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GREAT LAKES SHIPPING, TRADE, AND AQUATIC INVASIVE SPECIES

Ballast Water Treatment Technologies and Their Application for Vessels Entering the Great Lakes via the St. Lawrence Seaway

Prepared for
Committee on the St. Lawrence Seaway:
Options to Eliminate Introduction of Nonindigenous Species into the Great Lakes, Phase 2
Transportation Research Board and Division on Earth and Life Studies

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A review of the current status of ballast water treatment technologies since 1996 when the National Research Council's *Stemming the Tide* was published, and major impediments to the implementation of these technologies on a large scale, are presented. In addition, factors that affect implementation of the technologies on ocean-going vessels transiting in the St. Lawrence Seaway and the Great Lakes are identified. From the survey of peer-reviewed literature, many of the studies have focused on filtration/physical removal systems, biocides (oxidizing and non-oxidizing), or a combination of technologies, most often filtration/physical removal systems followed by organism inactivation via biocides or ultraviolet (UV) light. One major impediment to the implementation of technologies has now been resolved, with the establishment by the International Maritime Organization (IMO) in 2004, of ballast water discharge standards. Also underway is a joint effort by the US Environmental Protection Agency, NSF International, Battelle and the US Coast Guard to develop protocols and identify standard conditions for pilot-scale testing of ballast water treatment technologies. Once these procedures and standard conditions are well-defined and are in place, it is expected that progress on developing ballast water treatment technologies will accelerate. For ocean-going ships operating on the Great Lakes, the unique nature and configuration of vessels transiting the area (e.g., under No Ballast on Board, or NOBOB status), and physical/chemical water characteristics, pose challenges to the effectiveness of certain treatment options. Overall, given the current scientific and engineering knowledge base, and the fact that the Great Lakes serves as a drinking water source for 33 million people, it appears that a treatment technology capable of reliably achieving treatment standards is the most suitable system for ocean-going vessels operating on the Great Lakes. This infers that other often cited criteria such as cost and ease of operation should be secondary considerations for technology selection on these vessels. In addition, focus for effective treatment systems should be shifted to new ships being built for use in the Seaway.

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INTRODUCTION

The purpose of this white paper is to provide guidance to the members of the *National Academies Committee on the St. Lawrence Seaway* regarding the viability of various ballast water treatment technologies. In 1996, when the report on ballast water treatment options (*Stemming the Tide: Controlling Introductions on Nonindigenous Species by Ships' Ballast Water*, National Research Council, 1996) was published, it was noted that no system or practice in use at the time would prevent the introduction of unwanted nonnative aquatic species into port and estuarine waters. Since then, efforts to develop treatment technologies have continued worldwide. The recent issue in 2004 by the International Maritime Organization (IMO) of performance standards for ballast water treatment (IMO, 2004), has stimulated research and development in this arena. Furthermore, the shipbuilding industry appears robust, and it is expected that with a large number of new ships to be built in the near future, opportunities to design and implement effective and innovative ballast water treatment systems will increase substantially. Against this background, the white paper will address three specific objectives, namely to: 1) summarize current status, based on review of technical literature and relevant databases; 2) identify major impediments to implementation of treatment systems in general; and 3) discuss additional factors that affect implementation for ocean-going vessels operating in the Great Lakes.

DISCUSSION

1. Summary of Current Status of Ballast Water Treatment Technologies

To initiate the review of technical literature published since 1996, when ballast water treatment options were discussed in *Stemming the Tide* (National Research Council, 1996), the string "ballast water treatment" was used in several search engines (ISI Web of Science®, OCLC FirstSearch®, and Google Scholar® beta version). After eliminating replicated references, a master list of 234 references was compiled, as of January 2007. Of these references, approximately 25 were on ballast water treatment technologies that appeared in peer-reviewed journals, and 16 were government and institution reports. Approximately half of the references were of conference proceedings, and the rest included peer-reviewed literature on related topics (e.g., invasion biology, risk assessment), patents, news articles and editorials. Other information sources included the International Maritime Organization (IMO) Globallast R&D Directory (http://globallast.imo.org) which listed 66 projects worldwide, and the National Oceanic and Atmospheric Administration (NOAA) website, which listed projects funded under the Ballast Water Technology Demonstration Program from 1995 to 2006 (http://www.oarhq.noaa.gov/sgpr/ballast/project_list96-06.pdf).

From these information sources, an attempt was made to focus mainly on ballast water treatment systems as they appeared in the peer-reviewed literature to minimize bias regarding effectiveness of the technology. In the past, a number of vendors specializing in ballast water treatment systems have disseminated results that were not subjected to the rigorous scientific review process and could not be further substantiated. A scientific audit of four different ballast water treatment systems submitted by vendors was undertaken by the US Coast Guard Research and Development Center (USCG RDC). The resulting report noted that "the test programs lacked controls, sufficient replication, appropriate test protocols, adequate experimental design, and the level of rigor indicative of a scientifically sound test program" (Roderick, 2004). Thus, for purposes of this white paper, the emphasis was on evaluating ballast water treatment technologies that were reported in peer-reviewed journals.

1.1 Most Reported Technologies in the Peer-Reviewed Literature Since 1996

In *Stemming the Tide* (National Research Council, 1996), it was concluded that ballast water treatment options must meet a number of criteria: they must be biologically effective, environmentally acceptable, safe for the crew, and cost effective. Furthermore, the report identified ten candidate technologies for shipboard treatment: filtration systems, oxidizing and nonoxidizing biocides, thermal treatment, electric pulse and pulse plasma techniques, ultraviolet (UV) treatment, acoustic systems, magnetic fields, deoxygenation, biological techniques, and anti-fouling coatings. Of these ten technologies, four were identified that would meet the requirements for safety and effectiveness: filtration, biocides, heat, and electric pulse/pulse plasma systems. Biological treatment and antifouling coatings were not evaluated in any detail. The other systems were considered safe, but did not meet the criterion of effectiveness in treating the wide range of organisms found in ballast water.

Indeed, it appears that the conclusions reached in *Stemming the Tide* (National Research Council, 1996) influenced the direction of subsequent research on ballast water treatment technologies, as most of the current reports in the peer-reviewed literature are focused on filtration/physical separation systems, biocides, or combinations of different technologies, usually filtration/physical treatment followed by organism inactivation via biocides or UV treatment. In addition, these treatment options are currently used to remove or inactivate organisms in other applications, including drinking water, wastewater and biofouling treatment systems, thus much is already known about their biological effectiveness. Most of the research on ballast water treatment technologies has focused on shipboard use of these systems, since it potentially provides more flexibility in the management of ballast water.

1.1.1 Filtration and Physical Separation Systems For the removal of non-indigenous organisms from water, filtration and physical separation systems are perhaps the most environmentally benign, as they do not add any toxic substances (i.e., chemical biocides) to the ballast water. In experiments conducted on a large scale, filtration and physical separation systems were often tested in combination with UV light or the addition of chemical biocides to inactivate organisms (please see Section 1.1.4). Filtration technologies may also be designed to preclude sediments from being entrained in ships' ballast tanks, which would alleviate many of the problems associated with vessels in No Ballast on Board (NOBOB) status (please see Section 3). For optimal use, the treatment system would be applied as water is taken onboard a ship. The material collected by the physical separation systems or filtration media after backwashing would either be discharged in the area where the ballast water is being loaded, or in a less optimal scenario, kept and further treated (i.e., the organisms are inactivated) before disposal.

a. Screens Screens with continuous cleaning have been reported by a number of researchers as being effective in removing particles and organisms from test water. Using water from the Great Lakes at flows of 340 $m^3 h^{-1}$, Parsons and Harkins (2002) noted that both the screen-type and disk-type automatic backwash filter performed consistently, with particle removal efficiencies of over 90 %. Large scale experiments at flows of 340 $m^3 h^{-1}$ using a commercially available, self-cleaning 50 µm screen, showed that this technology removed 60 to 95 % of the ambient zooplankton assemblage of Biscayne Bay, FL (Waite et al., 2003). Scanning electron micrographs of material passed through the screen revealed however, that the screen was not effective in removing particles and organisms that were cylindrical in shape with minimum dimensions < 50 µm (e.g., pennate diatoms). More recently, Velduis et al. (2006) reported that at water flows of 530 $m^3 h^{-1}$, a self-cleaning 50 µm screen alone removed a significant fraction of zooplankton from waters of the Wadden Sea, but not enough to meet the International Maritime Organization (IMO) standard (please see Section 2.2).

b. Hydrocyclones As hydrocyclones have no moving parts, they were considered to be a viable treatment technology for shipboard installation, due to the ease of use, operation and maintenance. A number of large scale studies however, have shown that compared to self-cleaning screens, commercially available units were not effective in removing particles and organisms. Sutherland et al. (2001) found dead and moribund copepods after cyclonic treatment, but low densities and high variances precluded statistical analysis. Phytoplankton species were also not removed to any significant degree. Parsons and Harkins (2002) reported that particle removal performance was more erratic with the hydrocyclone compared to the self-cleaning screen, with an overall particle removal efficiency of 30 %. Waite et al. (2003) found no statistical difference in the amount of ambient bacteria, phytoplankton and zooplankton after treatment with the hydrocyclone alone. Velduis et al. (2006) noted that treatment with the hydrocylone had two different and opposing effects on the removal of the phytoplankton *Phaeocystis globosa*, which forms gelatinous colonies up to 1 cm in diameter, and produces harmful algal blooms: most of the large masses were removed, however, some colonies were disrupted, liberating colony cells which passed as single cells through the subsequent self-cleaning filter also being tested. Although hydrocyclones are used in other applications (e.g., removal of grit from oil in oil extraction operations), they are designed to separate particles according to mass, and are not as effective in removing plankton, which have a small mass and are neutrally buoyant in water.

c. Media Filters Physical separation technologies such as screens and hydrocyclones are limited by the size of particles they can effectively remove continuously, at high water flows as would be encountered in shipboard operations. The studies reviewed above have shown that these technologies will have difficulty in continuously removing particles less than 50 µm in size. Media filtration, however, can remove particles down to 1 µm in size, and have done so in other water treatment processes. In order to use this technology, however, new design parameters must be developed, as the mode of operation of these filters for ballast water treatment is radically different than those used in water treatment plants. Specifically, design relationships must be developed for media filters to involve extremely high unit filter loading rates, short filter runs, and rapid head loss development, in order to be incorporated successfully onboard a ship. New media types and effective size relationships must be investigated and developed to minimize the total weight of filtration material required for given applications.

Recent reports on compressible media (e.g., crumb rubber, made from waste tires) show that this technology may be suitable for potential shipboard installation due to its relatively low density and compact size, which would require less space than conventional media filters (Tang et al., 2006a; 2006b). Compressible media are different from conventional granular media filtration used in water and wastewater treatment in that the elasticity of compressible media allows for compression during filtration and reduces filter media porosity. The media porosity can be adjusted, depending on the amount of compression, and theoretically, particles down to 1 μm may be removed, although at lower flow rates. Because compressible media behaves differently from conventional media filtration, theories and models for the latter are being modified (Valdes and Liang, 2006; Tang et al., 2006a).

Tang et al. (2006b) investigated the removal of turbidity, particles, phytoplankton and zooplankton assemblages from lake water by crumb rubber filtration, and found that up to 70 % of phytoplankton and 45 % of zooplankton of zooplankton were removed, but that effluent organism concentrations exceeded the IMO performance standards. This was likely due to the larger pore size inside the crumb rubber filter bed used. For filter beds packed with 0.66, 1.2, and 1.9 mm (effective size) crumb rubber, the calculated pore sizes were 102, 186, and 294 μm, respectively. Clearly, reducing the crumb rubber media size would enhance organism removal. In addition, compared to conventional granular media filters, crumb rubber filters required less backwash because of the low density of rubber material, and developed lower head loss. Consequently, crumb rubber filters could be run for a longer time or allow a higher filtration rate. Tang et al. (2006b) also calculated that for a ship with ballast flow of 5000 $m^3\ h^{-1}$, the crumb rubber filtration system would require a surface area of 70 m^2 and a depth of 2 m. This size is several times smaller than a typical sand/anthracite filter (200 m^2 and 2 m deep, assuming a typical flux of 24 $m^3\ h^{-1}$ per m^2), and would have a relatively small footprint onboard a vessel. Thus, compressible media is a good candidate for adoption for shipboard applications, provided that enough space is available.

1.1.2 Biocides A number of biocides have been investigated for the removal of potentially invasive organisms from ballast water. To be considered suitable for this purpose, biocides need to be both effective in terms of inactivating organisms, and at the same time, readily degradable or removable in order to limit possible persistence of toxicity in the discharged water. Chattopadhyay et al. (2004) evaluated 32 chemicals in the literature for potential use in ballast water treatment in both marine and freshwater environments, and identified the following as showing "fair to good" biocidal activity against a broad spectrum of organisms: chlorine, chlorine dioxide, hydrogen peroxide, glutaraldehyde, SeaKleen®, Peraclean®, phenol, and cationic surfactants (such as C_{16}-alkyltrimethylammonium chloride). All but two of these biocides, SeaKleen® and phenol, are used to disinfect water systems and their effectiveness on large volumes of water has been well researched. Much of the collected information, however, did not specifically address the use of biocides in ballast water treatment applications, and the authors noted that further evaluation would be necessary prior to adoption for such applications.

Laboratory studies aimed at ballast water treatment (e.g., Sano et al., 2003, 2004, 2005; Faimali et al., 2006; Raikow et al., 2006) have shown various biocides to be effective against a broad taxonomic spectrum, though none were 100 % effective in terms of targeted organisms. For the most part, biocidal effectiveness was reported as LC_{90}, (lethal concentration required to kill 90 % of the population of test organisms), or LD_{50} (lethal dose required to kill 50 % of the population of test organisms) after a set period of time (usually 24 h). It is difficult to evaluate these findings in light of IMO discharge standards, which are based on concentration of organisms within certain size classes. Nevertheless, these studies provide a basis from which future efforts on biocidal effectiveness in the context of IMO regulations, can be carried out.

In addition, for reliable and effective treatment of ballast water with biocides onboard a vessel, biocide dose vs. contact times must be known. In drinking water treatment, for example, water treatment plant operators use established CT values (where C is the residual disinfectant concentration (mg L^{-1}) and T is the time (minutes) that water is in contact with the disinfectant) to meet microbial disinfection profiling and benchmarking provisions of the Federal Surface Water Treatment Rule. CT tables (e.g., US Environmental Protection Agency, 2003) relate CT values to log inactivation of microorganisms under various operating conditions, with different tables for different disinfectants. As the CT value is increased, a greater percentage of microorganisms are inactivated by chemical disinfection. The CT value, and thus the level of microorganism inactivation achieved, can be increased by applying greater doses of the disinfectant or by increasing the time that the water is in contact with the disinfectant. The underlying principle (Chick's Law) has been known for over 100 years, and has allowed water treatment plant operators to reliably and effectively disinfect large volumes of water. Thus, to inactivate unwanted organisms transported by ballast water and to meet the proposed IMO regulations, it is envisioned that CT values and tables could be established for use in this application.

a. Oxidizing Biocides Oxidizing biocides include chlorine, bromine and iodine, and their various halogenated forms, many of which are well recognized and thoroughly studied disinfectants. Among these are inorganic agents such as chlorine dioxide (ClO_2) and hypochlorites (e.g., NaOCl). Other oxidizing biocides include hydrogen peroxide (H_2O_2) and ozone (O_3). Oxidizing biocides are general disinfectants and act by destroying organic structures, such as cell membranes, or nucleic acids.

i. Sodium Hypochlorite Sano et al. (2004) reported that sodium hypochlorite was effective in freshwater against the oligochaete *Lumbricus variegatus* and the cladoceran, *Daphnia magna*. For these two organisms, the LC_{90} at 24 h was less than 5 mg L^{-1}. In contrast, hypochlorite was not as effective against adult zebra mussels, with a 24 h LC_{90} value of 130 mg L^{-1}. The low efficacy was thought to be due to the ability of adult mussels to avoid chlorine exposure by keeping their shell valves closed for an extended period of time.

ii. Hydrogen Peroxide Kuzirian et al. (2001) found that hydrogen peroxide at concentrations of 1, 3 and 10 ppm was lethal to a mixed assemblage of marine plankton (dominated by both planktonic adult and larval stages of benthic crustaceans) taken from waters around Woods Hole, MA. The time for 100 % mortality, indicated when swimming activity stopped and the organisms did not respond to tactile stimuli, ranged between 5 – 35 min, depending on the concentration of H_2O_2 used.

iii. Ozone Laboratory studies with ozone showed that dosages of 9 mg L^{-1} (at pH 7) and 14 mg L^{-1} (at pH 8.2) and 24 h contact time in seawater achieved 4-log inactivation of *Bacillus subtilis* spores, an indicator organism used for biocidally resistant spore-forming organisms in ballast water (Oemcke and van Leeuwen, 2004). A similar experiment using cysts from a marine dinoflagellate, *Amphidinium* sp. showed that high ozone doses of 5 to 11 mg L^{-1}, and up to 6 h of residual contact, were required for a 4-log inactivation of these cysts. The researchers concluded that "ozonation is likely to be a difficult technology to implement for organisms with this ozone requirement in combination with characteristics of ballast tanks, which contain areas of sediments high in detritus and areas of corrosion" (Oemcke and van Leeuwen, 2005).

Larger scale studies using a prototype ozone treatment system installed on a commercial oil tanker, the S/T Tonsina, demonstrated that ozone gas diffused into a ballast tank for 5 and 10 h inactivated up to 99.99 % of the culturable bacteria, > 99 % for dinoflagellates and 96 % for zooplankton (Herwig et al., 2006). Initially, ozone was thought to be the primary disinfection agent, but it subsequently became apparent that bromide in seawater was being converted by ozone to hypobromite ion and hypobromous acid, a less effective, but longer lasting disinfectant. Concerns about the formation of bromoform, a toxic disinfection byproduct produced by the reaction with natural organic matter in the water, were alleviated when the maximum bromoform concentrations were found to be 107 $\mu g\ L^{-1}$. From surveying the literature, the researchers concluded that this level was not expected to adversely affect marine organisms. Herwig et al. (2006) also noted that for effective treatment at large scales, the prototype ozone treatment system needed to be modified to improve ozone distribution in ballast tanks. This is not an insignificant problem as ozone is well known to have very poor diffusion characteristics in water.

Perrins et al. (2006) conducted studies with seawater obtained from Puget Sound, WA, Cape Fear, NC and San Francisco Bay to investigate how seawater characteristics, including organic content and ammonia, affected the amount of ozone required to achieve a desired total residual oxidant (TRO) level and rate of TRO decay. To eliminate the large diversity of organisms that are present in seawater, it was recommended that a minimum TRO concentration of at least 1 mg L^{-1} Br_2 be maintained in ballast tanks for an extended period of time, ideally throughout the length of the voyage. It was also determined that to due to the high organic matter content of San Francisco Bay waters, up to 3 times more ozone would be required to achieve the same TRO levels in Puget Sound and Cape Fear waters. Naturally occurring organic matter and ammonia can rapidly react with total residual oxidants to lower their biocidally effective concentrations. Thus, at least for ozone, chemical characteristics of the source water are of concern in determining the effective dose in the treatment of ballast water.

All the studies reported above for ozone treatment of organisms in seawater indicated that long contact times (hours to days) were required for effective treatment. These results were unexpected, since it is well known that ozone is a powerful oxidant (more so than free chlorine), with its biocidal effects taking place within seconds. Indeed, a rough estimate of contact time calculated from an established CT value for the 3-log inactivation of *Giardia* cysts with ozone (1.9 min mg L^{-1} at 5 °C; US Environmental Protection Agency, 2003) and from a report of an ozone concentration required for 4-log inactivation of marine dinoflagellate cysts (5 mg L^{-1}; Oemcke and van Leeuwen, 2005), indicates that biocidal treatment should have taken place within seconds (1.9 min mg L^{-1} / 5 mg L^{-1} = 0.38 min, or about 23 sec). Although a number of caveats must be taken into consideration (e.g., different species of test organisms) in the above calculation, it nevertheless points to the substantial difference between the contact time experimentally observed and that estimated from established CT values. Clearly, the relationship between biocide concentration vs. contact time for ozone was not applicable in this case, and establishment of CT values for biocides in seawater for the inactivation of marine organisms is needed for reliable and efficient treatment of ballast water.

b. Non-Oxidizing Biocides A number of non-oxidizing, or organic compounds have also been explored for potential use in the treatment of ballast water. These include glutaraldehyde, and commercially marketed agents such as SeaKleen® and Peraclean® Ocean. Non-oxidizing biocides exert their effect by interfering with reproductive, neural, or metabolic functions of organisms. The potential formation of possibly toxic by-products, including those derived from the biocides themselves, has been largely unstudied, and discharge of residuals into receiving waters warrants further investigation. Taken together with the variability in range of efficacy of these biocides, it is clear that much remains to be studied in the assessment of this technology for ballast treatment.

i. Glutaraldehyde Glutaraldehyde is commonly used as a medical disinfectant, and Sano et al. (2003) tested its biocidal efficacy against a number of freshwater test species (e.g., oligochaetes, cladocerans and amphipods). The researchers found that the biocidal effectiveness was variable, depending on the species. Additional experiments with sediments sampled from NOBOB (No Ballast On Board) ships resulted in a recommendation that a concentration of at least 500 mg L^{-1} of glutaraldehyde held for 24 h, would be effective in killing 90 % of organisms. Using this concentration estimate and an assumed treatment volume of 200 metric tons (typical of a ship operating in the Great Lakes), Sano et al. (2003) estimated the cost of treatment on the order of $5,000 per treatment (assuming a cost of about $17 per kg of glutaraldehyde). This cost did not take into account other expenses, including hardware installation, or field testing to show that biocidal concentrations were achieved.

ii. SeaKleen® SeaKleen® (Vitamar, Inc.) is a mixture of naphthoquinone, menadione (also known as Vitamin K_3), and its bisulfite. Laboratory studies have shown SeaKleen® to be effective against a freshwater amphipod, *Hyalella azteca* and an oligochaete, *Lumbriculus variegates*, with an estimated 24 h LC_{90} for these organisms less than 2.5 mg L^{-1} (Sano et al., 2004). Raikow et al. (2006) observed that SeaKleen® was also toxic to eggs of *Brachionus plicatilis* (a marine rotifer), *Daphnia mendotae* (a freshwater cladoceran), and *Artemia* sp. (a marine brine shrimp). *Daphnia* eggs were found to be the least sensitive, with a 24 h LD_{90} of 8.7 mg L^{-1}. Exposure of SeaKleen® to sunlight reduced the toxicity of the compound such that after 72 h of light exposure, SeaKleen® was not biocidally effective.

A related compound, menadione nicotinamide bisulphite (MNB), a biocide derived from alkylated naphthoquinones and a synthetic derivative of Vitamin K, has recently been reported by Faimali et al. (2006) as being highly water soluble and extremely photodegradable, with a half-life of < 6 h. Laboratory efficacy tests performed on a suite of ballast water surrogate organisms (planktonic active and resting stages) from different trophic levels (bacteria, dinoflagellates, green algae, and larvae of crustaceans and mollusks), showed 24 h LC_{50} in the range of 0.11 – 7.62 mg L^{-1}.

iii. Peraclean® Ocean Another commercially available biocide, Peraclean® Ocean (Degussa AG, Germany), has been purported to be effective in the killing of marine organisms. The main bioreactive component is peroxyacetic acid (PAA), with hydrogen peroxide (H_2O_2) as the secondary active ingredient that acts a weak biocide for bacteria. Concentration vs. contact time graphs showed that from an initial Peraclean® Ocean concentration of 150 mg L^{-1}, PAA rapidly decayed within the first 5 h and dropped to nearly to zero within 10 h, while H_2O_2 showed a slower decay, and was still present at 50 h (Veldhuis et al., 2006). In large scale tests, these researchers found that ambient phytoplankton were killed after the addition of Peraclean® Ocean and regrowth did not occur, even after 40 d. Phytoplankton and zooplankton were observed to be instantaneously disrupted. Bacterial growth decreased while H_2O_2 was present, but there was rapid regrowth when H_2O_2 was no longer present. The researchers noted that one limitation of this technology was the need to store chemically treated effluent for at least 6 d before discharge was considered safe, and calculated that an extremely large storage capacity (> 120 m^3) for holding the effluents would be required if the technology was conducted on a full scale (water flows of 530 m^3 h^{-1}).

c) Ultraviolet (UV) Light Ultraviolet treatment is a well-established technology for inactivating microorganisms, and acts by disrupting the DNA within cells, thereby prohibiting their replication. One advantage of UV treatment is that no residuals are formed as in chemical biocide applications. The efficacy of UV treatment, however, is reduced in the presence of turbidity (i.e., as would be encountered in some coastal ports). In addition, inactivation by UV of larger, aquatic organisms appears to be limited. The growth rate and relative abundances of three phytoplankton species were found to decrease after exposure to UV (Sutherland et al., 2001), but at doses of 60 mW sec cm^{-2}, UV treatment did not have a statistically significant effect on the abundance of a natural phytoplankton assemblage (Waite et al., 2003). Furthermore, visual observations of samples taken after UV treatment at that dose showed motile zooplankton in the sample (Waite et al., 2003). Oemcke et al. (2004) tested UV doses of 10 to 350 mW sec cm^{-2} in killing zoospores of a seaweed, a marine bacterium and dinoflagellate cysts, and found that doses of 37.5 to 60 mW sec cm^{-2} were effective in achieving 1 to 2 log kills of the seaweed zoospores and the marine bacterium, respectively. Even after irradiations of up to 1,600 mW sec cm^{-2}, dinoflagellate cysts were still viable, as indicated by hatching of the cysts. UV doses of up to 200 mW sec cm^{-2} were required to kill organisms in the size range of 60 to over 6000 µm, but the researchers note that the UV dose "exceeded the standard bactericidal UV doses by more than six times" (Wright et al., 2006). Thus, for effective UV treatment of ballast water, exceedingly high doses would be required, resulting in unreasonable energy costs.

1.1.3 Other Treatment Technologies The treatment technologies reported below are at an early stage and are not as widely documented in the peer-reviewed literature. These systems do not have the advantage of an extensive scientific and engineering research base as some biocides and filtration/physical separation systems, which are currently used to treat large volumes of water in other applications (e.g., drinking water treatment). In all cases reported below, it is difficult to evaluate the biological effectiveness in light of IMO regulations for ballast water discharge (please see section 2.2), as the research results are reported as percent, and not absolute, numbers of organisms killed.

a. Deoxygenation In shipboard experiments, oxygen was purged from ballast tanks with a continuous supply of nitrogen, demonstrating the engineering feasibility of deoxygenation as a potential ballast water treatment technology (Tamburri et al., 2002). In the laboratory, these researchers exposed three invasive invertebrates (*Ficopomatus enigmaticus*, a polychaete; *Carcinus maenas*, the European green shore crab; and *Dreissena polymorpha,* the zebra mussel) to hypoxic conditions (O_2 levels of 0.8 mg L^{-1}) for 2 – 3 days, and observed that there was 20 % survival of the polychaete and the zebra mussel. This technology would therefore not be a good option for ships with short transit times, but perhaps would be suitable for vessels that would undertake longer, transoceanic voyages.

b. Heat A shipboard experiment, using heated water from the ship's main engine and flushed through a ballast tank on the Bulk Carrier *Iron Whyalla*, was held at sea (Rigby et al., 1999). Microscopic observations of samples taken from heat-treated ballast tanks led the researchers to conclude that heat treatment of ballast water to temperatures of 38 °C for several days was sufficient to destroy all zooplankton and a major portion of the phytoplankton. Although some concerns regarding the effect of higher temperature on ballast tank corrosion were initially raised, the researchers found the effect to be minor.

c. Advanced Oxidation Technologies A pilot-scale experiment for treatment of ships' ballast water was conducted at water flows of 20 tonnes h^{-1} using pulse plasma to generate hydroxyl radicals at a concentration of 24.3 mg L^{-1} (Bai et al., 2005). The researchers reported that when the dissolved hydroxyl concentration was 0.63 mg L^{-1}, the kill efficiencies of bacteria, phytoplankton and protozoans reached 100 % within 2.67 s.

1.1.4 Combinations of Treatment Technologies A few large scale tests (i.e., at water flows of approximately 300 m^3 h^{-1}) have been conducted on the efficacy of several treatment technologies in sequence to remove or destroy the diverse group of organisms present in natural waters. The main idea behind these studies was to initially remove the larger particles and organisms (e.g., zooplankton), while smaller organisms (e.g., bacteria and phytoplankton) that pass through separation technologies are then killed by biocidal treatment. For example, Sutherland et al. (2001) evaluated a cyclonic first stage followed by UV treatment, and observed that invertebrates were dead or moribund after the separation phase (although there were not enough results for statistical analyses), and that "grow out" experiments conducted on phytoplankton showed lowest concentrations and growth rates in those samples subsequently treated with UV. Waite et al. (2003) conducted large scale experiments with Biscayne Bay (FL) water, using either a hydrocyclone or a self-cleaning 50 µm screen as a primary treatment step, followed by secondary UV treatment. Hydrocyclonic separation was found to be ineffective, while the 50 µm screen removed most of the zooplankton. Subsequent UV treatment initially reduced the viable counts of microorganisms, but bacterial regrowth was observed in samples held for 18 h.

In a recent study, Veldhuis et al. (2006) tested a ballast water treatment system with a hydrocyclone, screen and a biocide (Peraclean® Ocean), and found that the resulting treated water complied with IMO regulations for organisms in both size classes. Viitasalo et al. (2005) tested ozonation, UV, ultrasonication and H_2O_2 singly, and in combination on their biocidal efficacy against a natural assemblage of zooplankton from brackish waters, and found that the most effective treatment that met IMO standards was a combination of UV (dose of 140 mW s cm^{-2}) followed by exposure to 15 mg L^{-1} H_2O_2 for 48 h. They nevertheless recommended that to keep the energy costs reasonable, a preliminary physical separation step be in place to remove the larger organisms and particulate matter.

1.2 Other Demonstrations of Ballast Water Treatment Systems

In addition to the peer-reviewed literature reviewed above, a number of demonstrations of ballast water treatment technologies on a large scale have taken place. These demonstrations have been run by commercial interests who may not have had access to the appropriate scientific and/or engineering backgrounds necessary for successful implementation. Indeed, in an audit of ballast water treatment systems put together by vendors, Roderick (2004) summarized that there were "weaknesses in the experimental designs and analyses that made it difficult to draw definitive conclusions about the treatment performance" and that "a determination that any of the systems qualify as acceptable alternatives to ballast water exchange is premature". For completeness, however, some of the demonstrations are mentioned below. These include cyclonic filtration and UV treatment systems placed onboard several passenger vessels in the Princess Cruise Lines (Carnival Corp.) fleet (*Regal Princess, Sea Princess, Star Princess*), and tested at water flows between 200 to 255 m^3 h^{-1}. Similar systems were also placed onboard the container ship *R.J. Pfeiffer* (Matson Navigation Co.) and the parcel tanker *Stolt Aspiration* (NYK Stolt Tankers SA) and tested at water flows of 350 m^3 h^{-1}, and 250 m^3 h^{-1}, respectively. Filtration/UV treatment systems were installed on the cruise ships *Coral Princess* (Carnival Corp.) and the *Celebrity Mercury* (Royal Caribbean Cruises, Ltd.) and tested at water flows of 250 m^3 h^{-1}, and 210 m^3 h^{-1}, respectively. The chemical biocide, SeaKleen® has been tested aboard the double hulled oil tanker, *Seabulk Mariner* (SEACOR Holdings, Inc.). A three-step treatment system (OceanSaver®) consisting of filtration, nitrogen injection and cavitation has been installed on a roll-on, roll-off car carrier *Höegh Trooper* (Leif Höegh & Co., Ltd.).

NOAA has tasked the Volpe Center to conduct scientific audits of experimental ballast water treatment systems funded through the Ballast Water Technology Demonstration Program (please see section 2.1) as a way for the Government to assess full-scale or pilot scale systems tests, either onboard ships or shoreside. The audits will address the following: 1) technical quality of the auditees' projects, in both the engineering and biological treatment aspects; 2) validity of the auditees' experimental claims; and 3) status of the ballast water treatment systems' development, their feasibility for application in the shipboard working environment, and treatment effectiveness of the system in particular, and the technology generally (Dorn Carlson and Melissa Pearson, NOAA, Pers. Comm.) It is hoped that by conducting these audits, research results from such endeavors, which may not appear in the peer-reviewed literature, will also undergo a scientifically rigorous review process. At present, two treatment technologies, ozone injection, and electrolytic sodium hypochlorite generation, are planned to be evaluated.

1.3 Ballast Water Treatment Options Likely to Have Prevented Invasions in the Great Lakes

Of the ballast water treatment options reviewed thus far, a few may have prevented the majority of problematic invasions, had they been in use at the time. The Great Lakes have had several notorious invasions by non-indigenous species, including the zebra mussel (*Dreissena polymorpha)*, quagga mussel (*Dreissena bugensis)*, round goby (*Apollonia melanostomus)*, and most recently (discovered late 2006), bloody red mysid shrimp (*Hemimysis anomala)*. Both the zebra and quagga mussels are usually found in fresh water in salinities up to 1 ‰ (parts per thousand), can reproduce in salinities below 2 to 3 ‰, and are killed by salinities exceeding 6 ‰ (Wright et al., 1996). Thus, ballast water exchange of low salinity ballast water with open ocean water, which has salinities around 35 ‰, would have purged most of the fresh water organisms, and any remaining in the tank should have been killed when the tanks were refilled with seawater. In fact, regulations were enacted in 1993 to effectively require open-ocean ballast exchange for vessels inbound to the Great Lakes with freshwater or brackish water if the water is to be discharged into the lakes (US Coast Guard, 1993), but by that time, these two mussel species had already been introduced into the Great Lakes ecosystem.

One treatment technology that would have removed non-indigenous organisms from ballast water is filtration through new types of efficient and lightweight media. The juvenile stages of the zebra mussel are >200 µm in size, while the adults are 2.5 to 5 cm**;** the eggs of the round goby are about 4.4 mm x 2mm in size, while the adults are 10 to 25 cm; the juveniles of bloody red mysid shrimp are 1.4 mm in length and grow to 25 mm as adults (US Geological

Survey, 2007). Routine water treatment media (sand) filters are able to remove particles as small as one µm in diameter. In addition to avoiding the biocide residual discharge problem, filtration can theoretically remove all settleable material from ballast, keeping ballast tanks free of sediments. This reduces maintenance onboard vessels, as well as precluding sediments and associated organisms from posing a risk on NOBOB status ships.

2. Major Impediments to Implementation of Ballast Water Treatment Systems

At present, major barriers still exist in scaling treatment technologies to deal effectively with the huge quantities of ballast water (e.g., about 6,000 tonnes of ballast water on a 25,000 DWT bulk carrier plying the Seaway). There is still a substantial knowledge gap between lab- and pilot-scale studies, and full-scale, shipboard operations. Furthermore, research on engineering and operation parameters required for a given technology to function reliably on board a ship, is minimal or non-existent. Parsons (2003) discussed various ballast system design issues that must be considered in the selection and design of a treatment system on a typical Seaway size bulk carrier using 2000 $m^3 h^{-1}$ main ballast pumps, but since this report was published before the performance standards proposed by the International Maritime Organization (please see below for further discussion) it is difficult to evaluate in the context of the proposed standards.

2.1 Research Funding

In the absence of a major industry-wide effort and resources to develop ballast water treatment technologies, funding for research in this area has been limited, and has been primarily from the Ballast Water Technology Demonstration Program (BWTDP) run jointly by the National Oceanic and Atmospheric Service (NOAA), US Fish and Wildlife Service (FWS) and the US Maritime Administration (MARAD). The program supports projects to develop, test, and demonstrate technologies that treat ships' ballast water in order to reduce the threat of introduction of aquatic invasive species to US waters through the discharge of ballast water. The program objectives support NOAA's mission support goal of: "Ecosystems - Protect, Restore, and Manage Use of Coastal and Ocean Resources through Ecosystem-Based Management", and NOAA's Commerce and Transportation mission support goal of: "Support the Nation's Commerce with Information for Safe, Efficient and Environmentally Sound Transportation". NOAA funding is from Congressional earmarks, sometimes with directives on how the program funding should be spent (e.g., focus on ballast water treatment for waters of the Great Lakes or the Chesapeake Bay region).

Starting in 1998, and through 2005, the BWTDP has funded 54 proposals for total of US $11.8 million, with the following breakdown: $10.2 million from NOAA, $1.6 million from FWS, and MARAD contributing the use of its vessels. An additional $3.5 million was generated in matching funds. For 2007, the estimated total program funding is $1.5 million, with an award ceiling of $200,000. It is expected that eight awards will be made with this funding. The program is fairly diverse in scope and funds activities other than research and development of treatment technologies *per se*. Awards have been made for related projects such as a feasibility study of a treatment technology development site, an outreach campaign for ballast water best management practices, monitoring and verification technologies, and technology assessment methodologies (Dorn Carlson and Melissa Pearson, NOAA, Pers. Comm.). It is hoped that research results generated since 2004 (please see below for further discussion) will soon widely appear in the peer-reviewed literature, with an emphasis on meeting ballast water treatment goals proposed by the International Maritime Organization.

2.2 International Maritime Organization (IMO) Convention for the Control and Management of Ships' Ballast Water and Sediment

After more than a decade of discussion, negotiation and input from various stakeholders, the International Maritime Organization (IMO) promulgated in February, 2004, a set of proposed regulations for ballast water management practices. In the absence of such standards, the development of ballast water technologies was greatly impeded, due to the uncertainty of ballast water discharge conditions that needed to be met by a particular treatment practice. The proposed regulations state that until 2009, empty-refill or flow-through ballast water exchange (BWE) will be allowed as the main practice for ballast water management. After this time, and between 2014 and 2016, a performance standard for ballast water treatment technologies will need to be met such that the practice of ships loading or discharging untreated ballast water will be eliminated. The standard requires less than 10 viable organisms per cubic meter of minimum dimension greater than 50 µm, less than 10 viable organisms per milliliter of organisms between 10 and 50 µm in size, and specific standards for indicator bacteria and *Vibrio cholerae*. The setting of these proposed regulations is perhaps the most important driving force for ballast water treatment technology research worldwide, and it is expected that development and implementation of these systems will now proceed at a greatly accelerated rate.

In the US, a joint effort is underway by the US EPA, NSF International, Battelle and USCG to develop a protocol for pilot-scale testing of ballast water treatment technologies (Hunt et al., 2005). In order to verify the effectiveness of a treatment system under the Environmental Technology Verification (ETV) Program, it is proposed to test the technologies using standardized protocols and under well-defined conditions. Some of the challenge conditions that are being defined are water quality (e.g., salinity, temperature, and levels of dissolved organic carbon, particulate organic matter, and mineral matter), hydraulic conditions (must be capable of handling flows of 300 $m^3 h^{-1}$), and surrogate species to be used for biological testing (i.e., fresh and marine bacteria, zooplankton and protists). In addition, efforts to delineate sampling design are also underway. Although much progress has been made, until these protocols and standard conditions are better defined and are in place, development and implementation of ballast water treatment systems in the US will be impeded.

2.3 Adaptation of Treatment Technologies to Existing Ships

Another major impediment to the implementation of ballast water treatment technologies is the engineering challenges involved in redesigning and modifying technologies developed on land for shipboard use. Perhaps the greatest limitation is space on board a vessel, but power use, controls and piping must also be considered, and these are difficult, complex issues. Given the different configurations and remaining lifetimes of existing ships, retrofitting existing vessels with ballast water treatment technologies may not be cost-effective, and shipowners may not have an economic incentive to implement these technologies.

As older vessels are retired, new ships (new-builds) will be commissioned and designed to accommodate effective ballast water treatment technologies. According to a market report on *Shipbuilding and Repair* (Thomson Gale, 2006), orders for containerships as of May 2005 rose nearly 70 % over the previous year, due to increased trade in the Asia Pacific region. South Korea, Japan and China are the chief shipbuilding nations, with South Korea, the world's current shipbuilding leader, receiving orders for 159 ships from 26 countries during the first quarter of 2004 – up 31 % from the same period in 2003. By the end of 2004, there was a backlog of 847 vessels. In addition, China is investing billions of dollars to reach its goal of becoming the world's shipbuilding leader by 2015. These market conditions indicate that the shipbuilding industry is robust, and with infusion of new capital and recognition that IMO performance standards will need to be met, it is expected that in any new ships being built, ballast water treatment systems will be incorporated in the design. This means that previous engineering design challenges for existing ships (e.g., space, power, piping, etc.) will no longer be an issue, thus making way for innovative designs for effective ballast water treatment systems on new-builds.

3. Additional Factors Specific to the Great Lakes

Transport via ships, of various commodities to and from the ports in the St. Lawrence Seaway and the Great Lakes to other areas worldwide, has been essential for the economic development of the US during most of the 20th century. Because of this shipping activity, the Great Lakes ecosystem has also been the unfortunate recipient of non-indigenous aquatic species via discharge of ballast water from ocean-going ships carrying cargo from elsewhere. In order to prevent future invasions, effective ballast water management practices, and in particular, treatment systems, must be in place. The uniqueness of the Great Lakes, however, poses some technical challenges, and specific issues need to be considered for effective treatment of ballast discharge from ocean-going vessels transiting the area.

First of all, the Great Lakes basin is a freshwater system that supplies 32 million gallons per day for various uses, including as a supply of drinking water for millions of citizens living near the watershed (US Geological Survey, 2005). Currently, a few biocides (e.g., chlorine) are in widespread use for application in other water treatment processes (e.g., drinking water and wastewater), and have been well researched for their environmental acceptability, and effectiveness to disinfect large volumes of water. Other biocides (e.g., SeaKleen®) however, are still in the research phase, and further evaluation regarding efficacy, fate and toxicity of any residuals, will be required before being acceptable for discharge into the Great Lakes. Of note is that the proposed IMO regulations only take into consideration the number of organisms in discharged ballast water, and not concentrations of any residuals that may result from ballast water treatment. In most instances, when ballast water discharge is in brackish or sea water ports, residuals toxicity is an important, but not critical, issue. In the Great Lakes, however, residuals toxicity is of paramount significance because of its impact on drinking water. In fact, US EPA drinking water standards will also have to be considered in the selection of a ballast water treatment system for ships entering and discharging ballast water into the Great Lakes.

Secondly, "No Ballast on Board", or NOBOB ships dominate trade into the Great Lakes, and because of the structural and operational limitations of these vessels, they cannot completely empty their ballast tanks. As a result, these vessels carry tonnes of unpumpable water and sediments, and have been documented to carry viable organisms (e.g., invertebrate, fertilized embryos enclosed in protective egg case that can lie in a dormant state) in both residual water and sediments (Bailey et al., 2003, 2005).

The biological efficacy of chemical biocides was observed to be less in the presence of sediments taken from NOBOB ships than in water alone (Sano et al., 2004; Raikow et al., 2006). For example, a substantially (25,000 times) higher concentration of hypochlorite was necessary for the same lethal effect to be observed in freshwater test organisms when assayed in the presence of NOBOB sediments than in water alone (Sano et al., 2004). It was thought that the biological efficacy was reduced due to the sediments serving as protective refugia for the test organisms, and that the organic material in the sediments reacted with the hypochlorite, dramatically decreasing its effective concentration. Thus, for NOBOB ships, higher concentrations of biocides will be required for effective treatment to overcome the protective effect of the sediments and the oxidant demand of the sediment organic matter, if treatment of these residuals is anticipated. If these vessels, however, are practicing best ballast water management procedures, then residuals on NOBOB ships should not be a problem.

In addition, the effectiveness of some biocides will be impacted by the water chemistry of the Great Lakes if treatment of this water is attempted. Specifically, the biocidal efficacy of ozone will be affected. Ozone was initially thought to be the primary oxidant and causing mortality to some aquatic organisms, but it subsequently became apparent that bromine present in the seawater was reacting with ozone to form hypobromous acid, a more stable and effective disinfectant (Herwig et al., 2006). Since concentrations of bromine and other halides will not be as high in the fresh waters of the Great Lakes, it is thus unlikely that ozone alone will be an effective biocide when applied to these waters.

Although the volume of material to be treated in NOBOB ships (without a ballast water treatment system) would be relatively small, the frequency of discharge into receiving waters and the chronic effects of exposure to biocides would also need to be determined before it would be considered as a viable management alternative. Sano et al. (2005) observed that when environmental concentrations of glutaraldehyde approached 1 or 2 mg L^{-1}, growth rates of native algal populations were detrimentally affected, and that longer term releases at this concentration would affect the hatching success of sensitive fish species. Rapid degradation and dispersion are likely to ameliorate chronic effects, however, this will depend on the nature and location of releases.

Thirdly, NOBOB ships undergo multiple port cargo operations, and this situation is also unique to the Great Lakes. NOBOB vessels entering into the Great Lakes loaded with cargo and no pumpable ballast water on board, can unload cargo at one port, then take on ballast at that port to maintain trim and stability during operations. This ballast water, which now has been mixed with residual ballast water, sediment and any associated non-indigenous organisms, may then be discharged at another Great Lakes port. Thus, in these situations, treatment of ballast water during deballasting would be a more appropriate course of action. In this case, treatment systems with UV or chemical biocides would not be as effective due to the presence of particulate matter in ballast discharge from NOBOB vessels.

SUMMARY

Since the publication of *Stemming the Tide* in 1996, research and development of ballast water treatment technologies have continued globally. Most reports in the peer-reviewed literature are on lab-scale studies, with few at pilot- or full- scale (i.e. at water flows of approximately 300 $m^3 h^{-1}$), and there are no studies as yet addressing operational and engineering parameters required for ballast water treatment systems to be effective at ship-board scale. Research and development of treatment technologies have been stimulated by the IMO convention proposed in 2004, which sets discharge limits for organisms in ballast water. A few published reports on the efficacy of ballast water treatment systems have specifically addressed meeting these treatment goals, and it is anticipated that the number of reports evaluating technologies in this context will increase. The biological efficacy of treatment systems is difficult to determine at present, as there is a need for standardized protocols and tests to be implemented, but efforts are underway by a consortium from the US EPA, NSF International, Battelle and USCG.

As the Great Lakes is a source of drinking water for millions of people, perhaps the most environmentally benign ballast water treatment technology is media filtration, though further development is clearly needed before implementation at the large scale. An additional advantage of this technology is that if applied upon ballasting, it would also preclude sediments from entering the ballast tanks of NOBOB ships. In the nearer term, the addition of an oxidizing biocide is perhaps the most suitable option. Although higher concentrations will be required to overcome the oxidant demand of organic matter associated with sediments in NOBOB ships, and there is concern about residuals being released, an extensive literature base from other applications exists (e.g., drinking water treatment), from which these issues can be tackled. Therefore, because of the environmental sensitivity of the Great Lakes, appropriate shipboard treatment systems are those that can reliably and effectively remove unwanted organisms, and operational parameters (e.g., residual concentrations) are also able to be reliably and effectively monitored. This means that other considerations such as ease of use, and cost-effectiveness, should be secondary in the shipboard implementation of a treatment system.

Although there has been limited funding for the development of ballast water treatment technologies through federal sources, the ship-building industry is robust, and it is anticipated that ship new-builds will become an important driver in the design and implementation of effective treatment systems. Large numbers of all classes of ships, including those that will be entering the Great Lakes via the St. Lawrence Seaway, are being created, and will need some form of ballast water treatment. This affords opportunities for innovative treatment systems not available as retrofits on existing ships. Thus, ship new-builds should be the focus for new ballast water treatment technologies.

Ballast water treatment for the majority of ocean-going vessels (i.e., NOBOB ships) transiting the Great Lakes presents some challenges in that these ships carry smaller volumes, but highly sediment rich ballast water. If, however, an effective ballast water treatment system is already operational onboard, vessels entering the Great Lakes in NOBOB status will not be a vector for the transfer of non-indigenous organisms. Thus, discussions on unique treatment approaches for residuals on NOBOB vessels, should not be necessary.

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