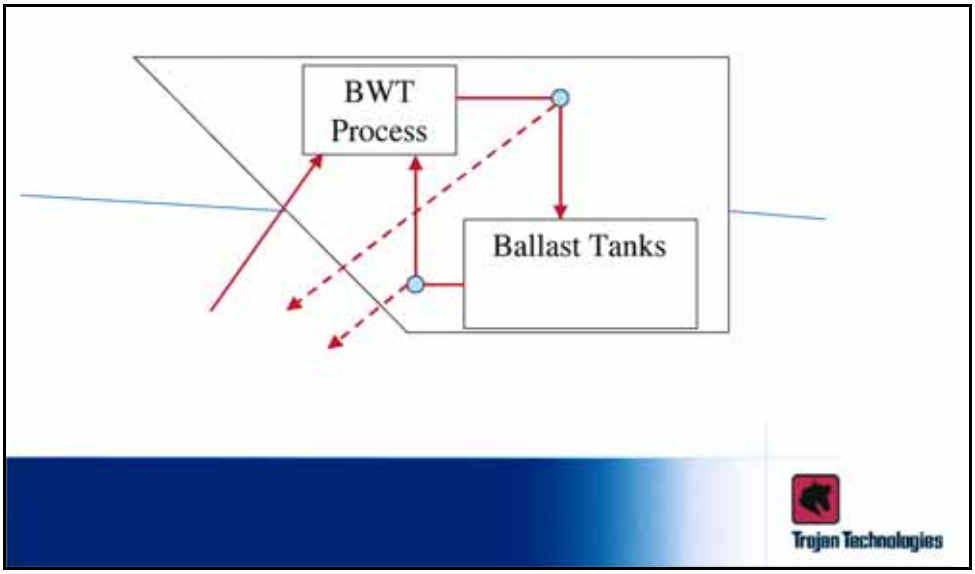


Figure.1 *Closed-Loop – an option for Ballast Water Treatment.*

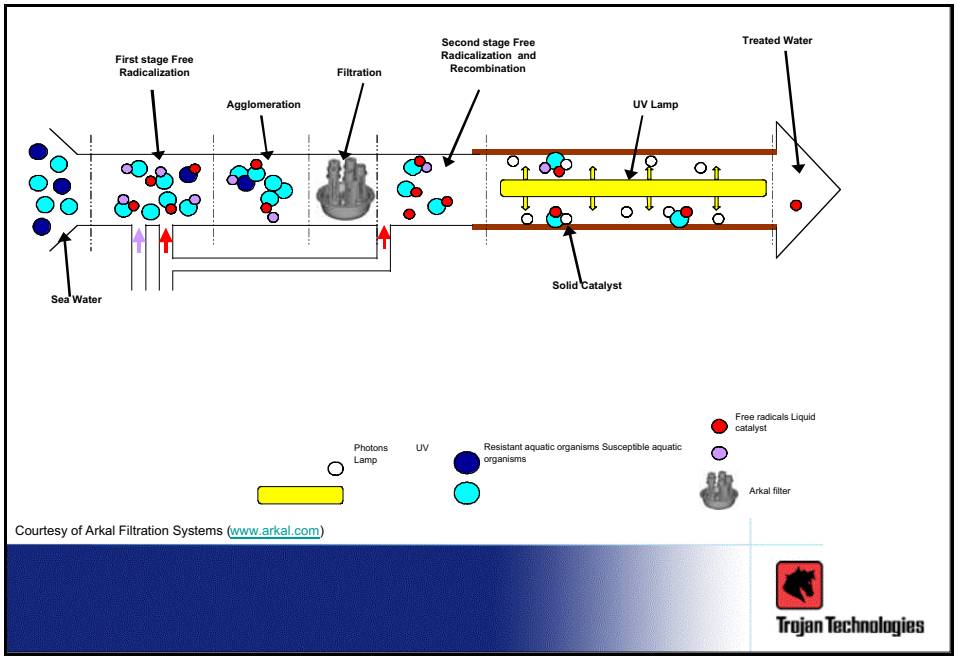


Figure 2. *General view of the process.*

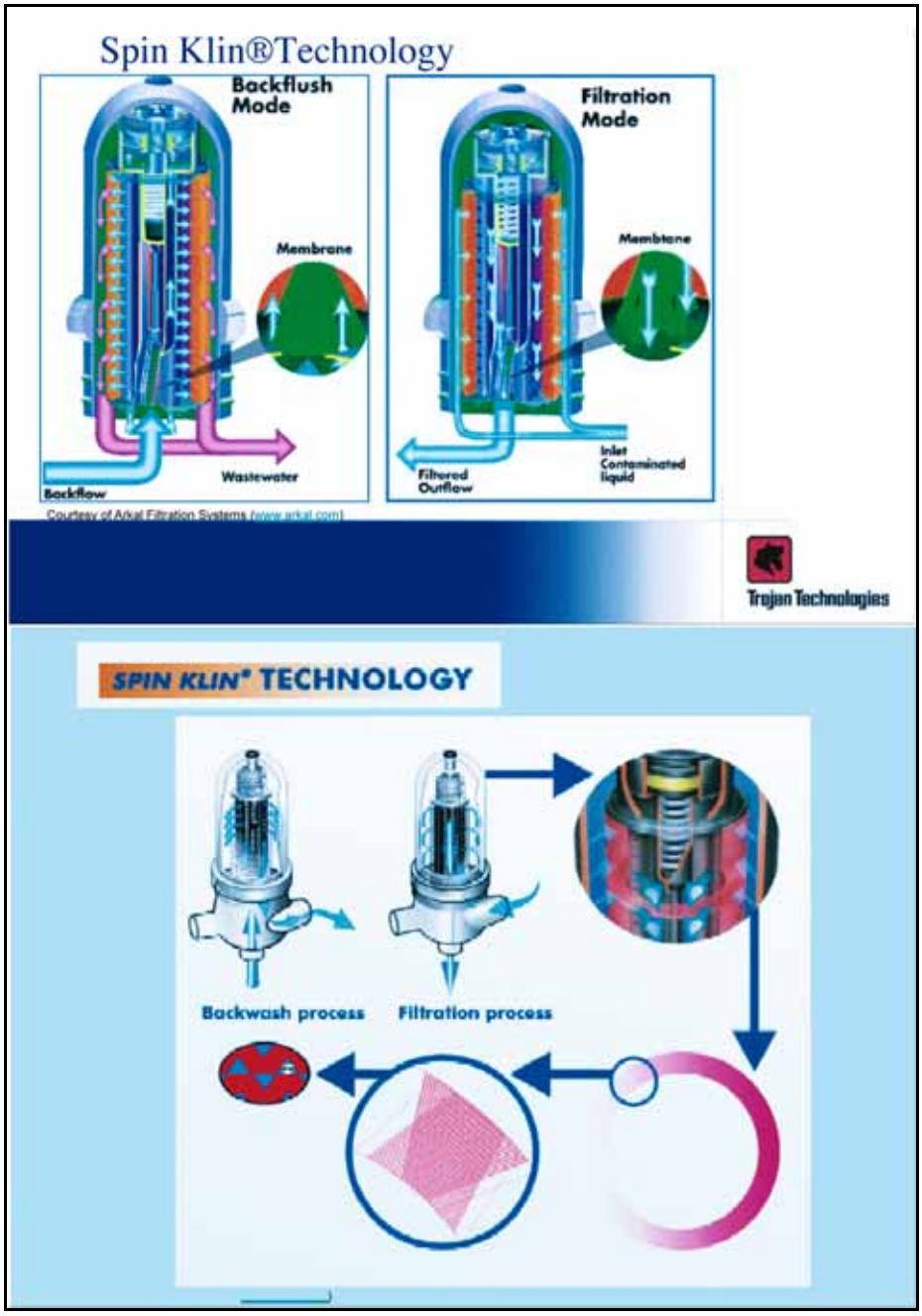


Figure 3. *Modular Backwashable Disk Filter: "Spin-Klin" Filter Technology.*

Figure 4. *Ganging together of modular disk filters.*

Figure 5. *UV technology configurations.*

Using MCDA methods in an application for outranking the ballast water management options

C. F. S. Gomes

CASNAV
(Brazilian Naval Center of System Analysis)
simoes@casnav.mar.mil.br or cfsimoes@fgvmail.br

Abstract

The Multicriteria Analysis Methodology has been developed in order to support and guide decision-makers in the evaluation and selection of alternatives/solutions. In this case, it can be used to evaluate and select ballast water exchange systems and treatment methods.

Introduction

Each individual is endowed with internal information processing and problem-solving capacity, which varies with time. The human hierarchy of values depends on the number of state variables, the human physiological and psychological conditions, social situation, and self-suggested goals.

When a set of Decision Makers (DM) and a set of objectives exist, the multiobjective decision analysis problem needs to obey three parameters[2]:

- MULTIPERIOD – the consequences of a decision are spread over N time periods, with x_t being the consequence x in time period t. For example, x_t may be the cash flow in year t from an investment opportunity. The STABILITY is a MULTIPERIOD interpretation.
- MULTIPERSON – the consequences are spread over N individuals. For example, x_i may be the investor i share of the partnership profit. EQUALITY is a MULTIPERSON interpretation. Decision Making problems that we encounter in the real world are often associated with several individuals or groups whose interests and/or preferences attitudes are different. In those situations, individual preferences should be aggregated.
- MULTIVARIABLE – the consequences are spread over several parts of an organization, over several economic activities, or over several categories of a problem. For example, x_n may be the market share of a product. BALANCE is a multivariable interpretation.

Decision Maker values

We can suggest some questions to help the DM identify their own values:

- What are the feasible alternatives for the decision problem? Can we expand the feasible set?
- What are the goal functions?
- What is the set of criteria?
- What are the consequences of the alternatives?
- How do we reduce uncertantainty and the risk? (A long-lasting consequence of the investment decision creates uncertainties. Ignoring uncertainties results in a severe oversimplification. Uncertainties create an environment in which risk attitudes play an important role)
- How can we rank the preferences?

- Do we have contingence plans for the undesirable consequences?
- Who are the decision actors?
- Who are the people who may change the outcomes of the decision?
- What are the reliable external information sources?
- How do we obtain accurate information from them?
- Are there conflicting interests?

The individual goals are:

- Self survival and security, physiological health (right blood pressure, body temperature and balance of biochemical states), safety and freedom from dangers; right level and quality of air, water, food, heat, clothes, shelter and mobility, acquisition of money and other economic goods.
- Perpetuation of the species: sexual activities, giving birth to the next generation, family love, health and welfare.
- Feeling of self-importance: self-respect ans. self-esteem, esteem and respect from others, power and dominance, recognition, prestige, achievement, creativity, superiority, giving and accepting sympathy and protectiveness.
- Social approval; esteem and respect from others, affiliation, friendship, conformity with a desired group, giving and accepting sympathy and protectiveness; conformity with group ideology, beliefs, attitudes and behaviors.
- Sensed gratification: sexual, visual, smell, taste, tactile etc.
- Cognitive consistency and curiosity: consistency in thought and opinions, exploring ans. acquiring knowledge, truth ans. Religion.
- Self-actualization: the ability to accept and depend on the self, or to rely on one's own standards, to cease identifying with others, to aspire to the "ego-ideal'.

Vind [20] proved that pre-order on a set of functions can be represented by the expect value of a utility function was an independence condition, and a similar result assuming that preferences were defined on a space which could be interpreted as a set of probability measures. Knoblauch[17] prove the nonexistence of representation via lexicographic orders for all preference relations.

Group values

In a group of DM we have:

- The degree of importance of each individual member of the group;
- The values for the attributes of the alternatives for each member of the group; and
- The coefficient vector of the additive utility function of each individual.

The final goal for the group decision making process is to aggregate mutually conflicting individual preferences into a group preferences and to decide an alternative to be chosen by the group. The context of group discussion includes Negotiation [5][6][7][8][9][20][21], which must take into account the following questions:

- Is the habitual domain of a one group able to absorb the habitual domains from other group?
- What are the common interests and the conflicting interests?
- Can we emphasize the common goals to encourage co-operation and reduce competition?

- Can we introduce news players, or change the rules, or can we influence the players in order to change the situation favorable to us?
- Can we form coalition?

Karni and Safra [16] propose Harsanyi´s Theory [20] that exist two preference relations, one representing the individual choice behavior among social-alternatives lotteries and the second representing moral value judgment, being the preference relation of an impartial observer on the set of extended lotteries. Harsanyi[15] assumes that the two preference relations satisfy the axioms of expected utility theory. Karni and Safra[16] proved that the impartial observer's preference relation may be viewed as a fair and reasonable procedure of aggregating individual preferences into a social preference relationship.

The Multicriteria Decision Making Aiding (MCDA) methodology

The literature about MCDA is vast and can be found in, for example, " Vincke, Philippe, 1992, Multicriteria Decision-Aid. Ed. John Wiley & Sons, Inc", and " Roy, Bernard, Bouysson, Denis, 1993, Aide Multiple a la Decision: Methods et cas, Ed. Econômica, France".

The Multicriteria[4] methodology accepts the following basic assumptions:

- complexity of the decision-making process, which involves many parties that define the relevant aspects of such process;
- inherent subjectivity of each party's opinion (value judgement);
- acknowledgement of the limits of objectivity and due consideration of the subjectivity; and
- inaccuracy due to the fact that the problem has not been clearly defined.

An understanding of the relationship between current decisions and future outcomes is crucial for the analysis of economic growth, the role for saving and investment, the properties of asset markets, and other important topics [18].

Considering, for example, the investment decision in a global economic world, with many influences changing the environment, we can assume that:

- Decisions are nonrepetitive;
- The criteria for evaluating the investment alternative are subjective, and they can be defined by the DM; and
- The alternatives can be evaluated by criteria, using a scale; the DM must choice the best scale for each criteria/alternative.

Economic constraints often push us to make difficult choices within a limited budget. This choice is rarely unique [19]. There is no one DM but several decision actors, who can be affect or not by the decision. Multicriteria Analysis is adapted for selection the optima strategy because:

- The actors have a set of tools which permit modeling the decision process;
- Models utilizing probabilities of success, risk, measurements of benefits or utility are helpful to guide the manager, but they only work for a limited number of cases, when the distributions are know; and
- The high number of parameters and the different possibilities for the weights.

We can use many MCDA methods in economics or market, for example:

- Outranking methods: that use concordance index to measures the intensity of the agreement between that average opinions of the group of decision makers, and the discordance index

which measures the intensity of the disagreement between the average opinions of the group of decision makers; and

- Utility Theory and Perspective Theory: one incompleteness market cause price fluctuations in financial markets [3]; or Project finance or project financing involves performing a set of security arrangements to reduce risk in large infra-structural investments [1].

Next, we are going to use the MCDA technique in a problem of the real world. The following section will describe the use of the MCDA as a toll to choose the best ballast water treatment system.

Aims and objectives of the project - example application of the MCDA methodology

Ballast water (BW) treatment options - the problem

The introduction of invasive marine species into new environments by ships' ballast water, attached to ships' hulls and via other vectors has been identified as one of the four greatest threats to the world's oceans. The other three are land-based sources of marine pollution, overexploitation of living marine resources and physical alteration/destruction of marine habitat. Shipping moves over 80% of the world's commodities and transfers approximately 3 to 5 billion tonnes of ballast water internationally each year. A similar volume may also be transferred domestically within countries and regions each year. Ballast water is absolutely essential to the safe and efficient operation of modern merchant ships, providing balance and stability to unloaded ships. However, it may also pose a serious ecological, economic and health threat.

Observation: Ballast is any material used to weight and/or balance an object. One example is the sandbags carried on conventional hot-air balloons, which can be discarded to lighten the balloon's load, allowing it to ascend. Ballast water is therefore water carried by ships to ensure stability, trim and structural integrity. Ships have carried solid ballast, in the form of rocks, sand or metal, for thousands of years. In modern times, ships use water as ballast.

It is estimated that at least 7,000 different species are being carried in ships' ballast tanks around the world (figure 1). The vast majority of marine species carried in ballast water do not survive the journey, as the ballasting and deballasting cycle and the environment inside ballast tanks can be quite hostile to organism survival. Even for those that do survive a voyage and are discharged, the chances of surviving in the new environmental conditions, including predation by and/or competition from native species, are further reduced. However, when all factors are favourable, an introduced species by survive to establish a reproductive population in the host environment, it may even become invasive, out-competing native species and multiplying into pest proportions.

As the situation is becoming more and more serious, the International Maritime Organization (IMO) has sponsored international meetings to determine courses of action to meet this challenge, where the subject is discussed by the IMO member States.

Research methods, test protocols and experimental design - MCDA in the Ballast Water Problem

The system proposed by this paper is based on the algorithm THOR[13], which has been the subject of a presentation given at the Symposium of the International Federation of Operational Research Societies (IFORS), 2002, in Edinburgh from 8 to 13 of July 2002 and 12th Mini-Euro Conference, Bruxelas, 2002 [14]

This paper submits a methodology of outranking ballast water treatment options. A result of the application of this methodology will be the indication, consensually, of the best treatment system.

When applied to group's decisions, the MCDA allows individual preferences (in this case represented by the proposals submitted by IMO Member States) to be combined in such way that it results in a group decision. The THOR[10][11] system, which uses the MCDA, has a module that allows the

group to reach a decision through the exchange of views of the group members, from which the negotiation[15][21] around the acceptable proposals starts (i.e. around the preliminary accepted BW treatment and exchange methods).

The Multicriteria aid helps the decision making process by incorporating the value judgement of the IMO Member States taking into account their preferences and interpreting the procedure as a learning process. Thus, it helps to select the best ballast water exchange and treatment methods.

In order to apply this methodology to the case under consideration, relevant factors have been identified. They are:

- Practicability;
- Biological effectiveness (including pathogens);
- Cost/benefits;
- Time frame within which the standards could be practically implemented;
- Environmental impact of the process' sub-products.

Criteria application

The detailed criteria, referring to the relevant factors identified, for quantitative measuring in association with a nominal scale or description, are reproduced in paragraph ***5.2.2) Questions.*** They are numbered from 1 to 26. Each criteria presented shall be analyzed and represented using quantitative measuring. It can be done by assigning a value in a nominal scale, by a value attributed to a **yes** or **no** answer, or by a description.

For this study the following was adopted:

a) Restriction (veto criterion) – the system to be incorporated or selected shall not present any restrictions unacceptable.

b) All criteria have the same weight.

c) Undesirable outcomes are taken with negative values as well as those that have a negative impact with higher absolute values. According to that:
   - In the items 3, 5, 20-24 and 25, negative values are assigned for the lowest desirable feature;
   - In the items 8 to 13, 17, 18, 19 and 26, where the answers should be either "Yes" or "No", a value of 1 was assigned to a "Yes" answer (desirable) and a value of 0 to a "No" answer (undesirable);
   - In the items 6, 7 and 14, verbal (or nominal) scales associated to a numerical scale have been created for test purposes.

Questions

a) Practicability

a.1) Quantitative Criteria

1 - at what ballast flow rate range is the system applicable? (m^3/hour) (Specify the minimum and maximum flow rate)

2 - what is the ship tonnage that the system can be applied to? (DWT) (Specify the minimum and maximum tonnage)

3 - what is the additional workload on board? (man/hours)

4 - what is the highest sea state (in the Beaufort wind scale) on which the system can operate?

5 - what is the increase in tank's sediment caused by the system? (specify percentage)

*a.2) Questions that need to be answered by a nominal scale, subject to association to a numerical scale of intervals or by a **yes/no** answer*

6 - does the system present any risks to the ship's crew safety or to the crew? (−3, high risk; −2, medium risk; −1, low risk; 0, no risk)

7 - does the system affect the tanks' corrosion rate? (−2, increases the rate; −1, does not increase the rate; 0, reduces the rate)

8 - does the system dispense with the need to keep chemical products on board? (Yes or No).

9 - can the system be used in short voyages (up to 12 h)? (Yes or No)

10 - can the system be operated without complete re-circulation of the ballast water? (Yes or No)

11 - is the system unaffected by incrustation that could lead to a drop in pressure and/or to a reduction in the flow rate? (Yes or No)

12 - is the system being applicable to existing ships? (Yes or No)

13 - are the ship's other functions independent from the system's operation? (Yes or No)

a.3) Questions that require detailed answers

14 - does the system present any occupational hazard to the operator? Describe and quantify. (−3, high; −2, medium; −1, low; 0, no hazard**).**

b) Biological effectiveness (including pathogens)

b.1) Quantitative Criteria

15 - how effective is the system in relation to the removal, elimination and inactivation/neutralization of aquatic organisms, apart from pathogens (according to the various taxonomic groups)? (quantify in terms of percentage, size and/or concentration of organisms)

16 - same as 15 for pathogens.

b.2) Questions for which the answers should be either Yes or No

17 - does the system eliminate cysts?

18 - does the system allow the elimination of organisms when the water enters the tank?

19 - is the system adequate for the elimination of all species or life stages that may present a hazard to the environment?

c) Cost-benefits

c.1) Quantitative Criteria

20 - what is the purchase cost? (US$)

21 - what is the cost of installation? (US$)

22 - what is the operational cost? (US$/ton)

23 - what is the cost variation per ship size? (US$/ton)

24 - what is the increase of fuel or oil consumption that is introduced by the use of this system on board? (Percentage)

d) Time frame within which the standards could be practically implemented

d.1) Quantitative Criteria

25 - within which time frame could the standards be practically implemented? (Months)

e) Impact of the system's sub-products on the environment

e.1) Question for which the answer should be either Yes or No

26 - is the system free from generating sub-products that can have an impact on the environment?

Example of the MCDA application

Table 1 presents an example utilization of this method using three management methods. It is difficult, in the following table, to find out the best management method. This problem becomes even more complicated if we consider that there are several ballast water treatment methods currently being discussed at IMO and not just the three ones used as example.

Table 1. *Criteria and management alternatives.*

Criteria	Management Method 1	Management Method 2	Management Method 3
1	Maximum 15,000 m^3/hour Minimum 100 m^3/hour	Maximum 14,000 m^3/hour Minimum 200 m^3/hour	Maximum 13,000 m^3/hour Minimum 300 m^3/hour
2	Maximum 450,000 DWT Minimum 450 DWT	Maximum 350,000 DWT Minimum 350 DWT	Maximum 250,000 DWT Minimum 450 DWT
3	90 man/hours	80 man/hours	90 man/hours
4	7	8	10
5	10%	12%	5%
6	–1	–2	–3
7	–2	–1	0
8	1	1	0
9	1	1	0
10	1	1	0
11	0	1	1
12	0	1	1
13	0	0	1
14	0	–1	–2
15	93%	92%	90%
16	90%	88%	91%
17	1	0	1
18	1	0	0
19	0	1	1
20	US$ 200,000.00	US$ 210,000.00	US$ 220,000.00
21	US$ 10,000.00	US$ 21,000.00	US$ 1,000.00
22	0.02 US$/ton	0.03 US$/ton	0.04 US$/ton
23	US$ 9	US$ 8	US$ 6
24	3%	8%	1%
25	6 months	8 months	9 months
26	0	1	0

Results (using the software THOR)

It is possible to outrank the worst management methods and identify the best ones applying the THOR[12] methodology to the data from the Table I, as shown in the Figure 2 and 3 further shown.

Using the software THOR (Figure 3), it can be seen that the management method 1 is the best method, slightly better than method 3.

Conclusions and recommendations

In order to apply this methodology to the problem of ballast water, the IMO Member States could consider taking the following steps:

a) Define which criteria will be used to evaluate the management methods. The Committee can, then, decide on the value to be assigned to each criterion and can also define the initial restriction (veto). (We suggest, as a starting point for the discussions on the restriction, that the docking time should not exceed 10% of the time allowed for before the introduction of the system. The same time limit should be observed with regards to the increase in the time of ship's construction. Please note: any system presented for evaluation should have been tested on board, and laboratory tests should not be accepted for this purpose);

b) Stipulate the deadlines for disputing the outcome of the evaluation of the management methods (the outcome shall be disputed by means of a new evaluation carried out by the disputing party);

c) Establish the relative value to be assigned to each evaluation criteria and apply the data obtained through the evaluation of each treatment method to the THOR[14] system and outrank the worst methods.

Based on the above steps one could select the best course of actions based on scientific methodology avoiding taking decisions based on misleading individual preferences expressed by voting.

References

[1] Ballestero, E. 2000. Project Finance: a multi-criteria approach to arbitration, *Journal Of The Operational Research Society*, n 51, pp. 183-197.

[2] Bodily, Samuel E. 1978. "Police sector design incorporating preferences of interest groups for equality and efficiency, *Management Science*, vol. 24, no 12.

[3] Calvet, Laurent E. 2001. Inclopete Markets and Volatility, *Journal of Economic Theory* 98, pp. 295-338.

[4] Gomes, Luiz Flavio Autran Monteiro, Carlos Francisco Simões Gomes & Adiel Teixeira 2002. *Tomada de Decisão Gerencial o Enfoque Multicritério*, Editora Atlas.

[5] Gomes, C. F. S., Gomes, L. F. A. M. 1996. Aplicação da Teoria dos Conjuntos Aproximativos à Modelagem Analítica de Apoio à Negociação, *VIII CLAIO - Latin-Iberian-American Congress on Operations Research and Systems Engineering e XXVIII Simpósio Brasileiro de Pesquisa Operacional (SBPO)*, Rio de Janeiro.

[6] Gomes, C. F. S., Gomes, L. F. A. M., Moreira, A. M. M. 1997. Modelos Analíticos para a Negociação, *XXIX Simpósio Brasileiro de Pesquisa Operacional*, 1997, Salvador.

[7] Gomes, C. F. S., Gomes, L. F. A. M., Moreira, A. M. M *1998 Modelos Analíticos para Negociação. Pesquisa Naval*. Rio de Janeiro, RJ: , v.11, pp.151 - 157.

[8] Gomes, C. F. S., Gomes, L. F. A. M. 1999. *Uma Aplicação de Conjuntos Aproximativos ao Apoio Multicritério à Negociação. Pesquisa Naval*. Rio de Janeiro, RJ: , v.12, p.263 - 270.

[9] Gomes, L. F. A. M. 1991. *Conflito e Negociação no Planejamento Participativo: Uma Formulação de Análise de Decisões com Múltiplos Critérios*; Investigacion Operativa; Vol. 2; No 2; Deciembre pgs 111-119.

[10] Gomes, Carlos Francisco Simões 1999. THOR - Um Algoritmo Híbrido de Apoio Multicritério à Decisão para Processos Decisórios com Alternativas Discretas, tese de doutorado, Engenharia de Produção, Coppe-Ufrj.

[11] Gomes, Carlos Francisco Simões, Gomes, L. F. A. M, Valle, Rogerio A. B 2000. Aplicação do THOR em um Processo de Seleção de Pessoal, *XXXII Simpósio Brasileiro de Pesquisa Operacional*, Viçosa.

[12] Gomes, Carlos Francisco Simões, Gomes, L. F. A. M, Valle, Rogerio A. B2001. Nova Proposta de Aplicação do Apoio Multicritério à Decisão (Algoritmo THOR) em Ordenação de Alternativas*, XI Encontro Nacional dos Estudantes de Engenharia de Produção* - ENEGEP-2001.

[13] Gomes, Carlos Francisco Simões, Gomes, L. F. A. M, Valle, Rogerio A. B. 2002. One Application of Thor in a Process of Personal Evaluation, *The Sixteenth Triennial Conference of The International federation of Operation Research Societies.* , IFORS-2002, Edinburgh.

[14] Gomes, Carlos Francisco Simões, Gomes, L. F. A. M, Valle, Rogerio A. B. 2002. One Application THOR (A Multicriteria Decision Aiding Hybrid Algorithm Applied to the Decision Process with Discrete Alternatives) In: *12th. Mini-Euro Conference, Bruxelas.*

[15] Haranyi, J.C. 2000. *Rational Behaviour and Bargaining Equilibrium in Games and Social Situations.* Cambridge Uni. Press, Cambridge.

[16] Karni, Edi, Safra, Zvi 2000. An extension of a theorem of Von Neumann and Morgenstern with an application to social choice theory, Journal of Mathematical Economics, 34, pp. 315-327.

[17] Knoblauch, Vicki 2000. Lexicographic orders and preference representation, *Journal of Mathematical Economics* 34.

[18] Noussair, Charles, Matheny, Kenneth 2000. An Experimental study of decisions in dynamic optimisation problems, Economic Theory 15, page 389-419. Savage, L. J.*, The foundation of Statistics*, Wiley.

[19] Varlan, E., Paillier, R. Le 1999. Multicriteria Decision making for contract research organisation choice in the pharmaceutical industry, journal of the operation research society, 50, page 943-948.

[20] Vind, K. & von Neumann M. 2000. Preferences, *Journal of Mathematical Economics* 33, pp. 109-122.

[21] Von Neumann, J., Morgenstern, 1944. *The Theory of Games and Economics* 20.

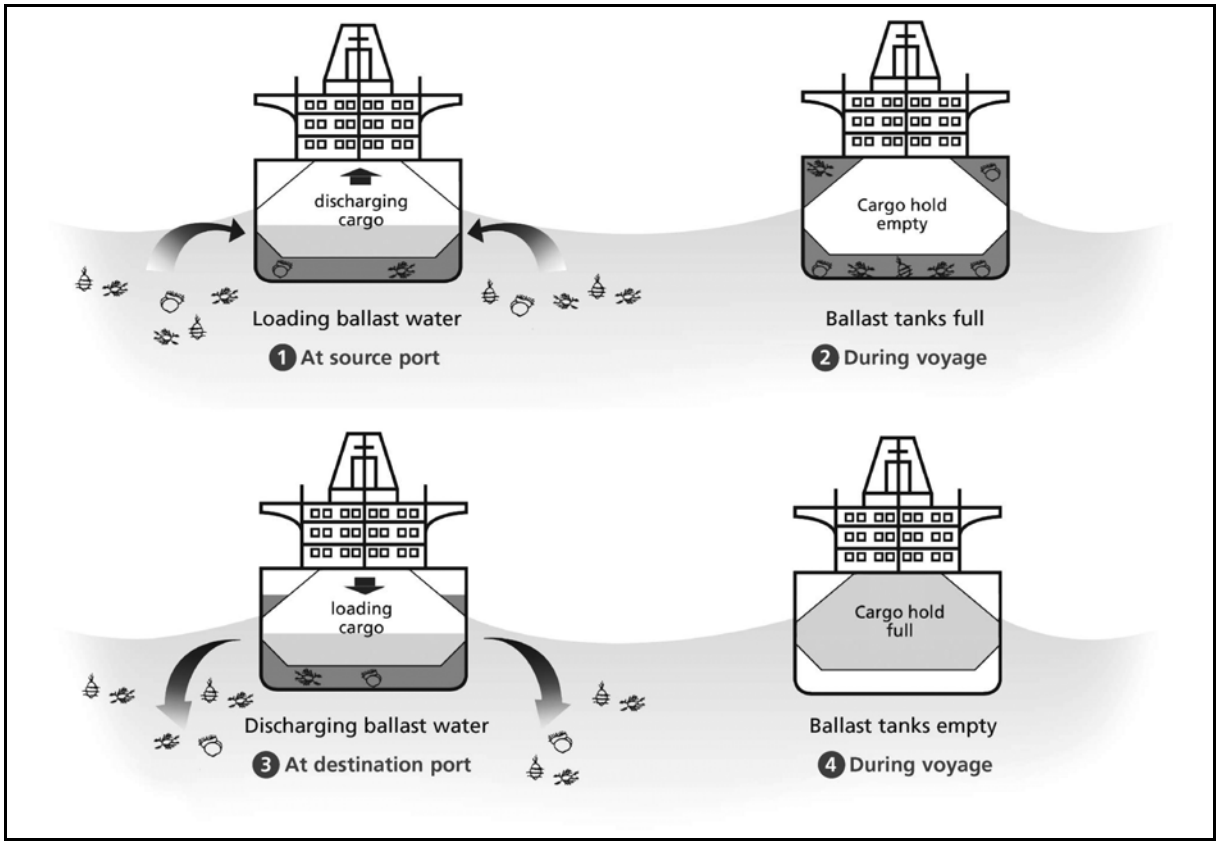


Figure 1. *Ballast water cycle (source: IMO GloBallast).*

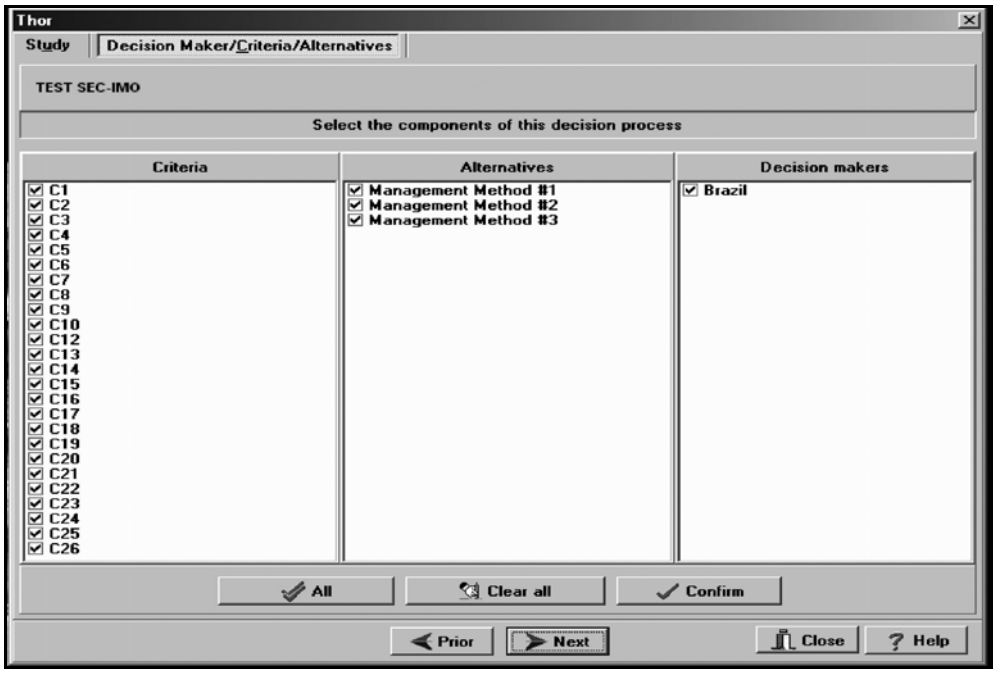


Figure 2. *Criteria and alternatives.*

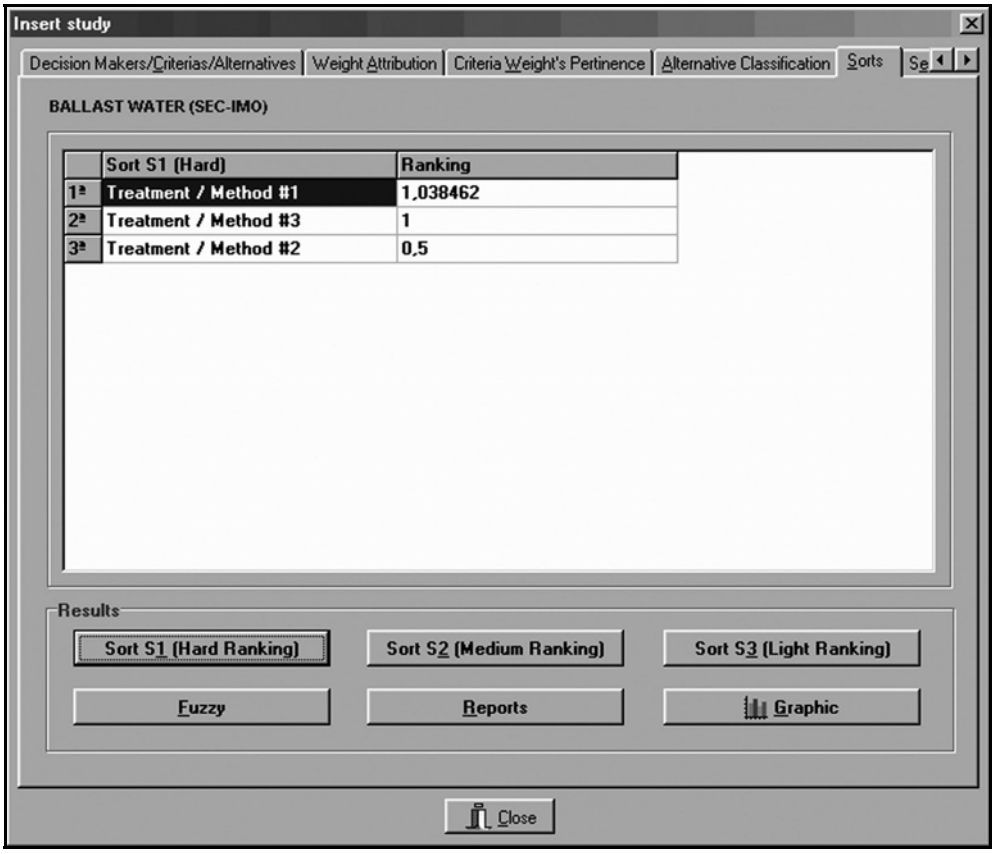


Figure 3. *THOR results.*

The eco-friendly ship of the future

K. V. Subba Rao

Freelance Management and Maritime Teacher, India
maps1711@yahoo.com

Treatment options being researched

This research paper deals with a vision of future ships in 2015 meeting sustainable sea trade and environment needs. Only the aspect dealing with ballast water is included in the subsequent paragraphs. This paper *does not deal with Ballast water treatment* but gives solutions to provide stability in the ballast passage by other means (Figure 1).

By Newton's law namely, Force = Mass × Acceleration, the ballast water contributes to the downward thrust as a mass. In this paper the emphasis is shifted to provide downward thrust and due to gravity, the second variable in the formula (Figure 2).

Lowering centre of gravity

The aim is to lower the centre of gravity of the ship, due to bottom heavy hull design and better hull shape like a submarine (Teardrop shape). This will improve the metacentric height, and righting lever. The double bottom tanks of the hulls will need redesigning before 2015. They will have to be optimised for dynamic ballast stresses, guides for solid ballast of the size of containers. The smooth contours as in silent submarines, will give better engine power to speed ratio (Figure 3).

Hydrodynamic ballast

The vessels presently use seawater as ballast and the water is discharged in the load port. If the sea water is taken from watertight doors in the front and discharged continuously the problem of migration of species will be solved. The downward thrust is proposed to be incorporated by baffles in the flow in double bottom tanks suitably modified in double hulls ships of 2015. The size of DB tanks may have to be increased to lower centre of gravity and redesigned in shape and strength. The free flow technology exists in about 45 metres long catamaran hulls vessels. The watertight doors in the bow and stern will permit continuous Replenish And Overboard (RAO) system of dynamic ballast giving a downward thrust by baffles. The free flow at 14 knots is already present in a submarine design between the pressure hull and casing, so the technology exists for such stresses (Figure 4).

Solid ballast

Solid ballast is already being used in some small ferries. This research paper recommends the double hulls to be suitably redesigned to load Twenty feet containers, with the help of guide rails .The maritime containers are of standardised size suitable for handling in all ports of the world. The ballast weight may be in the shape of containers. A concrete slab in a 20 feet by 8 feet container will be 1/3 in height and can be used solid ballast, in a container or may be bunkers in tanker containers (shown in Figure 5). The proven battery technology in submarines may be adopted in form of TEU size batteries for maritime use and ballast weight

Steering in the vertical plane

This innovation is based on a basic steering servo system; this technology is presently in use to steer the ship in the horizontal plane. The safe ballast draft can be calculated and similar automation can hold the vessel at ballast draft by control surfaces as is done presently in a submarine (Figure 6).

Promulgation of ballast water exchange zones

The promulgation of suitable zones on international sea routes for exchange by sequential or flow through method is recommended. This will restrict the environment degradation to only certain areas; this can be promulgated and marked on navigational charts and in notices, as done in traffic separation schemes (Figure 7).

Timeframe of the project

The time frame has been **worked backwards from 2015** when double hulls come in force:

- 2015 Eco friendly new design ships in trade
- 2010 Commence production of new design ships
- 2007 On completion of successful trials
- 2006 promulgate results of trials on prototype
- 2005 publish the road map if duly approved by IMO in accordance with E 3 (Long Term Plan)
- 2004 commence implementation plan to modify ships as data collection platforms
- 2003 present new ship design to the international maritime community

Aims and objectives of the project

To innovate an Eco friendly ships by 2015 to comply with implementation double hulls, adopting submarine technology and basic Hydrodynamics and known technologies for sustainable Sea transportation vis a vis Environmental Degradation. The ship will be designed using eco-friendly parameters. This includes solar panels for emergency lighting. Batteries as used in submarine propulsion for power supply, to conserve fossil fuel.

Research methods, test protocols and experiments

The research is planned in two phases:

Phase I

Theoretical research for the tacit approval of maritime community of seafarers, owners, and classification society. Only proven technology will be considered for incremental innovation. The specifications are worked on theoretical considerations and mathematical calculations and computer simulations. This phase will need funding from an external agency.

Phase II

Experiments on a prototype in a water tunnel, corrections of defects in hypothesis in Phase I. Commence construction to coincide with implementation of double hulls in 2015. This phase will need funding from an external agency.

Results

The final results of the research depend on successful of PHASE II by about 2007. This research has adopted the normal channel of scientific discovery, propagating a hypothesis, proving it by models/calculations. Trials on a prototype, and finally manufacture of the NEW PRODUCT**.**

Conclusions

The methods of ballast water treatment can be considered as a clean up operation within a ship; other alternative solutions may be found, however, by lowering the centre of gravity by other known technologies. These include:

- Solid ballast in standard 20 feet container size
- Dynamic ballast with baffles
- Steering in the vertical plane

Recommendations

- This project will need the setting of specifications by a central body like IMO.
- It is suitable for long-term implementation of Ballast water management coordinated with double hulls.
- This research can contribute significantly to long term goals of ballast water management and further research should be conducted.
- It recommends a proactive and not reactive approach to the promulgation of legislations in this case.

References

Smith, R. Munroe 1975. *Elements of ship design*. Marine Media Management LTD, London.

Model Ballast Water Management Plan, (1998) International Chamber of Shipping, London.

Ballast Water Newsletters, Global Ballast Water Management Programme, IMO, London.

Derrett D.R. 1967. *Ship Stability for Masters and Mates*. The Maritime Press limited, London.

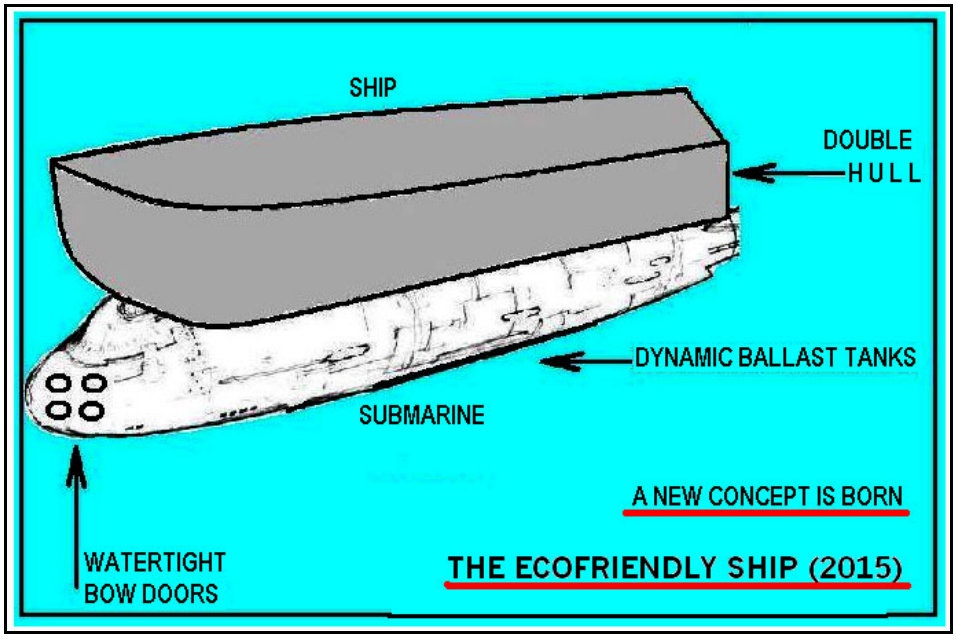


Figure 1. *The eco-friendly ship concept is born as a hybrid from proven technologies used in submarines and surface ships, both suitably modified prior to adoption.*

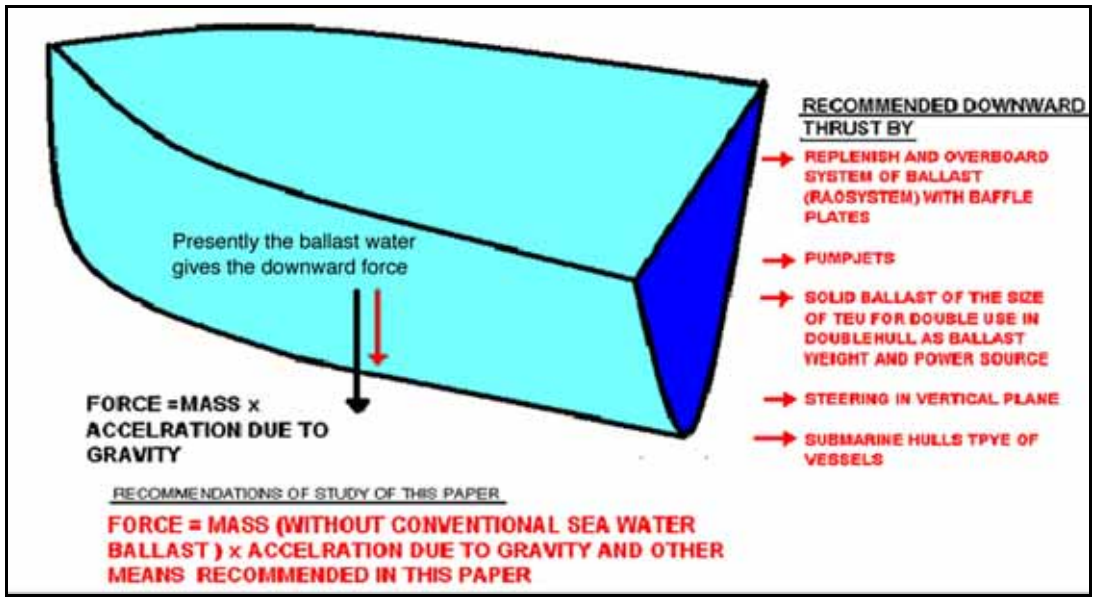


Figure 2. *Various means of creating a downward thrust.*

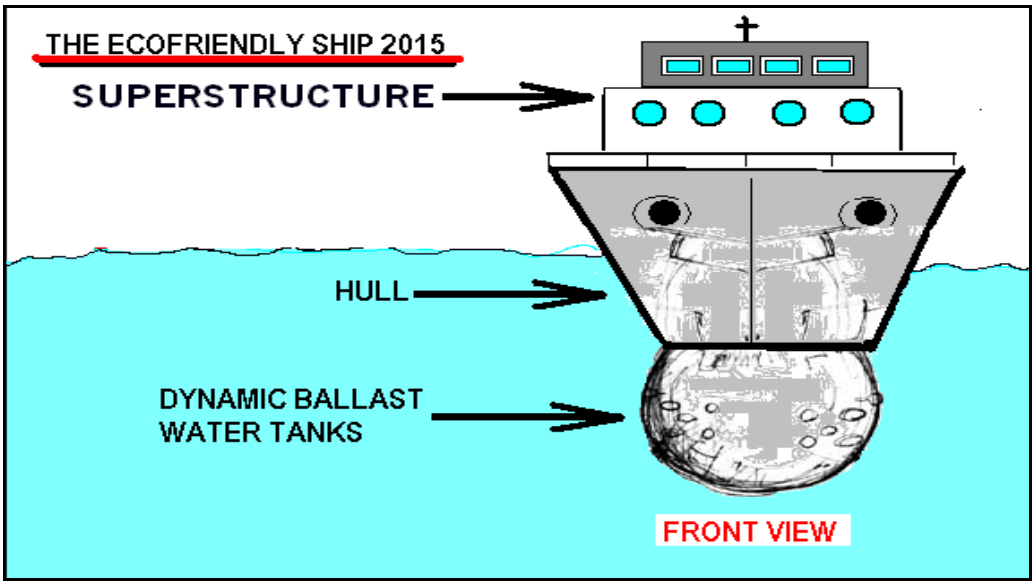


Figure 3. *Front view of the eco-friendly ship – 2015.*

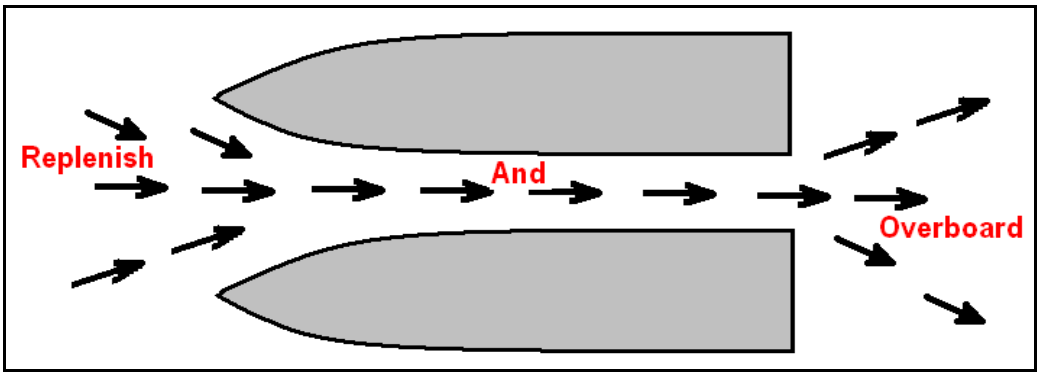


Figure 4. *The hydrodynamic flow in case of small vessels is known for catamaran hulls. The idea for the Replenish And Overboard system (RAO system) is based on hydrodynamic ballast. This idea will have to tested after computer simulations and prototype trials.*

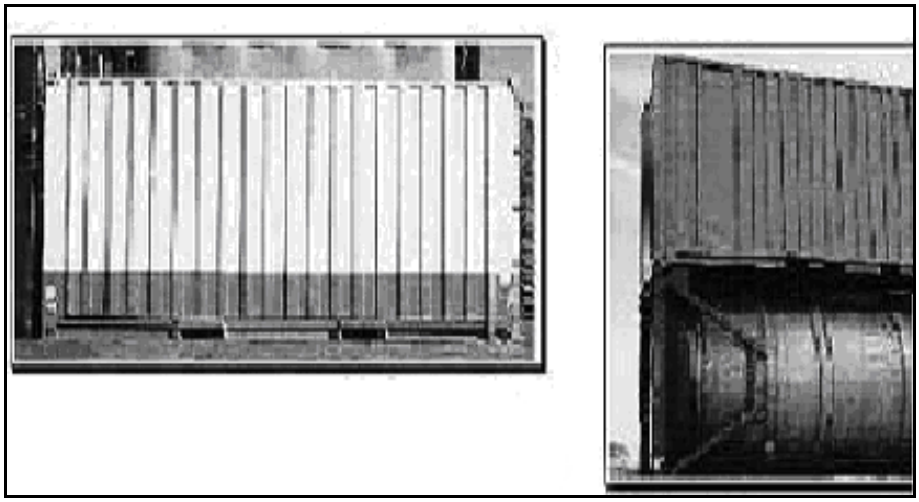


Figure 5. *20 ft standard container (left) atop a 20 ft tank container (right) for bunkers in ballast passage.*

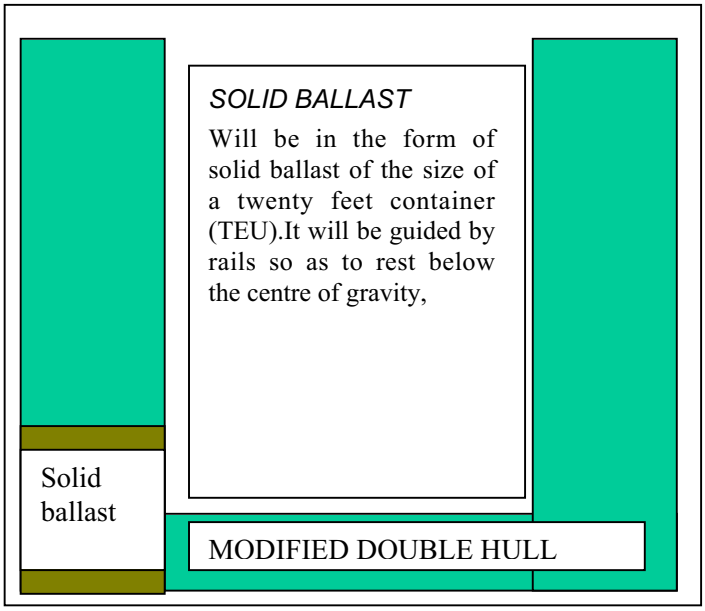


Figure 5a. *Solid ballast.*

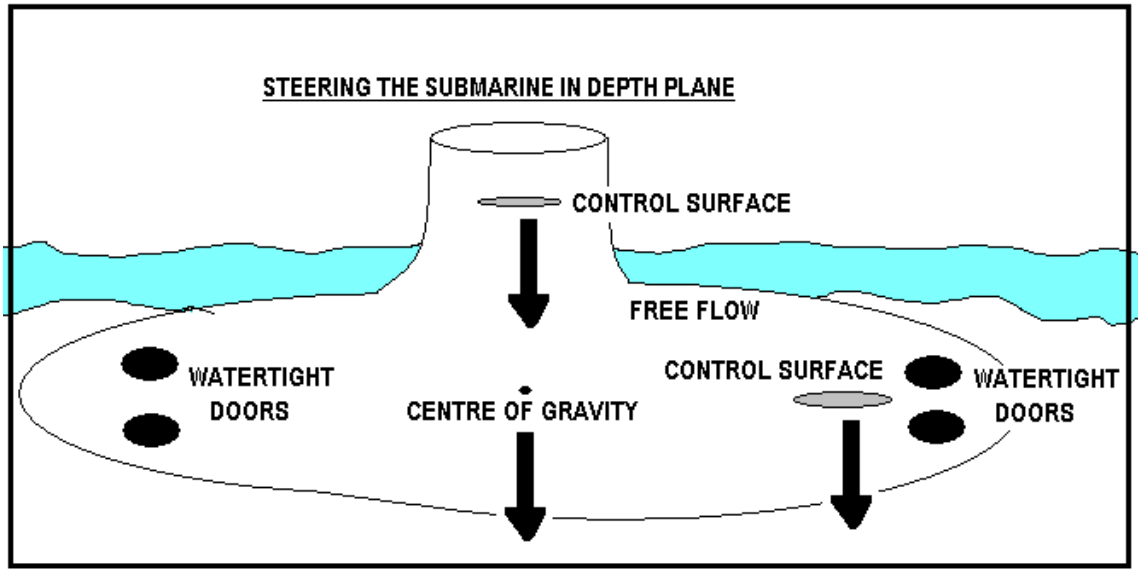


Figure 6. *Steering the submarine in depth plane.*

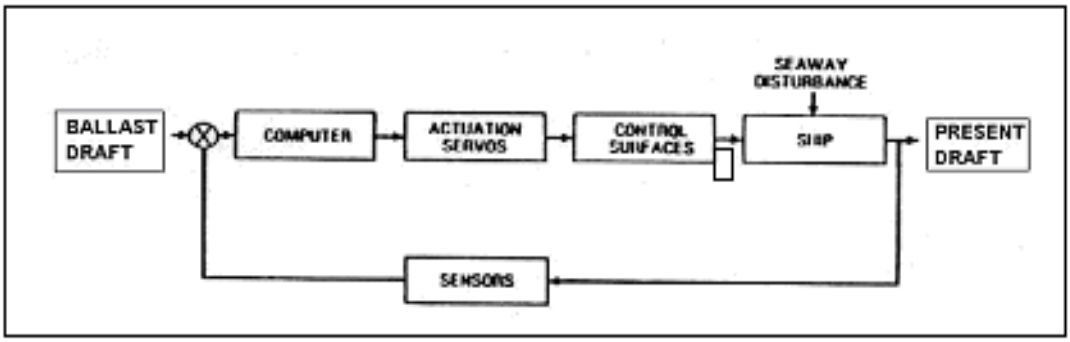


Figure 6a

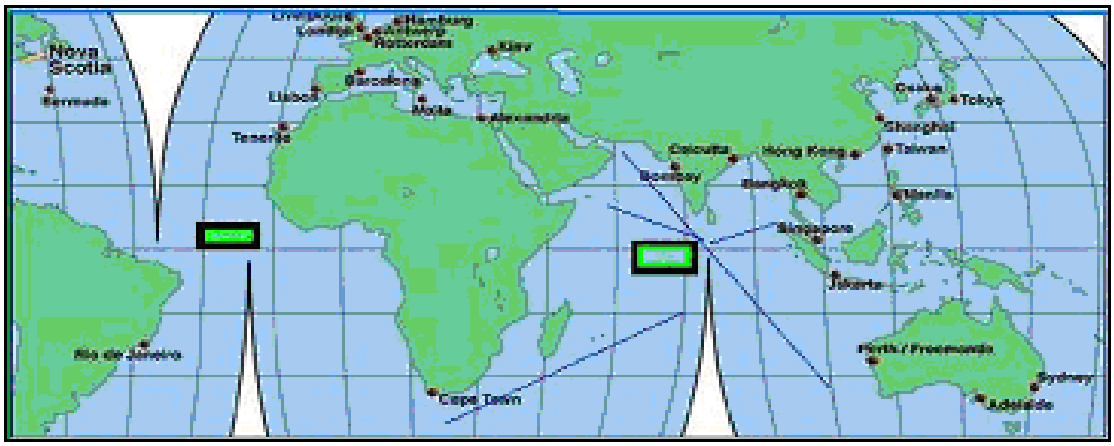


Figure 7. *Propose establishing ballast water exchange areas on ocean passages of the world, to limit the areas of environmental degradation, as a short-term measure.*

Appendix 1:
List of Participants

Mr Adanggiak Akanteyam
Chief Ship Surveyor
Ministry of Ports Harbours & Railways
PO Box M38
Accra
Ghana
Tel: +233 21 671 594
Fax: + 233 21 677702
Email: aakanteyanm@hotmail.com

Mr Aage Andersen
Principal Consultant
DNV
Verigasveien 1
Høvik 1324
Norway
Tel: +47 6757 9900
Fax: +47 6757 9911
Email: Aage.Bjorn.Andersen@dnv.com

Mr Petros Andriotis
MSc Student in Marine & Offshore Engineering
John Moores Liverpool University
Marybone Project
7 Marybone
Liverpool L3 2BX
UK
Tel: +44 (0)7967 140622
Email: enrpandr@livjm.ac.uk

Mr Anatolyi Andryushchenko
Director
Engineering Center 'TRANSZVUK'
Ukraine
Tel: +380 482 220 931
Fax: +380 482 220 401
Email: transsound@paco.net

Mr Arga Chandrashekar Anil
Scientist
National Institute of Oceanography
Dona Paula
Goa 403 004
India
Tel: +91 832 245 6700
Fax: +91 832 245 6702
Email: acanil@darya.nio.org

Dip Ing Jan Arlemark
Managing Director
Ozone Technology
Sallerupsv 152
S212 28 Malmö
Sweden
Tel: +46 40 326660
Fax: +46 40 928990
Email: j.arlemark@ozonetech.se

Dr Graeme Armstrong
General Manager Engineering
Three Quays Marine Services Limited
12-20 Camomile Street
London EC3A 7AS
UK
Tel: +44 (0)20 7929 2299
Fax: +44 (0)20 7929 1650
Email: graeme.armstrong@threequays.com

Dipl Ing Filiz Aslan
Project Manager
Centre for Technology Transfer (ttz)
Bremerhaven
An der Karlstadt 6
Bremerhaven 27568
Germany
Tel: +49 471 9448 714
Fax: +49 471 9448 722
Email: faslan@ttz-bremerhaven.de

Mr Adnan Awad
Country Focal Point Assistant
GloBallast
c/o NBI
Private Bag X7, Claremont
Cape Town 7735
South Africa
Tel: +27 21 799 8815
Fax: +27 21 797 1561
Email: awad@nbict.nbi.ac.za

Mr Harry Barnes-Dabban
Estate & Environment Manager
Ghana Ports and Harbours Authority
Port of Tema
PO Box 488
Tema
Ghana
Tel: +233 22 216473
Fax: +233 22 202812
Email: hbarnes-dabban@ghanaports.net

Dr Michael Barnett
Head of Maritime Research Centre
Southampton Institute
East Park Terrace
Southampton SO14 ORD
UK
Tel: +44 (0)23 80 319790
Fax: +44 (0)23 80 319722
Email: mike.barnett@solent.ac.uk

Dipl Ing Claus Beiersdorfer
Area Manager
Boll & Kirch Filterbau GmbH
Siemensstr 10-14
50170 Kerpen Sindorf
Germany
Tel: +49 2273 562 220
Fax: +49 2273 562 176
Email: claus.beiersdorfer@bollfilter.de

Mr Alec Bilney
Marine Manager
International Chamber of Shipping
12 Carthusian Street
London EC1M 6EZ
UK
Tel: +44 (0)207 417 2856
Fax: +44 (0)207 417 8877
Email: alec.bilney@marisec.org

Lt Cdr Stephen Blackburn
Maritime Waste Management Team Leader
Ministry of Defence
Warship Support Agency
MAES3B #4206
Abbey Wood
Bristol BS34 8JH
UK
Tel: +44 (0)117 913 9041
Fax: +44 (0)117 913 9944
Email: maesiptmaes3b@wsa.dlo.mod.uk

Mr Michel De Blois
Research & Development
Polygo
35 Chemin Royal
St-Laurent Ile d'Orléans-Québec
GOA 3ZO
Canada
Tel: +1 418 828 1588
Fax: +1 418 828 1357
Email: mdtech@qc.aira.com

Ms Bonnie Bonnivier
Manager Acrolein Programs
Baker Petrolite Corporation
5145 Boylan Street
Bakersfield CA 93308
USA
Tel: +1 661 325 4138
Fax: +1 661 323 0879
Email: bonnie.bonnivier@bakerpetrolite.com

Miss Ulrika Borg
Environmental Administrator
Swedish Maritime Administration
Slottsgatan 82
Norrköping SE-601 78
Sweden
Tel: +46 (0)11 191000
Fax: +46 (0)11 23 9934
Email: ulrika.borg@sjofartsverkef.se

Mr Jack Brabban
Project Co-ordination Manager
Teekay Shipping (Canada) Ltd
#2000 Bentau 5
550 Burrard 8
Vancouver BC V6C 2KZ
Canada
Tel: +1 604 609 4758
Fax: +1 604 642 5890
Email: jack.brabban@teekay.com

Mr Leo Brouwer
Head Advisory Group
Royal Haskoning
Hoofdweg 490
PO Box 8520
Rotterdam 3000 AM
The Netherlands
Tel: +31 (0) 10 2865680
Fax: +31 (0) 10 4562312
Email: leo.brouwer@royalhaskoning.com

Mr Robert Brown
Program Development
Naval Research Laboratory
P O Box 1739
Key West FL 33040
USA
Tel: +1 305 293 4220
Fax: +1 305 293 4213

Mr Will Browning
Chief Operations Officer
AquaHabiStat
223 East City Hall Avenue
#200
Norfolk VA 23510
USA
Tel: +1 757 223 7278
Fax: +1 757 965 2419
Email: willbrowning@aquahabisrat.com

Mr Wilson Browning
Chairman
AquaHabiStat
223 East City Hill Avenue
#200
Norfolk VA 23510
USA
Tel: +1 757 223 7278
Fax: +1 757 965 2419
Email: wilsonbrowning@aquahabistat.com

Mr John Butchers
Group Managing Editor
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Email: john.butchers@imarest.org

Dr Calay Calay
Senior Research Fellow
University of Hertfordshire
UK

Mr Robson Calixto de Lima
Adviser
Ministry of Environment
Esplanada dos Ministérios, Bloco B, 8-andar
Sala-831
Brasília - DF
CEP:70068-900
Brazil
Tel: +55 61 344 2256
Fax: +55 61 22 42 466
Email: robson-jose.calixto@mma.gov.br

Dr Michael Champ
President & CEO
ATRP Corporation
7000 Vagabond Drive
Falls Church VA 22042
USA
Tel: +1 703 237 0505
Fax: +1 703 241 1278
Email: machamp@aol.com

Mr Stephen Chapman
Director
Marine Information Limited
Steeplefield
Marlpost Road
Southwater
Horsham RH13 9BZ
UK
Tel: +44 (0)1403 733070
Fax: +44 (0)1403 733165
Email: schapman@marine-info.co.uk

Mr John Chapman-Fortune
Director
Hi Tech Marine Pty Ltd
Nantucket
Lake View Road
Dormans Park
East Grinstead RH19 2LR
UK
Tel: +44 (0)1342 870229
Fax: +44 (0)1342 870307
Email: jcf@htmarine.fsnet.co.uk

Mr Ajoy Chatterjee
Chief Surveyor
The Government of India
Jahaz Bhavna
Walchand Hirachand Marg
Mumbai 100 001
India
Tel: +91 22 2261 1788
Fax: +91 22 2261 3655
Email: cs@dgshipping.com

Miss Christina Chen
Secretary
Panama's Permanent Mission to IMO
40 Hertford Street
London W1Y 7SH
UK
Tel: +44 (0)207 629 6166
Fax: +44 (0)207 629 6366
Email: seastar029@yahoo.com

Mr Krishna Chidambaram
Honorary Editor
Institute of Marine Engineers (India)
38 Second Line Beach
Chennai 600001
India
Tel: +91 44 2522 7265
Fax: +91 44 2522 0080
Email: kc.shipcare@vsnl.com

Mr René Coenen
International Maritime Organization
Marine Environment Division
4 Albert Embankment
London SE1 7SR
UK
Email: rcoenen@imo.org

Miss Sarah Colgan
Customer Service Technologist
Solvay Interox Ltd
PO Box 7
Warrington
Cheshire WA4 6HB
UK
Tel: +44 (0)1925 643514
Fax: +44 (0)1925 643514
Email: sarah.colgan@solvay.com

Mr Martin Cooper
President
Qwater LLC
3901 Airport Freeway
Suite 100
Bedford
Texas 76021
USA
Tel: +1 281 639 3544
Fax: +1 734 758 7296
Email: martin.copper@qwatercorp.com

Mr Hamish Cubitt
Technical Director
Anglo-Eastern Technical Services (UK)
107-115 Milton Street
Glasgow G4 ODN
UK
Tel: +44 (0)141 353 1020
Fax: +44 (0)141 572 1459
Email: hcubitt@angloeasterngroup.com

Dr Stephen Cutler
President
Garnett Inc
240 Nestor Crescent
Roswell GA 30076
USA
Tel: +1 770 552 9895
Email: cutlers1@bellsouth.net

Mr Etai Dagan
Managing Director
Amiad Australia
15 Brisbane Street
Eltham
Australia
Tel: +61 3 9439 3533
Fax: +61 3 9439 1612
Email: etai@amiad.com.au

Mr Patrick Dahl
President
Benrad Marine Technology AB
PO Box 17086
10462 Stockholm
Sweden
Tel: +46 (0)8 772 0588
Fax: +46 (0)8 772 0788
Email: patrick.dahl@benradmarine.com

Mr Dang Kun
Associate Professor
Dalian Maritime University
1 Linghai Road
Dalian 116026
Liaoning Province
People's Republic of China
Tel: +86 (0)411 4729967
Fax: +86 (0)411 4696252
Email: david-dangkun@hotmail.com / dkxeme@dlmu.ed.cn

Mr Matej David
University of Ljubljana
Faculty of Maritime Studies
and Transporation
Pot Pomorscakov 4
Portoroz SI-6320
Slovenia
Tel: +386 5 6767222
Fax: +386 5 6767130
Email: matej.david@fpp.uni-lj.si

Mr Parker Davis
CEO
AquaHabiStat
223 East City Hill Avenue
#200
Norfolk VA 23510
USA
Tel: +1 757 223 7278
Fax: +1 757 965 2419
Email: parkerdavis@aquahabisrat.com

Prof Rodger Dawson
University of Maryland
Chesapeake Biological Laboratory
Box 38
Solomons MD 20688
USA
Tel: +1 410 257 2840
Fax: +1 410 326 7210
Email: rodgerdawson@netzero.com

Miss Tracy Edwards
Offshore Industries Advisor
JNCC
Dunnet House
7 Thistle Place
Aberdeen AB10 1UZ
UK
Tel: +44 (0)1224 655707
Fax: +44 (0)1224 624188
Email: tracy.edwards@jncc.gov.uk

Mr David Eley
President
Cape International
3300 Foster Avenue
Juneau
Alaska 99801
USA
Tel: +1 907 586 2685
Fax: +1 907 586 2692

Mr Brian Elliott
Senior Policy Advisor
Maritime and Coastguard Agency
Bay 2/01
Spring Place
105 Commercial Road
Southampton SO15 1EG
UK
Tel: +44 (0)23 8032 9481
Fax: +44 (0)23 8032 9204
Email: brian_elliott@mcga.gov.uk

Ms Joanne Ellis
Project Manager
SSPA Sweden AB
PO Box 24001
Göteborg SE-40022
Sweden
Tel: +46 31 772 9073
Fax: +46 31 772 9124
Email: joanne.ellis@sspa.se

Mr Han Elskamp
Safety Manager
P&O Nedlloyd
PO Box 240
Rotterdam 3000 DH
The Netherlands
Tel: +31 10 400 6263
Fax: +31 10 400 7315
Email: j.elskamp@ponl.com

Dr Oivind Enger
Business Advisor
Forinnova AS
Thormohlensgate 55
N5008 Bergen
Norway
Tel: +47 55 54 38 42
Fax: +47 55 54 38 99
Email: oivind.enger@forinnova.no

Mrs Suzie Essomba Mbarga
SITEAU
Po Box 2315
Yaounde 237
Cameroon
Tel: +237 223 16 44
Fax: +237 250 52 98

Dr Richard Everett
USCG
2100 2nd Street SW
G-MSO-4 Rm 1601
Washington DC 20593
USA
Tel: +1 202 267 2243
Fax: +1 202 267 4690
Email: reverett@comdt.usc.mil

Dr Horst Felbeck
Professor
Scripps Institution of Oceanography
Marine Biology Division 0202
8750 Biological Grade
University of California
SD La Jolla CA 92093-0202
USA
Tel: +1 858 534 6647
Fax: +1 858 534 7313
Email: hfelbeck@ucsd.edu

Ms Liliana Fernadez
IMO Representative
Panama's Permanent Mission to IMO
40 Hertford Street
London W1Y 7SH
UK
Tel: +44 (0)20 7629 6166
Fax: +44(0)20 7629 6366
Email: l.fernadez@panama.uk.org

Dr Flavio Fernandes
Head of Marine Biology Division
IEAPM - Brazilian Navy
253 Kioto Street
Arraial do Cabo
RJ 28930-000
Brazil
Tel: +55 22 2622 9013
Fax: +55 22 2622 9093
Email: flaviocofe@yahoo.com

Dr Luciano Fernandes
Senior Lecturer
Taxonomy & Ecology of Phytoplankton
Federal University of Paraná (UFPR)
Setor de Ciéncias Biológicas - Botánica - CP 19031
Jardim das Amèricas
Curitiba – Paraná
Brazil
Tel: +55 21 41 36 11 759
Fax: +55 21 41 26 62 042
Email: lff@ufpr.br

Ms Francis Fernandez Estarlich
Research
Southampton Institute
East Park Terrace
Southampton SO14 ORD
UK
Tel: +44 (0)23 80319721
Email: francis.fernandez@solent.ac.uk

Mr Carlton Formby
President
Vitamar LLC
2095 Exeter Road #80
Germantown TN 38138-3919
USA
Tel: +1 901 844 6231
Fax: +1 901 844 6240

Mr Stein Foss
Managing Director
Foss & Varenhed Enterprises AS
PO Box 592
Drammen N-3002
Norway
Tel: +47 32 244220
Fax: +47 32 841395
Email: sfo@fve.no

Mr Richard Fredricks
Vice President
Maritime Solutions Inc
17 Battery Place
Suite 913
New York NY 1004
USA
Tel: +1 212 747 9044
Fax: +1 212 747 9240
Email: rfredricks@maritimesolutionsinc.com

Dr Rainer Fuchs
Senior Manager Enironment Chemistry
Degussa AG
BW-AO-AT
Rodenbacher Chaussee 4
D 63457 Hanau
Germany
Tel: +49 6181 593892
Fax: +49 6181 593311
Email: rainer-g.fuchs@degussa.com

Dr Yasuwo Fukuyo
University of Tokyo
Asian Natural Environmental
Science Center
Yayoi 1-1-1
Bunkyo-ku
Tokyo 113-8659
Japan
Tel: +81 3 5841 2782
Fax: +81 3 5841 8040
Email: ufukuyo@mail.ecc.u-tokyo.ac.jp

Mr Satya Ganti
Sarva Bio Remed LLC
36 South Broad Street
Suite #7
Trenton NJ 8608
USA
Tel: +1 609 6795 4922
Fax: +1 419 710 5831
Email: sales@sarvabioremed.com

Ms Alison Gatland
Administrative Officer
Maritime and Coastguard Agency
Bay 2/01
Spring Place
105 Commercial Road
Southampton SO15 1EG
UK
Tel: +44 (0)23 803 29191
Fax: +44 (0)23 8032 9204
Email: alison_gatland@mcga.gov.uk

Dr Stephen Gollasch
Marine Biologist
GoConsult
Bahrenfelder Street 73a
Hamburg 22765
Germany
Tel: +49 40 3905460
Fax: +49 40 3603094767
Email: sgollasch@aol.com

Prof Primitivo González
Naval Architect
University of A Coruña
Avda 19 de Febrero-Serantes S/N
Ferrol (A Coruña) 15405
Spain
Tel: +34 609 841 668
Fax: +34 981 337401

Ms Kathy Goodrich
Manager Eng/Sci/Tech
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Email: kathy.goodrich@imarest.org

Mr Richard Graber
Consultant
Seaworthy Systems
PO Box 965
Essex CT 06426
USA
Tel: +1 860 767 9061
Fax: +1 860 767 1263
Email: mtoyen@seaworthysys.com

Capt Graham Greensmith
Lloyd's Register of Shipping
71 Fenchurch Street
London EC3 4BS
UK
Tel: +44 (0)1372 813324
Email: graham.greensmith@lr.org

Ms Letitia Greyling
Manager - Environmental Research & Best Practices
National Ports Authority
P O Box 32696
Braamfontein
Johannesburg 2017
South Africa
Tel: +27 11 242 4144
Fax: +27 11 242 4260
Email: LetitiaG@npa.co.za

Mr Tom Gross
Consultant
QWater
3830 Fordham Park
Houston TX 77058
USA
Tel: +1 281 282 0791
Email: tom.gross@shell.com

Mrs Juliana Gunwa
Chief Marine Environment Protection Officer
National Maritime Authority
Number 4 Burma Road
Apapa
Lagos
Nigeria
Tel: +234 1 7757006

Dr Cato ten Hallers-Tjabbes
NIOZ
PO Box 59
1790 AB den Burg
The Netherlands
Tel: +31 222 369 574
Fax: +31 222 319 674
Email: cato@nioz.nl

Dr John Hamer
Maritime Policy & Advice Team Leader
Countryside Council for Wales
Maes y Ffynnow
Penrhos Road
Bangor LL57 2DN
Wales
UK
Tel: +44 (0)1248 385735
Fax: +44 (0)1248 385510
Email: j.hamer@ccw.gov.uk

Mr Shinichi Hanayama
Consultant
Japan NUS Co Ltd
Loop-X Bldg
8F 3-9-15 Kaigan Minato-ku
Tokyo 108-0022
Japan
Tel: +81 3 5440 1852
Fax: +81 3 5440 1870
Email: hanayama@janus.co.jp

Miss Sarah Harden
Senior Events Organiser
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Tel: +44 (0)20 7382 2636
Fax: +44 (0)20 7382 2667
Email: sarah.harden@imarest.org

Mr Ian Harris
Lloyd's Register of Shipping
71 Fenchurch Street
London EC3M
UK

Ms Teresa Hatch
Manager Operations & Environment
Australian Shipowners Association
Level 1
4 Princes Street
Port Melbourne 3207
Australia
Tel: +61 3 9646 0755
Fax: +61 3 9646 2256
Email: teresa.hatch@asa.com.au

Ms Penny Herring
Program Manager
USCG R&D Center
1082 Shennecossett Road
Groton CT 06340
USA
Tel: +1 860 4412868
Fax: +1 860 441 2792
Email: pherring@rdc.uscg.mil

Capt Klaus Hesse
Managing Director
Reederei Hesse GmbH & Co
Garrelsstr 22-24
26789 Leer
Germany
Tel: +49 491 919 3330
Fax: +49 491 919 333 79
Email: info@reederei-hesse.de

Mr David Hill
Engineering Manager
Severn Trent de Nora
1110 Industrial Blvd
Sugar Land TX 77478
USA
Tel: +1 281 274 8473
Fax: +1 281 240 6762
Email: dhill@severntrentdenora.com

Dr Rob Hilliard
Principal Marine Environmental Science
URS
Level 3
Hyatt Centre
20 Terrace Road
East Perth WA 6004
Australia
Tel: +61 8 9326 0246
Fax: +61 8 9221 1639
Email: robert_hilliard@urscorp.com

Mr Steve Hillman
Principal Project Officer ABWTC
James Cook University
CRC Reef Research
Townsville 4811
Australia
Tel: +61 7 4781 4997
Fax: +61 7 47751184
Email: steve.hillman@jcu.edu.au

Capt Geoff Hindmarch
Stephenson Clarke Shipping
Eldon Court
Percy Street
Newcastle Upon Tyne NE99 1TD
UK
Tel: +44 (0)191 232 2184
Fax: +44 (0)191 2603208

Mr Graham Hockley
Director Technical and Corporate Affairs
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Tel: +44 (0)20 7382 2600

Mr Michael Hollmann
UK Correspondent
Deutsche Verkehrszeitung DVZ
167 Milkwood Road
London SE24 OJB
UK
Tel: +44 (0)779 629 26 08
Fax: +49 89 2443 17 669
Email: mphollmann@aol.com

Mr Mike Hunter
Maritime and Coastguard Agency
2/21 Spring Place
105 Commercial Road
Southampton SO15 1EG
UK
Tel: +44 238 0329 199
Fax: +44 2370 329 204
Email: mike_hunter@mcga.gov.uk

Mr Mo Husain
President
MH Systems Inc
10951 Sorrento Valley Road
Suite 2F
San Diego CA 92121
USA
Tel: +1 858 452 1280
Fax: +1 858 452 6035
Email: corporate@mhsystemscorp.com

Dr Dhandayuda Pani Ilangovan
Scientist
National Institute of Oceanography
Dona Paula
Goa
403004
India
Tel: +91 832 245 6700
Fax: +91 832 245 6702

Mr Iver Iversen
Business Development Manager
UNITOR ASA
PO Box 300
Skoyen
N-0213 Oslo
Norway
Tel: +47 22131415
Fax: +47 221 34507
Email: iver.iversen@unitor.com

Mr Robert Jellinggaard
Area Manager
Boll & Kirch Filter Skandinavien
Skovlyoften 26
DK-2840 Holte
Denmark
Tel: + 45 45421200
Fax: +45 45421299

Mr Anders Jelmert
Research Scientist
Institute of Marine Research
Flodevigen
N-4817 His
Norway
Tel: +47 37 05 90 00
Fax: +47 37 05 90 01
Email: anders.jelmert@imr.no

Capt Rajko Jurman
ass. Captain of Port Authority
Port of Rijeka Authority
Riva 1
Rijeka 5100
Croatia
Tel: +385 51 333600
Fax: +385 51 332195
Email: rajko.jurman@portauthority.hr

Capt D Kabanakis
Consultant/Marine Surveyor
Independent Shipping Research
253 Cowley Road
Oxford OX4 1XQ
UK
Tel: +44 (0)1865 243476
Fax: +44 (0)1865 243476
Email: demosk2@aol.com

Mr Claude Kamdem
General Secretary
SITEAU
PO Box 2315
Yaounde 237
Cameroon
Tel: +237 223 16 44
Fax: +237 230 52 98

Mr Nasser Keivan Rad
Marine Environment Senior Expert
Ministry of Roads and Transportation
Ports and Shipping Organization
of the I.R. Iran
751 Enghelab Ave.
Tehran 159966 1464
Islamic Republic of Iran
Tel: +98 21 8809326
Fax: +98 21 8809555
Email: kayvanrad@ir-pso.com

Mrs Sarah Kenny
Project Manager
QinetiQ
Haslar Marine Technology Park
Gosport
Hampshire PO12 2AG
UK
Tel: +44 (0)23 92 33 5129
Fax: +44 (0)23 92 335102
Email: slkenny@qinetiq.com

Dipl Ing Oliver Kerschek
Project Manager
GAUSS mbH
Institute for Environmental
Protection & Safety in Shipping
Werderstr 73
28199 Bremen
Germany
Tel: +49 421 59054850
Fax: +49 421 59054151
Email: gauss@gauss.org

Capt Takeaki Kikuchi
General Manager
The Japan Association of Marine Safety
Marine Pollution Prevention
Research Department
15-16 Toranomon 1-Chome
Minato-ku
Tokyo 105-0001
Japan
Tel: +81 3 3502 3643
Fax: +81 3 3581 6136
Email: kikuchi@oak.ocn.ne.jp

Mr Kim In Soo
Environmental Engineering Course
Korea Maritime University
Bosan
Republic of Korea
Tel: +82 51 410 4416
Fax: +82 51 405 7708

Mr Seiji Kino
Manager
Marine Technology Institute Co Ltd
2269-53 Seto-cho
Imari City
Saga pref 848-0043
Japan
Tel: +81 955 23 2266
Fax: +81 955 23 2223
Email: mti@felco.ne.jp

Mr Edward Kleverlaan
Assistant Director
Environment Australia
GPO Box 787
Canberra ACT 2601
Australia
Tel: +61 2 62741750
Fax: +61 2 62741006
Email: edward.kleverlaan@ea.gov.au

Dip Ing Vojko Kocijan
Expert
Port of Rijeka Authority
Riva 1
Rijeka 51000
Croatia
Tel: +385 51 351123
Fax: + 385 51 213112
Email: vojko.kocijan@ri.hinet.hr

Mr Martin Kondrup
Port Captain
Lauritzen Bulkers A/S
Sankt Annae Plads 28
Copenhagen K 1291
Denmark
Tel: +45 33 96800
Fax: +45 33 96 8305

Dr Ing Anja Kornmüeller
R&D - Manager Ballast Water Treatment
Berkefeld Water Tech/RWO Marine Water Tech
Lückenweg 5
D-29227 Celle
Germany
Tel: +49 5141 803 273
Fax: +49 5141 803 201
Email: a.kornmueller@berkefeld.de

Mr Itay Kreisel
Chief Technologist
ARKAL Filtration Systems
Bet Zera
Jordan Valley 15135
Israel
Tel: +972 4 677 5140
Fax: +972 4 677 5461
Email: itayk@arkal.com

Mr Ian Laing
Senior Scientist
CEFAS
Weymouth Laboratory
The Nothe
Weymouth
Dorset DT4 8UB
UK
Tel: +44 (0)1305 206711
Fax: +44 (0)1305 206601
Email: i.laing@cefas.co.uk

Mr Malcolm Latarche
Editor
Fairplay Solutions
3 Princess Way
Redhill
Surrey RH1 1UP
UK
Tel: +44 (0)1737 379147
Fax: +44 (0)1737 379007
Email: malcolm.latarche@fairplay.co.uk

Mrs Melissa Law
Group Leader
Baker Petrolite
12645 West Airport
Sugarland TX 77478
USA
Tel: +1 281 276 5416
Fax: +1 281 276 5492
Email: Melissa.Law@Bakerpetrolite.com

Capt Bud Leffler
President & CEO
Marine Environmental Partners Inc
3874 Fiscal Court #200
West Palm Beach FL 33404
USA
Tel: +1 561 842 9900
Fax: +1 561 842 9922
Email: Bud@MEPI.net

Mr Tony Leigh
Technical Director
ATG-WILLAND
Enterprise House
Pemberton
Wigan WN5 8AA
UK
Tel: +44 (0)1942 216161
Fax: +44 (0)1942 213131
Email: tony.leigh@atgwilland.com

Mr Edward Lemieux
Naval Research Laboratory
Center for Corrosion Science & Engineering
USA
Tel: +1 305 2934214
Fax: +1 305 293 4213

Mr Sergey Limanchuk
Country Focal Point Assistant
GloBallast
Odessa GloBallast Demonstration Site
Ukraine
Tel: +38 482 219 488
Fax: +38 482 219 483
Email: rabotn@te.net.ua

Prof Olof Lindén
Professor - Marine Environment Management
World Maritime University
Citadellsvägen 29
PO Box 500
SE -201 24 Malmö
Sweden
Tel: +46 40 35 63 30
Fax: +46 40 12 84 42
Email: olof.linden@wmu.se

Mr Keith Lucas
Head
Centre for Corrosion Sea & Engineering
Naval Research Laboratory
4555 Overlook Avenue SW
Washington DC 20375
USA
Tel: +1 202 767 0833
Fax: +1 202 404 3881

Capt Stanislaw Lunkiewicz
Maritime Office Gdynia
10 Chrzanowskiego Str
Gdynia 81-338
Poland
Tel: +48 58 620 5825
Fax: +48 58 620 6743
Email: ios@umgdy.gov.pl

Mr Gordon Mackay
Director
BWM
Birchbeck
Ulgham Grange
Ulgham
Northumberland NE61 3AU
UK
Tel: +44 (0)1670 790 237
Email: bwmacka@btopenworld.com

Mr Thomas Mackey
President
Hyde Marine Inc
28045 Ranney Pkwy
Cleveland OH 44145
USA
Tel: +1 440 871 8000
Fax: +1 440 871 8104
Email: tmackey@hydemarine.com

Mr Rajachandran Madhan
Scientist
National Institute of Oceanography
Dona Paula
Goa 403 004
India
Tel: +91 832 245 6700
Fax: +91 832 245 6702

Dipl Ing Thomas Mann
Senior Engineer
Hamann Wassertechnik GmbH
Brookdamm 6
21217 Seevetal
Germany
Tel: +49 40 769182 16
Fax: +49 10 7690182 28
Email:
thomasmann@hamannwassertechnik.de

Dr Jose Matheickal
Senior Research Scientist
Institute of Environmental Science and Engineering
Nanyang Technological University
Innovation Centre
Block 2 Unit 237
18 Nanyang Drive
Singapore 637723
Tel: +65 6794 1556
Fax: +65 6792 1291
Email: jtmath@ntu.edu.sg

Mr Celso Mauro
Petroleum Chemist
Brazilian Petroleum Company/Research Centre
Avenida Jequitiba 950
21949-900
Brazil
Tel: +55 3865 6659
Fax: +55 3865 6973
Email: celso@cenpes.petrobras.com.br

Ms Tracy McCollin
Plankton Ecologist
FRS Marine Laboratory
PO Box 101
375 Victoria Road
Aberdeen AB11 9DB
UK
Tel: +44 (0)1224 295573
Fax: +44 (0)1224 295511
Email: t.a.mccollin@marlab.ac.uk

Mr William McCracken
Consultant
BMT Fleet Technology
311 Legget Drive
Kanata ON K2K 1Z8
USA
Tel: +1 613 592 2830
Fax: +1 517 241 8133
Email: mccrackw@state.mi.us

Mr Peter McNulty
President
NEI Treatment Systems
900 S. Serrano Avenue
Ste 701
Los Angeles CA 90006
USA
Tel: +1 213 383 5855
Fax: +1 213 383 5755
Email: pmcnulty@nei-marine.com

Dr Husain Mehdi
General Manager
Kinectrics Inc
800 Kipling Avenue
Toronto M8Z 6C4
Canada
Tel: +1 416 207 6987
Fax: +1 416 207 6094
Email: husain.mehdi@kinectrics.com

Capt Virendea Mehta
Managing Director
Sea Scan Marine Services Pvt Ltd
Airport Road
Chicalim
Goa 403711
India
Tel: +91 832 2541244
Fax: +91 832 5642532
Email: scanacad@goatelecom.com

Miss Ioanna Meinetis
Executive
Corner Shipping Company Ltd
66 Sfaktirias Street
Piraeus 18545
Greece
Tel: +30 210 4030078
Fax: +30 210 4080079
Email: info@corner-shipping.gr

Dr Ehsan Mesbahi
Senior Lecturer
University of Newcastle
School of Marine Science
and Technology
Armstrong Building
Newcastle upon Tyne NE1 7RU
UK
Tel: +44 191 222 6723
Email: ehsan.mesbahi@newcastle.ac.uk

Capt William Millar
Liberian Shipowners Council
c/o Stolt-Nielsen
Transportation Group
Schiedam 3100 AE
The Netherlands
Tel: +31 10 409 0827
Fax: +31 10409 0821
Email: wmillar@sntg.com

Mr Samuel Moamissoal Fouma
Engineer
Cameroon Ministry of Mines Water and
Power
PO Box 2315
Yaounde 237
Cameroon
Tel: +237 223 16 44
Fax: +237 230 52 98
Email: siteau@asdep.zzn.com

Ms Fiona Morris
Events Manager
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Email: fiona.morris@imarest.org

Mr Peter Morris
Senior Director
Minerals Council of Australia
216 Northbourne Avenue
Canberra 2603
Australia
Tel: +61 262 79 3600
Fax: +61 262 793699
Email: p.morris@minerlas.org.au

Mr Tom Morris
Manager Environmental Protection
Transport Canada
Tower C, Place de Ville
Marine Safety Division
11th Floor 330 Sparks Street
Ottawa Ontario K1A - ON8
Canada
Tel: +1 613 991 3170
Fax: +1 613 993 9196
Email: morrist@tc.gc.ca

Dr Doug Mountfort
Senior Research Scientist
Cawthron Institute
98 Halifax Street East
Private Bag 2
Nelson
New Zealand
Tel: +64 3 548 2319
Fax: +64 3 546 9464
Email: doug@cawthron.org.nz

Mr Eiichi Muraoka
Assisstant to the Director
Ministry of Land Infrastructure & Transport
Ocean Division Policy Bureau
2-1-3 Kasumigaseki
Chiyoda-ku
Tokyo 100-8918
Japan
Tel: +81 3 5253 8267
Fax: +81 3 5253 1349
Email: fmuraoka-e63m3@mlit.go.jp

Mr Sefa Nawadra
Marine Pollution Adviser
South Pacific Regional Environment Programme
PO Box 240
Apia
Samoa
Tel: +685 21929
Fax: +685 20231
Email: sefanajan@sprep.org.ws

Mr Birgir Nilsen
Optimarin AS
400 Main Street #714
Stamford CT 06901
USA
Tel: +1 203 973 0678
Fax: +1 413 683 3240
Email: bnilsen@optimarin.com

Mr William O'Neil
Secretary-General
International Maritime Organization
4 Albert Embankment
London SE1 7SR
UK
Tel: +44 20 7587 3100
Fax: +44 20 7587 3210
Email: secretary-general@imo.org

Mr Martin O'Reilly
Stantec Consulting
361 Southgate Drive
Guelph ON N2G 2M5
Canada
Tel: +1 519 836 6050
Fax: +1 519 836 2493
Email: moreilly@esg.net

Mr Gerald O'Shaughnessy
Chairman of the Board
The Globe Resources Group
8301 E. 21st Street N. Suite 420
Wichita KS 67206
USA
Tel: +1 316 630 0247
Fax: +1 316 630 0248
Email: clahar@iz.netcom.com

Mr Eugene Pam
Research Student
Liverpool John Moores University
Faculty of Technology &
Environment
Byrom Street
Liverpool L3 3AF
UK
Tel: +44 (0)151 2312028
Email: engepam@livjm.ac.uk

Dr Foroogh Papan
Assistant Professor
Faculty of Science Shahid Chamran
University
I R Iran
Tel: +98 21 88 09 326
Fax: +98 21 88 09 555
Email: papan_p@hotmail.com

Mr Ron Payton
Chief Executive Officer
Qwater LLC
3901 Airport Freeway
Suite 100
Bedford TX 76021
USA
Tel: +1 281 639 3544
Fax: +1 734 758 7296
Email: ron.payton@qwatercorp.com

Mr Todd Payton
Consultant
Corona General Consulting
3901 Airport Freeway
Suite 300
Bedford TX76021
USA
Tel: +1 817 540 9322
Fax: +1 817 545 6598
Email: todd.payton@corona-gc.com

Dr Joseph Penkala
Product Specialist
Baker Petrolite Corporation
12645 West Airport Blvd
Sugar Land TX 77478
USA
Tel: +1 281 276 5674
Fax: +1 281 276 5492
Email: joseph.penkala@bakerpetrolite.com

Mr Tom Perlich
President
Ecochlor Inc
4389 Milner Road
Birmingham AL 35242
USA
Tel: +1 205 980 1131
Email: tperlich@aol.com

Mr David Peters
Managing Director
Wilson Taylor & Co Ltd
23 Green Lane
Dronfield
Sheffield S18 2LL
UK
Tel: +44 (0)1246 290899
Fax: +44 (0)1246 290896
Email: davidpeters@wilson-taylor.co.uk

Mr Yoram Pinner
Applications Engineer
Amiad Filtration Systems
Galil Elyon 1
12335
Israel
Tel: +972 4 6909382
Fax: +972 4 6909602
Email: yoram@amiad.com

Capt Dandu Pughiuc
Chief Technical Adviser
GloBallast Programme
4 Albert Embankment
London SE1 7SR
UK
Tel: +44 (0)20 7587 3247
Fax: +44 (0)20 7587 3261
Email: dpughiuc@imo.org

Miss Gemma Quilez Badia
Researcher
University of Newcastle
School of Marine Science and Technology
Armstrong Building
Newcastle upon Tyne NE1 7RU
UK
Tel: +44 (0)191 222 6723
Fax: +44 (0)191 222 5491

Mr Vladimir Rabotnyov
Head of Information & Analytical Centre for Shipping Safety
State Dept. of Maritime & Inland Water Transport
Ministry of Transport
1, Lanzheronovskaya str.
65026 Odessa
Ukraine
Tel: +38 482 219 488
Fax: +38 482 219 483
Email: rabotn@te.net.ua

Mr Keith Read
Director General
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Email: kfr@imare.org.uk

Dr Gill Reynolds
Principal Environmental Specialist
Lloyd's Register of Shipping
71 Fenchurch Street
London EC3M 4BS
UK
Tel: +44 (0)20 7423 1854
Email: gill.reynolds@lr.org

Eng David Reznik
President
RAZTEK
586 Weddell Drive
Sunnyvale CA 94089
USA
Tel: +1 408 745 1466
Fax: +1 408 734 4420
Email: raztek@aol.com

Dr Geoff Rigby
Director
Reninna Pty Limited
36 Creswell Avenue
Charlestown
New South Wales 2290
Australia
Tel: +61 249430450
Fax: +61 249478938
Email: rigby@mail.com

Mr Georges Robichon
Senior Vice-President & General Counsel
Fednav Limited
1000 de La Gauchetière W
3500 Montreal QC H3B 4W5
Canada
Tel: +1 514 878 6608
Fax: +1 514 878 6687
Email: grobichon@fednav.com

Ms Gail Roderick
ANS Project Manager
USCG R&D Center
1082 Shennecossett Road
Groton CT 06340
USA
Tel: +1 860 441 2658
Fax: +1 860 441 2792
Email: groderick@rdc.uscg.mil

Dipl Ing Hauke Röpell
Eng. Research & Development
Hamann Wassertechnik GmbH
Brookdamm 6
21217 Seevetal
Germany
Tel: +49 40 769182 16
Fax: +49 40 769182 28
Email:
haukeroepel@hamannwassertechnik.de

Prof Tony Roskilly
Chair of Marine Engineering
Newcastle University
Department of Marine Technology
Armstrong Building
Newcastle upon Tyne NE1 7RU
UK
Tel: +44 (0)191 222 5531
Fax: +44 (0)191 222 5532
Email: tony.roskilly@ncl.ac.uk

Capt Ronald Ruzic
Shipping consultant
Polic Kamova 13/I
5100 Rijeka
Croatia
Tel: +385 911702952
Fax: +385 51 216248
Email: 385911702952@vip.hr

Mr Norihide Saho
Chief Researcher
HITACHI Ltd
502 Kanduatsu
Tsuchiura
Ibaraki 300-0013
Japan
Tel: +81 29832 4209
Fax: +81 29832 8229
Email: saho@merl.hitachi.co.jp

Prof Yoel Sasson
Scientific Advisor
The Hebrew University of Jerusalem
Givat Ram Campus
Ross Building
91904 Jerusalem
Israel
Email: ysasson@huji.ac.il

Dr Ahmad Savari
Associate Professor
University of Marine Science and Technology
I R Iran
Tel: +98 63 242 333 21
Fax: +98 21 88 09 555
Email: savari53@yahoo.com

Mr Niv Shimron
Director BWT Division
ARKAL Filtration Systems
Bet Zera
Jordan Valley
15135
Israel
Tel: +972 4 677 5140
Fax: +972 4 6775461
Email: niv@arkal.com

Mrs Anna Shotadze
Deputy Head
Convention Inspection for Protection of the Black Sea
N6 Fuiad Gamsackaqurdiast
Batumi 6019
Georgia
Tel: +995 222 72850
Fax: +995 222 72850
Email: sc@batumi.net

Ms Julieta da Silva
Research
IEAPM
Rua Kioto, 253 - Arraial do Cabo
Rio de Janeiro – RJ, CEP: 28930-000
Brazil
Tel: +55 22 26 22 90 13
Fax: +55 22 26 22 90 93
Email: julieta@mar.com.br

Mr Jonathan Simpson
Assistant Policy Advisor
Maritime and Coastguard Agency
Environmental Quality Branch
Bay2/01, Spring Place
105 Commercial Road
Southampton SO15 1EG
UK
Tel: +44 (0)23 8032 9100
Fax: +44 (0)23 8032 9204
Email: jonathan_simpson@mcga.gov.uk

Ms Asha Singh
Student
University of Plymouth
Drake Circus
Plymouth
Devon P24 8AA
UK
Tel: +44 (0)1752 233005
Fax: +44 (0)1752 232406
Email: asha.singh@plymouth.ac.uk

Dr Geoff Smith
Technology Chief
QinetiQ
Haslar Marine Technology Park
Gosport
Hampshire PO12 2AG
UK
Tel: +44 (0)23 92 33 5438
Fax: +44 (0)23 92 33 5102
Email: gcsmith@qinetiq.com

Mr Glenn Smith
President & CEO
Bell-Smith & Associates
22500 SE 56th Street
Suite 41-300
Issaquah WA 98029
USA
Tel: +1 425 391 6844
Fax: +1 425 391 6844
Email: bellsmith2@msn.com

Mr Scott Smith
Biologist
Washington Dept. of Fish & Wildlife
600 Capitol Way N
Olympia WA 98501-1091
USA
Tel: +1 360 902 2724
Fax: +1 360 902 2845
Email: smithsss@dfw.wa.gov

Mr Danny-Sorek
Business Development Manager
ARKAL Filtration Systems
Bet Zera
Jordan Valley
15135
Israel
Tel: +972 4 6775140
Fax: +972 4 6775140
Email: sorek@arkal.com

Mr Tom Stevens
Manager Federal Programs
NSF International
789 North Dixboro Road
PO Box 130140
Ann Arbor
Michigan
USA
Tel: +1 734 769 5347
Fax: +1 734 769 5195
Email: stevenst@nsf.org

Dipl Ing Sonja Stiglic
Environmental Specialist
Adriatic Pipeline
Ulica Grada Vukovara 14
Zagreb 10000
Croatia
Tel: +385 (0)1 3039 409
Fax: +385 (0)1 3095 482
Email: sonja.stiglic@janaf.hr

Mr David Stocks
BMT Fleet Technology Ltd
311 Legget Drive
Kanata
ON K2K-1Z8
Canada
Tel: +1 613 592 2830
Fax: +1 613 592 4950
Email: dstock@fleetech.com

Mr Kallakuri Subba Rao
Consultant
51 Argent Street
Grays
Essex RM17 6NZ
UK
Tel: +44 (0)1375 385101
Email: maps1711@yahoo.com

Mr Igor Subbofin
Vice President
Fisonie Co
71 Sadovwicheskaya Street
Moscow 115035
Russia
Tel: 70959536356
Fax: 70959536376

Ms Lena Sundquist
Application Manager
Alfa Laval Tumba AB
Hans Stahles väg 14780
Sweden
Tel: +46 8 530 65228
Fax: +46 8 530 34555
Email: lena.sundquist@alfalaval.com

Mr Hirofumi Suzuki
Technical Manager
Mitsui Zosen Europe Limited
14th Floor
St Alphage House
2 Fore Street
London EC2Y 5DA
UK
Tel: +44 (0)20 7588 9277
Fax: +44 (0)20 7726 4359
Email: hirofumi@dial.pipex.com

Mr Chris Swanson
Managing Editor
CQD Journal Inc
123 Columbia Tpke
Ste 104A
Florham Park NJ 07932
USA
Tel: +1 973 377 0085
Fax: +1 973 377 3312
Email: cswanson@cqdjournal.com

Dr Mario Tamburri
Chesapeake Biological Laboratory
One Williams Street
Solomons MD 20688
USA
Tel: +1 410 326 7440
Fax: +1 410 326 7428
Email: tamburri@cbl.umces.edu

Mr Ravi Tandon Surendranath
MSc Student
Southampton Institute
c/o 115A Saint Mary's Street
Southampton SO14 1PF
UK
Tel: +44 (0)7817 958691
Email: 2tandr42@solent.ac.uk

Ir Maurice Tax
General Manager
Bright Spark
Slufter 21
Sneek 8602 DA
The Netherlands
Tel: +31 515 434 370
Fax: +31 515 434 211
Email: m.tax@brightspark.nl

Dr Cato ten Hallers-Tjabbes
Associated Scientist
Royal Netherlands Institute for Sea Research (NIOZ)
P O Box 59
1790 AB Den Burg
The Netherlands
Tel: +31 222 369574
Fax: +31 222 319674
Email: cato@nioz.nl

Mr Glenn Thornton
Managing Director
Hi Tech Marine Pty Ltd
PO Box 215
Cooma NSW 2630
Australia
Tel: +61 2 6452 6850
Fax: +61 2 6452 6520
Email: gthornton@htmarine.com.au

Mr Audun Thorstad
Sales Engineer
VEKOS AS
PO Box 1265
N-3254 Larvik
Norway
Tel: +47 33 14 00 20
Fax: +47 33 14 0030

Mr Sergey Tishkin
President
Fisonic Innovation Company
Sadovniches Kaya Street 71
Moscow 115035
Russia
Tel: +7 0 959536356
Fax: +7 0 959536376
Email: fisonic@fisonic.ru

Mr Frans Tjallingii
Co-ordinator International Affairs
North Sea Directorate
Public Works & Water Management
Ministry of Transport
PO Box 5807
2280 HV Rijswijk
The Netherlands
Tel: +31 (0)70 3366846
Fax: +31 (0)70 3090691
Email: f.j.tjallingii@dnz.rws.minvenw.nl

Mr David Tongue
Marine Adviser
International Chamber of Shipping
12 Carthusian Street
London EC1M 6EZ
UK
Tel: +44 (0)207 417 2862
Fax: +44 (0)207 417 8877
Email: david.tongue@marisec.org

Mr Leif Ivar Tonnessen
Staff Engineer
Statoil ASA
Stavanger N-4035
Norway
Tel: +47 51 996889
Email: litoe@statoil.com

Mr Martin Toyen
President
Seaworthy Systems Inc
PO Box 965
Essex CT 06475
USA
Tel: +1 860 767 9061
Fax: +1 860 767 1263
Email: mtoyen@seaworthysys.com

Miss Simona Trimarchi
Environmental Coordinator
Ports Corporation of Queensland
GPO Box 409
Brisbane QLD 4001
Australia
Tel: +61 7 3224 4344
Fax: +61 7 3224 7234
Email: strimarchi@pcq.com.au

Mr Carl Tullstedt
Project Manager
Benrad Marine Technology AB
PO Box 17086
10462 Stockholm
Sweden
Tel: +46 (0)8 772 0588
Fax: +46 (0)8 772 0788
Email: carl.tullstedt@benradmarine.com

Mr Val Usifoh
Member Governing Board
Joint Maritime Labour Industrial Council
1a Kingsway Road
Ikoyi
Lagos
PO Box 1884 Apapa
Nigeria
Tel: +234 01 545 5950
Fax: +234 01 5455950

Mr André Valois
President
Polygo Inc
1210-505 Cure Poirler est
Longueuil
Quebec J4J 5J2
Canada
Tel: +1 514 994 2909
Fax: +1 450 448 7684
Email: avalois@videotron.ca

Mr Kjell Varenhed
Director of Research & Developement
Foss & Varenhed Enterprises AS
PO Box 592
Drammen N-3002
Norway
Tel: +47 32 244220
Fax: +47 32 841395
Email: kva@fve.no

Mr Meindert Vink
Senior Policy Advisor
Shipping Inspectorate
'S Gravenweg 665
3065 SC Rotterdam
The Netherlands
Tel: +31 10 2668631
Fax: +31 10 2022616
Email: meindert.vink@ivw.nl

Dr Matthias Voigt
Owner
dr. voigt-consulting
Kampstr. 7
24601 Stolpe
Germany
Tel: +49 4326 98737
Fax: +49 4326 98738
Email: m.voigt@drvoigt-consulting.de

Mr Antony Vourdachas
Researcher
University of Newcastle
School of Marine Science and
Technology
Armstrong Building
Newcastle upon Tyne NE1 7RU
UK
Tel: +44 (0)191 222 6723
Fax: +44 (0)191 222 5491

Mr Ian Vroom
Magnetic Hydrodynamic CC Water
Treatment Systems
South Africa
Tel: +27 21 552 0427
Fax: +27 21 552 6346
Email: ian-vroom@mweb.co.za

Capt Masahito Wada
Senior Researcher
The Japan Association of Marine Safety
Marine Pollution Prevention
Research Department
15-16 Toranomon 1-Chome
Minato-ku
Tokyo 105-0001
Japan
Tel: +81 3 3502 3543
Fax: +81 3 3581 6136
Email: m-wada@oak.ocn.ne.jp

Mrs Claire Wainwright
IMarEST
80 Coleman Street
London EC2R 5BJ
UK
Email: claire.wainwright@imarest.org

Dr Thomas Waite
Program Director
National Science Foundation
4201 Wilson Blvd
Arlington VA 22202
USA
Tel: +1 703 292 7499
Email: twaite@nsf.gov

Capt Joris van de Water
Station Manager
Anglo Eastern Ship MAN
126 Dokter van de Perrelei
Borgerhout 2140
Belgium
Tel: +32 3 270 0180
Fax: +32 3 2700181
Email: aesm.ant@angloeastergroup.com

Mr Guy Weladji Monthe
NGO Developer
SITEAU
PO Box 2315
Yaounde 237
Cameroon
Tel: +237 223 16 44
Fax: +237 230 52 98
Email: siteau@asdep.zzn.com

Mr Barry Whitehead
Head of Section - Pumps & Waste Management
Ministry of Defence
Warship Support Agency
MAES3 #4206, Abbey Wood
Bristol BS34 8JH
UK
Tel: +44 (0)117 913 9023
Fax: +44 (0)117 913 9944
Email: maesiptmaes3@wsa.dlo.mod.uk

Mr Tim Wilkins
Environment Manager
Intertanko
38 Street Mary Axe
London EC3A 8BH
UK
Tel: +44 (0)207 623 4311
Fax: +44 (0)207 626 7078
Email: tim-wilkins@intertanko.com

Dr Ed Williams
Technical Director
Ed Williams Consultancy Ltd (EWCL)
24 Birch Close
Killamarsh
Sheffield S21 1FW
UK
Tel: +44 (0)144 3380 140
Fax: +44 (0)114 2280 140
Email: ed@ewcl.co.uk

Mr Michael Wilson
General Manager Fisheries & Forestry Environment
Department of Agriculture Fisheries & Forestry
Edmund Barton Building
Barton ACT
GPO Box 858
Canberra ACT 2601
Australia
Tel: +61 2 6272 4300
Fax: +61 2 6272 4875
Email: michael.wilson@affa.gov.au

Dr David Wright
Professor
University of Maryland
Center for Environmental Studies
Chesapeake Biological Laboratory
P O Box 38
Solomons MD 20688
USA
Tel: +1 410 326 7240
Fax: +1 410 326 7210
Email: wright@cbl.umces.edu

Mr Tetsuya Yamaji
Chief
The Japan Association of Marine Safety
London Research Office
Dexter House
Royal Mint Court
London EC3N 4JR
UK
Tel: +44 (0)207 488 3168
Fax: +44 (0)207 7488 3169
Email: cxq05210@nifty.ne.jp

Dr Vahid Yavari
Country Focal Point Assistant
GloBallast
University of Marine Science and Technology
Islamic Republic of Iran
Tel: +98 21 88 09 326
Fax: +98 21 88 09 555
Email: yavari@ir-pso.com

Mr Yook Keun Hyung
Researcher
Korea Maritime Institute
NFFC B/D 11-6
Shinchun-Dong
Song Pa-Ku
Seoul 138-730
Republic of Korea
Tel: +82 2 2105 2757
Fax: +82 2 2105 2779
Email: ykh690@kmi.re.kr

Mr Katsumi Yoshida
Senior Researcher
The Japan Association of Marine Safety
Marine Pollution Prevention
Research Department
15-16 Toranomon 1-Chome
Minato-ku
Tokyo 105-0001
Japan
Tel: +81 3 3502 3543
Fax: +81 3 3581 6136
Email: yoshida@lasc.co.jp

Ms Zhang Shuohui
Associate Professor
Dalian Maritime University
Dalian, Liaoning Province 116026
People's Republic of China
Tel: +86 411 472 8372
Fax: +86 411 472 8372
Email: ivyou@mail.dlptt.ln.cn

Mr Zhao Dianrong
Country Focal Point Assistant
GloBallast
China Maritime Safety Administration
11 Jianguomennei Ave
Beijing 100736
People's Republic of China
Tel: +86 10 6529 2862
Fax: +86 10 6529 2875
Email: vkdmdzhao@vip.sina.com

Mr Zheng Heping
Deputy Director General
China Maritime Safety Administration
11 Jianguomennej Avenue
Beijing 100736
People's Republic of China
Tel: +86 10 652 92466
Fax: +86 10 652 92245
Email: zhengheping@msa.gov.cn

Mr Nikolaos Zografos
MSc Student
John Moore's University
Naylor Street
Atlantic Point House 103.5
Liverpool L3 6LS
UK
Tel: +44 (0)790 9957639
Email: enrnzogr@livjm.ac.uk

More Information?

Programme Coordination Unit
Global Ballast Water Management Programme
International Maritime Organization
4 Albert Embankment
London SE1 7SR United Kingdom

Tel: +44 (0)20 7587 3247 or 3251
Fax: +44 (0)20 7587 3261
Web: http://globallast.imo.org

Cover designed by Daniel West & Associates, London. Tel (+44) 020 7928 5888 www.dwa.uk.com