

# **Ballast water treatment techniques: review and suggestions regarding use in the Arctic and Great Lakes**

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## **Contents**

Contents.....	3
Summary .....	4
1. Introduction .....	5
2. Methods .....	6
3. Treatment techniques applied in Ballast Water Management Systems .....	7
3.1 Mechanical systems .....	7
3.1.1 Filtration.....	7
3.1.2 Hydrocyclones .....	8
3.2 Physical disinfection .....	9
3.2.1 Ultraviolet light.....	9
3.2.2 Cavitation .....	9
3.3.3 De-oxygenation .....	10
3.3.4 Electric field technology (pulsed and plasma) .....	10
3.3 Chemical treatment.....	11
3.3.1 Oxidizing Biocides .....	11
3.3.2 Non-Oxidizing Biocides .....	13
4. Discussion and Conclusions .....	15
5. Quality Assurance .....	16
References.....	17

## ***Summary***

The retreating ice cover opens up the opportunity for new shipping routes, and consequently shipping traffic in the Arctic region is increasing and with this the risk of introducing non-indigenous species (NIS) via ballast water. Ballast water must therefore be treated to prevent the transport of NIS in an environmentally friendly way to minimise the environmental impact of the treatment. There is, however, limited information on the suitability of different ballast water treatment methods for use specifically in Arctic conditions. A literature study was conducted to identify and summarise different ballast water treatment methods, evaluate their potential for use in the Arctic, and to identify gaps in the current knowledge on Arctic ballast water treatment for further investigation. As winter conditions on the Great Lakes present a useful analogue for Arctic operation, these conditions were also included in the scope of work.

Three basic methods for ballast water treatment were addressed: mechanical systems, physical disinfection, and chemical treatments. In ballast water treatment systems often a combinations of these techniques is applied. From the literature, each technique was described and evaluated regarding key environmental conditions present in the Arctic and Great Lakes regions, such as salinity, temperature and turbidity.

It became clear that the ideal ballast water treatment system for application in the Arctic region and the Great lakes is not yet available.

The use of filters or hydrocyclones forms a good first treatment step in ballast water treatment that can be applied at all conditions that can be expected during transport between the freshwater Great lakes and the marine Arctic, although ice forming can affect the performance. However, since filters and hydrocyclones do not remove the smallest organisms additional physical or chemical treatment is always required.

For this second treatment step most existing techniques have pros and cons. A combination is necessary to cope with all conditions that can be encountered when traveling between the Great Lakes (fresh water) and the marine Arctic. Electric field technology and cavitation might be future methods with good performance under all conditions. However, these need further development and testing.

From the study it was concluded that there are major knowledge gaps in terms of the effect of Arctic conditions on the treatment methods, especially with respect to the impact of low water temperatures. Therefore, the recommendations are based on information collected in other environments and on expert judgement. Further research is necessary to develop more reliable conclusions.

## 1. Introduction

Climate change is causing strong changes in the Arctic region. The retreating ice cover is leaving larger areas of open sea exposed. This opens up the opportunity for new shipping routes, and consequently shipping traffic is increasing in the Arctic. With this, also the risk of introducing non-indigenous species (NIS) to the Arctic via ballast water increases. Various examples are known where the introduction of invasive non-indigenous species had substantial impact on local ecosystems. This could also apply for the delicate arctic ecosystems and the livelihoods of Northern Canadian communities, where settlement of NIS and climate change may have negative, synergistic effects.

In order to prevent transportation of non-indigenous species with ballast water, ballast water management systems (BWMS) are being developed to remove living organisms during ballasting or before discharge of the ballast water.

The different voyage scenarios likely to be encountered by ships entering the Arctic and Great Lakes areas include various changes in environmental conditions that may influence the suitability/effectively of the ballast water treatment techniques. Ships travelling on typical shipping routes may experience significant changes in water salinity and temperature en route (Table 1). In order to protect the Arctic, it is necessary to evaluate ship-mediated biological invasions in the Canadian Arctic, which includes evaluating the operational efficacy of BWMS for cold, and freshwater environments. This will allow regulatory agencies to determine if current policies provide sufficient protection for the Arctic ecosystem against NIS invasions (Bailey, 2013).

Table 1. Typical shipping routes terminating in the Canadian Arctic and Great Lakes.

Scenario	Environment encountered
Europe → Canadian Arctic	Freshwater, brackish or marine source port → Arctic marine destination port
St. Lawrence River → Canadian Arctic	Freshwater, brackish or marine source port → Arctic marine destination port
St. Lawrence River → Great Lakes	Freshwater, brackish or marine source port → freshwater destination port
Europe → Great Lakes	Freshwater, brackish or marine source port → freshwater destination port

This report summarises different techniques that are applied in ballast water treatment methods and discusses how their performance can be influenced by the conditions that can be encountered along the shipping routes as listed in Table 1, with special focus on the Canadian Arctic. As winter conditions on the Great Lakes present a useful analogue for arctic operation, these conditions are also included in the scope of work. Most challenging water conditions will include the broad range of salinity (fresh to marine water), temperature (from moderate to close to 0°C), and turbidity/transmission.

Most BWMSs combine a mechanical with a chemical or physical treatment to maximise the effectiveness. In this report the treatments are treated individually. For the assessment of the theoretical effectiveness of a complete BWMS the conclusions for the different treatments as presented in this report should be combined.

## ***2. Methods***

A literature search was performed using and public publications on the Internet and databases of peer-reviewed literature for information about the most commonly used ballast water treatment techniques. The process of each technique was described along with advantages and disadvantages when known, with a focus on the possible environmental impacts. The techniques were separated into three treatments types; mechanical systems, physical disinfection and chemical treatments. In practice, complete BMWS in general involve a combination of two or more of these techniques.

### **3. Treatment techniques applied in Ballast Water Management Systems**

The most recent review of Ballast Water Management Systems has been published by Lloyd's Register (LR, 2012), based upon data of 67 BWMSs supplied by the vendors. This identified 45 systems using mechanical treatment (filtration) and 1 additionally using hydrocyclones. Twelve systems did not use mechanical treatment, while 10 systems did not give sufficient information on that point. In most BWMS mechanical treatment (filtration) is used as a pre-treatment and is combined with physical and/or chemical treatments for disinfection.

The final disinfection methods are more or less equally divided between physical and chemical treatments. The physical treatments used are: UV (21 systems), cavitation (8), ultrasonic treatment (4), de-oxygenation (5), heating (1) and coagulation (1). The chemicals treatments are dominated by electrochlorination (22). Ozone is used by 6 systems, while 10 systems directly apply chemicals, 3 of which are chlorine-based.

In the following paragraphs, the characteristics of most treatment techniques and their limitations are described.

#### **3.1 Mechanical systems**

##### **3.1.1 Filtration**

Order of operations: During ballasting

Filtration is the process of passing the ballast water through disc or screen filters to remove particles and organisms from the water (ABS 2011, Kazumi 2007, Werschkun *et al.* 2012). Larger particles and organisms are retained in automatic filter systems with mesh sizes of about 20-50  $\mu\text{m}$  (Kazumi 2007, Werschkun *et al.* 2012). These filters are often self-cleaning with a back-flushing cycle and the filtrate is returned overboard so that there is minimal need for storage (ABS 2011). However, due to the self-cleaning properties of the filtration system, and the resistance in the filter elements, these systems create drops in pressure and a reduced flow rate of the ballast water system (ABS 2011).

Filtration using the current filter mesh sizes could achieve the standard of removing particles of 50  $\mu\text{m}$  as described by the 2004 International Convention for the Control and Management of Ships' Ballast Water and Sediments (Lloyd 2010). With water flows of 340  $\text{m}^3\cdot\text{h}^{-1}$ , 60 to 95 % of particle removal from the water has been reported (Waite *et al.* 2003). Reports also show that with filtration alone through a self-cleaning 50  $\mu\text{m}$  screen with water flows of 530  $\text{m}^3\cdot\text{h}^{-1}$ , a significant fraction of zooplankton was successfully removed from waters of the Wadden Sea, but this was not enough to meet the International Maritime Organization (IMO) standard (Kazumi 2007, Valdes & Liang 2006). Furthermore, analysis of material passed through the screen using scanning electron micrographs revealed that a filter with a mesh size of 50  $\mu\text{m}$  was not effective in removing particles and organisms that were cylindrical in shape with minimum dimensions smaller than 50  $\mu\text{m}$  (e.g., pennate diatoms) (Kazumi 2007). Filtration will therefore be ineffective in removing organisms smaller than the mesh size and bacteria and pathogens could remain in the ballast water (Werschkun *et al.* 2012). Removing smaller organisms or particles would require finer mesh and this would seriously impact flow rate and back pressure (Lloyd 2010).

Using compressible media such as crumb rubber (made from waste tires) to filter the water is a treatment technique currently under development. In principle, the elasticity of the filter allows for compression during the filtration process and reduces the size of the filter pores, thereby enhancing particle removal.

While conventional filters are limited in their efficiency at removing particles smaller than 50 µm, compressible media filtration could theoretically remove particles as small as 1 µm in size (at lower flow rates). Crumb rubber filters were found to take up less space on board a ship and require less maintenance and cleaning due to the low density of the material, and could therefore be used for a longer time or at a higher filtration rate compared to conventional filters (Kazumi 2007, Tang *et al.* 2006). However, these filters are primarily applied in water treatment plants and the system needs development for the typical conditions in BWMS.

A filtration step is usually incorporated into BWMS as an initial removal of organisms and suspended solids. In addition filtration at ballasting has the advantage that it reduces the amount of sediment settling in the ballast tank. A sediment layer in a ballast tank can form a breeding ground for micro-organisms that could induce microbial induced corrosion, and reduces the available 'dead weight tonnage' (DWT) for cargo carriage (Lloyd 2010). The costs of removing sediment from ballast tanks and appropriate disposal is therefore reduced by filtration of the ballast water on uptake. However, filters are prone to blockages and require regular replacement and back flushing (Lloyd 2010). Logically the advantage of filtration, but also the necessary effort increases with the concentrations of suspended solids, including organisms of the water.

The effectiveness of filtration will not be influenced by the salinity of the water. As long as no ice is formed, it is unlikely that the performance of screen or disc filters will be affected by the water temperature. Crumb rubber filters might be more sensitive to arctic conditions as it can be expected that low temperatures will reduce the flexibility of the filtering material. However, we have no data showing this in practice.

### 3.1.2 Hydrocyclones

Order of operations: During ballasting

Cyclonic separation or 'hydrocyclones' use gravity and centrifugal force to separate solid particles from the water (ABS 2011, Werschkun *et al.* 2012). During this process, the ballast water enters a cylindrical chamber with a circular flow and then through a 'venturi passage' between the interior chamber and the separation chamber (Rodriguez 2012, Werschkun *et al.* 2012). The centrifugal action forces the larger particles to the walls and then to the collection chamber. The particles are then expelled through an outflow pipe (Rodriguez 2012). Finer or less dense particles remain in the water and are exit through a tube that extends into the centre of the cyclone (Werschkun *et al.* 2012).

Hydrocyclones were considered a viable method for removing large organisms from ballast water due to the ease of use, operation and maintenance. However, various studies have shown them to be less effective than simple self-cleaning filtration techniques (Kazumi 2007). As hydrocyclones are designed to separate particles according to mass they are highly ineffective at removing organisms that have specific gravities very close to that of their liquid environment and particles smaller than 100 µm (Water-Smart Environmental, 2001; Kazumi 2007). Reports have shown dead and moribund copepods and phytoplankton still present in the ballast water following cyclonic separation (Sutherland *et al.* 2001), as well as more variable success when compared with filters with an overall particle removal efficiency of 30% (Parsons & Harkins 2002), no significant difference in the amount of ambient bacteria, phytoplankton and zooplankton (Waite *et al.* 2003) and even adverse effects when colonies of harmful organisms were disrupted (Valdes & Liang 2006).

The effectiveness of hydrocyclones will not be affected by water temperature as long as no ice is formed. Hydrocyclones may become less effective with increasing salinity as this increases the specific weight of the water.



## 3.2 Physical disinfection

### 3.2.1 Ultraviolet light

Order of operations: During ballasting and de-ballasting

Ultraviolet (UV) treatment is a method of sterilization commonly used for the treatment of both fresh and sea water (Lloyd 2010). Most UV radiation methods use UV lamps that provide photons as the only active substance which can attack and break down cell membranes of aquatic micro-organisms and pathogens, or destroying their ability to reproduce (ABS 2011, Lloyd 2010). The UV-lamps include automatic wipers to maintain the quality of the light (Lloyd 2010).

There are two basic types of UV-lamp technology:

- Medium-pressure UV lamps. These emit highly intense polychromatic light across a wide range of the UV spectrum.
- Low-pressure UV lamps. These emit less intense monochromatic light in the lower end of the UV spectrum. These lamps are particularly efficient in killing organisms (Lloyd 2010), but have a low working temperature which may result in reduced UV-intensity when operating at low temperatures (Hallett 2010).

All UV lamps exhibit a tendency toward scaling in effectiveness and hence require regular maintenance as the tubes lose half of their biocidal effectiveness after six months of use. Apart from these maintenance costs, especially medium-pressure UV-lamps show a considerable power consumption as the tubes use mercury as a fuel source (ABS 2011, Lloyd 2010, Water-Smart Environmental 2001, Werschkun *et al.* 2012)

UV treatment has a high potential to destroy (micro)organisms, and is applied for this reason in various types of water treatment. The effectiveness of UV radiation on larger, aquatic organisms is limited. To be effective the UV light must be able to penetrate the (ballast)water in order to reach the organisms. High turbidity resulting from suspended matter can impair the transmission of UV light. However, even water with low turbidity can have limited UV transmission due to the presence of dissolved organic matter (DOM; humic substances that leach from decaying organic matter) that can effectively absorb UV-radiation (Muller & Lem, 2011). UV radiation by itself can cause degradation of suspended organic matter into DOM and thereby reduce the effectiveness of the treatment method. Prior to UV-treatment ballast water must therefore be pre-treated by filtration or hydrocyclonage. However, when the poor UV-transmission of the ballast water is caused by DOM filtration these pre-treatments will not solve the problem.

Disinfection is relatively insensitive to temperature changes (Severin et al. 1983), but low-pressure UV lamps may have reduced efficacy in very cold water due to the low working temperature. Medium pressure UV-lamps perform better at low temperatures but are less efficient in killing organisms. Salinity will not affect the performance of the UV-treatment in a BWMS.

### 3.2.2 Cavitation

Order of operations: During ballasting and/or deballasting

Cavitation is a process which occurs when a liquid flows into a space where its pressure is reduced to vapour pressure. This rapid decrease in pressure causes the liquid to boil and the formation of numerous micron sized vapour bubbles (cavities). These bubbles are carried in the liquid until a region of higher pressure is reached where they then expand and collapse in the liquid. If the bubbles collapse near to a solid boundary, the force of the liquid rushing into the cavities leads to a considerable energy release and highly localized pressures which destroy particles or the cytoplasmic membranes of the cell walls of

organisms, effectively killing them (ABS 2011, Brennen 1995, Kodura 2013, Rodriguez 2012, Werschkun *et al.* 2012).

Two types of cavitation generate sufficient intensity for water disinfection:

- Hydrodynamic cavitation: The bubbles are generated by the interchange of pressure and kinetic energy from flow through outlets such as venturi pipes or slit plates which create variations in pressure in the liquid (ABS 2011, Gogate 2007).
- Acoustic cavitation: The pressure variations in the liquid are generated using the high frequency sound waves, usually ultrasound (16 KHz–100 MHz) which cause cavities through vibrations in the liquid (Gogate 2007, Werschkun *et al.* 2012).

Cavitation can destroy particles and organisms immediately and without environmental risk. However, homogenous treatment of a larger water volume is technically difficult. In addition the process is very energy intense (Werschkun *et al.* 2012).

The performance of the cavitation treatment is not related to salinity, or turbidity of the water (CT Systems Ltd 2012). No information is available on the impact of water temperature. As Werschkun *et al.* 2012 indicate that this treatment is used in Norway, it is likely that it is not substantially affected by low temperatures.

### 3.2.3 De-oxygenation

Order of operations: During voyage

Various ballast water treatment methods are used to remove the dissolved oxygen in the water and replace it with inert gases, such as nitrogen. This removal of oxygen kills the aerobic organisms present in the water, as well as reducing corrosion rates, provided that the oxygen content is maintained at the correct levels. De-oxygenation may require a prolonged period of treatment (even up to four days; Lloyd 2010) to ensure that the organisms and pathogens are rendered harmless to the receiving waters. As the voyage must exceed the necessary treatment period, short voyages can be a problem when using this technique (ABS 2011). De-oxygenation plants installed on board a ship can be used for both fresh and salt water (ABS 2011, Lafontaine *et al.* 2013) and clear or turbid water (ABS 2011). Time to achieve hypoxia was found to be inversely related to temperature with much longer times needed in cold water (e.g. half a day at 25 °C to nearly seven days at 4–5 °C; ABS 2011, Lafontaine *et al.* 2013). In addition low temperatures reduce the metabolic rate of organisms enabling them to cope better with low oxygen levels.

Using this system may require carrying hazardous chemicals on board, but no toxic by-products are released in the discharged ballast water (Lloyd 2010). Some vendors, such as Coldharbour Marine use the inert gasses in the vessel's own exhaust to replace the oxygen in the head space above the cargo as a means to limit the requirement of carrying hazardous chemicals (Coldharbour Marine Ltd. 2013).

### 3.2.4 Electric field technology (pulsed and plasma)

Order of operations: During ballasting and/or deballasting

Electrical field techniques use technology involving short voltage impulses in a fixed volume of water that creates pores in cell membranes, killing the organism. These short pulses of energy with pulse widths of 130–500 ns can inactivate spores, bacteria and viruses in water (Harvey 2005, Werschkun *et al.* 2012). There are two types of electric field techniques which differ in how the energy is generated, but result in a similar effect on the organisms in the water:

- Pulsed electrical field technology involves the water passing between two metal electrodes. An electric pulse in the water produces short bursts of energy at a very high power density and pressure. This energy is transferred to the water and effectively electrocutes an organism.
- Pulse plasma technology operates using a mechanism placed in the water that delivers a high energy pulse, creating a 'plasma arc' in the water. The energy created by the plasma arc kills the organism (Harvey, 2005).

Electric and plasma pulse technologies are still in the experimental stage of development, with little experience in the application of this technology to ballast water treatment. However, both technologies appear to be very promising as an effective control of organisms in ballast water with no negative impact on the environment. Reports on early research show that these technologies are effective to 99% killing of brine shrimp (Harvey 2005). However these systems require considerably high energy consumption for effective application (Harvey 2005, Werschkun *et al.* 2012). Furthermore, filtration or cyclonic separation may be necessary to increase the effectiveness of electric field technologies, and there are residual effects including the generation of electrolytic chlorine and gaseous decomposition products such as carbon dioxide, hydrogen and oxygen (Harvey 2005).

### 3.3 Chemical treatment

Biocide chemicals are intended to be added to the ballast water flow and kill the living organisms by chemical poisoning or oxidation. Common ballast water biocides include chlorine (chloride ions, chlorine dioxide, sodium hypochlorite) and ozone. The main environmental drawback with chemical biocides is the residual chemicals remaining in the water and discharged into the environment. Residual biocides used in ballast water treatment are obliged to meet ballast water discharge standards which may require neutralisation techniques (ABS 2011).

#### 3.3.1 Oxidizing Biocides

Order of operations: During ballasting/voyage

Oxidising biocides are well recognised and thoroughly studied general disinfectants and work by destroying organic structures such as cell membranes or nucleic acids, thereby killing the organism. Common oxidising biocides include chlorine, bromine and iodine and their various halogenated forms including inorganic agents such as chlorine dioxide (ClO<sub>2</sub>) and hypochlorites (e.g., NaOCl). Other oxidizing biocides include hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ozone (O<sub>3</sub>). The effectiveness of all oxidizing biocides is reduced by the presence of (dissolved) organic matter in the water (Kazumi 2007).

*Ozone:*

Ozone (O<sub>3</sub>) is one of the strongest known oxidising agents. Because of its effectiveness, ozone disinfection has been very common in drinking and waste water treatment for decades. Ozone decomposes by producing oxygen radicals (O•) that form the primary toxic substances (Peleg 1976). In seawater the ozone converts bromide, that is naturally present in seawater, into hypobromite ions and hypobromous acid, a less effective, but longer lasting disinfectant (Kazumi 2007). As a result ozone might thus be even more effective as disinfectant in marine water than in fresh water. The drawback however is that these by-products may cause residual toxicity at discharge. Various studies have reported success of treating salt ballast water with ozone in the inactivation of aquatic organisms. Reports show the inactivation of *Bacillus subtilis* spores within 24 h and cysts from a marine dinoflagellate, *Amphidinium* sp. after 6 h (Kazumi 2007, Oemcke & Leeuwen 2005). Large scale studies using an ozone treatment system on a commercial oil tanker showed that ozone gas diffused into a ballast tank for 5 and 10 h resulted in the inactivation of up to 99.99 % of the

culturable bacteria, > 99 % of the dinoflagellates and 96 % of the zooplankton (Herwig *et al.* 2006). Herwig *et al.* (2006) also concluded that the amount of bromoform (a toxic by-product) would not be produced at a level to adversely affect marine organisms.

Although increasing temperatures significantly reduce the solubility of ozone and increases its decomposition rate, temperature by itself has virtually no effect on the disinfection rate of bacteria. (Katzenelson *et al.* 1974, Kinman 1975)

The application of ozone in BWMS is difficult due to the high dosages required and the fact that ballast tanks usually contain areas of corrosion and of sediment high in detritus (Oemcke & Leeuwen 2005). Ozone is also known to have poor diffusion in water, so the effect in ballast water can be inhomogeneous without appropriate distribution (Herwig *et al.* 2006). Furthermore, the effective dose of ozone in disinfecting the water depends on the chemical characteristics of the source water because naturally occurring organic matter and ammonia can react with the residual oxidants and decrease their effectiveness as biocides (Kazumi 2007). Probably due to these aspects effective treatment of organisms in seawater in larger scale studies requires long contact times (hours to days) (Kazumi 2007), while in laboratory experiments the biocidal effects of ozone can occur within seconds.

#### *Chlorine:*

Chlorine is one of the most commonly used disinfectants. When dissolved in freshwater, chlorine forms hydrochloric acid and hypochlorous acid which, along with their corresponding anions, act as oxidising agents and are effective in deactivating organisms by disrupting various biomolecules including DNA, RNA, fatty acids, cholesterol and proteins (Werschkun *et al.* 2012). Chlorine can easily be applied as the relatively cheap chlorine dioxide, sodium hypochlorite, or calcium hypochlorite, and concentrations can easily be measured and controlled.

Furthermore, in seawater the raw material for chlorine production is already present in the form of sodium chloride (Werschkun *et al.* 2012), and chlorine can be produced through electrolytic chlorination. For this an electrical current is applied directly to the ballast water flow by an electrolytic cell composed of typically titanium anodes and cathodes using DC power to provide the energy. This results in the generation of free chlorine, sodium hypochlorite and hydroxyl radicals, causing electrochemical oxidation through the creation of ozone and hydrogen peroxide (ABS 2011, Lloyd 2010, Werschkun *et al.* 2012). This is a relatively safe, non-hazardous (provided there is sufficient venting of gaseous oxygen and hydrogen by-products), and on-demand method of producing hypochlorite in sufficient amounts to be an effective biocide. The residual biocide remains in the ballast water tanks during the voyage, which prevents the regrowth of organisms during transit. These are then actively neutralised into non-toxic substances during deballasting (Lloyd 2010). At concentrations of 1, 3 and 10 ppm hydrogen peroxide was lethal to a mixed assemblage of marine plankton (mostly planktonic adult and larval stages of benthic crustaceans) taken from waters around Woods Hole, MA. These organisms were killed after 5-35 min depending on the concentration of biocide used (Kazumi 2007). The system functions optimally above 15°C, but between 10-15°C the generation of hypochlorite is reduced and below 5°C no chlorine, only oxygen and hydrogen gas is produced by the process. Some manufacturers of electrolytic ballast water treatment systems pass the entire ballast flow through the electrolytic cells, while others divert a side stream in which the hypochlorite is generated and then reintroduced into the rest of the ballast water. In cold water, with incoming water <15°C, this side stream can be heated to increase the hypochlorite production rate as well as extend the life of the electrodes (Lloyd 2010).

As the electrolytic chlorination technique depends on the presence of sufficient amounts of sodium chloride, it is only effective in salt or brackish water. In fresh water, or seawater with too low temperatures for electrolytic treatment, chlorine can be added as chlorine dioxide, sodium hypochlorite, or calcium hypochlorite. Sodium hypochlorite was reported to be effective in freshwater

against the oligochaete *Lumbricus variegatus* and the cladoceran, *Daphnia magna*, but not against adult zebra mussels (most likely due to the mussels ability to seal its shell valves for extended periods) (Kazumi 2007).

#### *Peraclean® Ocean*

Peraclean® Ocean (Evonik Degussa AG, Germany) is a commercially available biocide claimed to be effective as a ballast water disinfectant. The primary active substance is peroxyacetic acid with hydrogen peroxide as a secondary active substance. Large scale tests have shown that phytoplankton and zooplankton were observed to be immediately disrupted after the addition of Peraclean® Ocean and regrowth did not occur, even after 40 days. Bacterial growth decreased while hydrogen peroxide was present, but there was rapid regrowth after the hydrogen peroxide had degraded. The effectiveness of Peraclean Ocean is reduced by low water temperatures (6°C compared to 17°C; Gregg & Hallegraeff 2007), and as all other oxidising biocides by presence of humus-rich seawater and ballast water sediments (Gregg & Hallegraeff 2007)

The active substances in Peraclean® Ocean rapidly degrade in the water. From an initial concentration of Peraclean® Ocean of 150 mg.L<sup>-1</sup>, peroxyacetic acid degraded rapidly within five hours, and was almost completely gone within 10 hours. Hydrogen peroxide degraded more slowly and was still detectable 50 h after application. As a consequence treated effluent has to be stored on board a ship for at least six days before discharge is considered safe. Because of this very large effluent storage capacity would be required (Kazumi 2007). Hydrogen peroxide may be removed with catalase, leaving only peroxyacetic acid as active substance (De Lafontaine *et al.* 2008).

### 3.3.2 Non-Oxidizing Biocides

Order of operations: During voyage (ballasting)

Various non-oxidising, or organic compounds have also been investigated as potential ballast water disinfectants. These include glutaraldehyde, and commercially marketed agents such as SeaKleen®. These substances act by interfering with reproductive, neural or metabolic functions of organisms. There is variable efficacy reported for these biocides and concern about the potential formation of toxic by-products, including derivatives of the biocides themselves, and the effect of residuals discharged into the receiving environment. Chemical neutralisation may sometimes be possible. Further investigation is required to thoroughly assess this technology for ballast treatment.

#### *Glutaraldehyde*

Glutaraldehyde is commonly used as a medical disinfectant. As a biocide, its effectiveness was variable and dependent on species (Sano *et al.* 2003). The ability to penetrate the suspended sediments and kill viable organisms is likely to be limited in high turbidity (Sano *et al.* 2003). Following an investigation using NOBOB (No Ballast On Board) ships Sano *et al.* (2003) recommended a concentration of at least 500 mg L<sup>-1</sup> of glutaraldehyde held for 24 h, to deactivate 90 % of organisms, but the high costs of this treatment made it an unfeasible option.

#### *SeaKleen®*

SeaKleen® (Vitamar Inc.) is a mixture of naphthoquinone, menadione (also known as Vitamin K<sub>3</sub>), and its bisulfite. SeaKleen® has been shown to be effective against the freshwater amphipod *Hyalella azteca* and an oligochaete, *Lumbriculus variegatus*, at a concentration less than 2.5 mg.L<sup>-1</sup> after 24 h contact (Sano *et al.* 2004). SeaKleen® was also found to be effective against eggs of the marine rotifer *Brachionus plicatilis*, the freshwater cladoceran *Daphnia mendotae*, and the marine brine shrimp *Artemia* sp. (Raikow *et al.* 2006).

The disinfection effectiveness is influenced by low water temperatures and the presence of humus-rich seawater and ballast water sediments (Gregg & Hallegraeff 2007).

Exposure to sunlight decreases the toxicity of SeaKleen® so that 72 h of exposure renders it biocidally ineffective (Kazumi 2007), for ballast water treatment this is not relevant since no sunlight will penetrate the ballast water tanks.

#### **4. Discussion and Conclusions**

A complete BWMS normally utilises a combination of techniques, usually combining a mechanical system with a physical or chemical treatment (ABS 2011, Kazumi 2007, Werschkun *et al.* 2012).

Based on the information presented in this report and summarised in Annex 1, the techniques with the highest potential for successful application in the Arctic and in the Great lakes are presented. For this, emphasis is on the performance of the technique in fresh and marine water, at low temperatures and at variable water composition with respect to turbidity and (dissolved) organic matter.

The use of filters or hydrocyclones forms a good first treatment step in ballast water treatment that can be applied at all conditions that can be expected during transport between the freshwater Great Lakes and the marine Arctic, although ice forming can affect the performance. These methods removes the large organisms and other material so that whichever treatment that follows has a better chance of successful disinfection (Lloyd 2010) and is therefore recommended as a first step for any ballast water treatment method. However, since filters and hydrocyclones do not remove the smallest organisms additional treatment physical or chemical is always required.

As additional physical treatment electric field technology and cavitation are in theory the most suitable since there are no indications that their effectiveness is affected by water composition (including salinity) or temperature. However both techniques are relatively new and performance in BWMS still has to be proven.

The effectiveness of UV-light in disinfection is not influenced by salinity, and when the right lamps are used neither by temperature. However, performance is reduced in turbid water or water that is rich in (dissolved) organic matter which might cause problems under specific circumstances.

De-oxygenation is the final physical treatment that was considered in this report. It is not dependent on water composition but at low temperatures it takes longer for this treatment to become effective. In Arctic conditions this treatment is therefore only applicable during long travels.

Chemical treatments that are based on the use of oxidising biocides like the application of chlorite, ozone or the commercial product Peraclean® Ocean, all show reduced performance in water with high concentrations of (dissolved) organic matter. Low water temperature has no strong impact on the effectiveness of this type of treatments, although it might reduce the effectiveness of Peraclean® Ocean and other biocides. Oxidising biocides can be applied in both fresh and salt water. In the marine environment it is possible to produce chlorine electrolytic from the seawater, which reduces the amount of chemicals that have to be carried and the costs.

Chemical treatment with non-oxidising biocides, like glutaraldehyde and SeaKleen® shows decreased efficiency in cold temperatures and may also be negatively affected by (organic rich) suspended matter in the water. The disinfection capacity is not affected by salinity.

From the above it is clear that the ideal BWMS for application in the Arctic region and the Great lakes is not yet available. Most techniques have their pros and cons and with the existing techniques a combination is necessary to cope with all conditions that can be accounted traveling between the Great lakes and the Arctic. Electric field technology and cavitation might be future methods that can be applied at all conditions. However, these need further development and testing.

There is a noticeable lack of information available regarding to their use in Arctic conditions, especially with respect to the impact of low water temperatures on the effectiveness of the treatments. Therefore, the recommendations are based on information collected in other environments and on expert judgement. Further research is necessary to develop more reliable conclusions.

## ***5. Quality Assurance***

IMARES utilises an ISO 9001:2008 certified quality management system (certificate number: 57846-2009-AQ-NLD-RvA). This certificate is valid until 15 December 2012. The organisation has been certified since 27 February 2001. The certification was issued by DNV Certification B.V. Furthermore, the chemical laboratory of the Environmental Division has NEN-AND-ISO/IEC 17025:2005 accreditation for test laboratories with number L097. This accreditation is valid until 27 March 2013 and was first issued on 27 March 1997. Accreditation was granted by the Council for Accreditation.



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## Annex Summarising table

To be suitable for use in the Arctic and Great Lakes, ballast water treatment methods must work in different salinities, extreme cold temperatures and in varying levels of turbidity. Table 1 evaluates each method from the available literature with specific reference to these environmental conditions. Where no literature was available, an expected or suggested effect is given.

Table 2. Effects of different conditions present in the Arctic/Great Lakes on different ballast water treatment techniques.

Treatment	Salinity	Temperature	Turbidity	Other
Filtration	No expected effect	In general no expected effect Although in Crumb rubber filter the rubber may lose flexibility at low temperatures.	Maintenance costs increases and treatment capacity reduces with turbidity (Kazumi 2007, Werschkun <i>et al.</i> 2012)	Due to the effectiveness in removing larger organisms, but limitations in removing small organisms, filtration is often used as an initial treatment prior to other treatments.
Hydrocyclones	No expected effect	No expected effect	No expected effect	Limited in removing organisms with gravities similar to water. However is sometimes used as an initial treatment prior to other treatments.
UV Lamps	Works in both fresh and salt water (Lloyd 2010).	Disinfection is relatively insensitive to temperature changes (Severin <i>et al.</i> 1983). Low-pressure UV lamps may function less well in cold waters.	Effectiveness is dependent on low turbidity (ABS, 2011 Lloyd 2010, Werschkun <i>et al.</i> 2012).	Bacterial regrowth has been found to occur quickly after treatment (within 48 h) (Wright 2011). Effectiveness depends on transmission (UV-t). Especially when dissolved molecules cause low UV-t, system may not function properly (Muller & Lem, 2011). Presence of water in solid or slush form is likely to greatly impair effectiveness.
Cavitation	Not influenced by salinity (CT Systems Ltd 2012)	Used in Norway (Werschkun <i>et al.</i> 2012), so likely to be effective in low temperatures	Not influenced by turbidity (CT Systems Ltd 2012)	The bactericide influence of cavitation is directly proportional to its intensity, flow rate and number of stages of cavitation excitors (CT Systems Ltd 2012)

Treatment	Salinity	Temperature	Turbidity	Other
De-oxygenation	Works in both fresh and salt water (ABS 2011, Lafontaine <i>et al.</i> 2013)	Time to hypoxia inversely related to temperature, ranging from half a day at 25 °C to nearly 7 days at 4–5 °C. (Lafontaine <i>et al.</i> 2013) Sensitivity of organisms temperature dependent (Vaquer-Sanyer & Duarte, 2011)	Works in both clean and turbid water (ABS 2011)	Generally does not pose a toxic risk to natural receiving waters (Lafontaine <i>et al.</i> 2013).
Electric field technology	No expected effect	No expected effect	No expected effect.	The method is still in the experimental stage and requires further testing (Harvey 2005).
Ozone	Ozone decay rate is slower in higher salinities (30‰) than lower salinity (river water) (Richardson <i>et al.</i> 1981).	Increasing the temperature from 0 to 30°C can significantly reduce the solubility of ozone and increases its decomposition rate. However, temperature has virtually no effect on the disinfection rate of bacteria. (Katzenelson <i>et al.</i> 1974, Kinman 1975).	Effect decreases in water with high turbidity/organic concentration/ammonia concentration (Cefas 2012)	Likely to have a wide range of efficacy against possible ballast tank organisms (Sano <i>et al.</i> 2003).
Chlorine chlorine dioxide (ClO <sub>2</sub> )	Works in freshwater (Takahashi <i>et al.</i> 2008) and saltwater (Lloyd 2010)	Increase in temperature results in better inactivation of organisms (Le Dantec <i>et al.</i> 2002). Organism mortality rate varies with changes in temperature between 2°C and 20°C (Pughiuc 1998). Reduced effects due to lower concentrations can be compensated for with	High turbidity required high concentration of chlorine for disinfection. Suspended matter may shield organisms and compromise the effectiveness of the chlorine (Gollasch 1997).	Reacts with ammonia, organic matter, iron and manganese, thereby increasing the necessary dosage for disinfection (Armstrong 1997) Effective disinfection requires the chlorine to be calculated in an overdose resulting in negative effects for the receiving environment on discharge. Chlorine effectiveness reduces with

Treatment	Salinity	Temperature	Turbidity	Other
		increased exposure time (Tuncan 1993).		increasing pH (Gollasch 1997).
Electrolytic chlorination	Limited to salt or brackish water as salt is required for chlorine generation (Lloyd, 2010).	Functions optimally above 15°C. Reduced function 10-15°C. Does not function <5°C and >35°C (Lloyd, 2010)	Unaffected by turbidity (BALPURE®, 2011)	The presence of manganese in solution in seawater will impair electrode efficiency (Gollasch, 1997).
Glutaraldehyde	Has been shown to be effective against both fresh and marine organisms (Werschkun <i>et al.</i> 2012)	Most active at higher temperatures (Sagripanti & Bonifacino 1996).	Ability to penetrate the suspended sediments and kill viable organisms likely to be limited in high turbidity (Sano <i>et al.</i> 2003).	Most active above a pH of 7.5 (Sagripanti & Bonifacino 1996). Some ballast water organisms may be resistant to glutaraldehyde treatment; consequently eliminating most organisms may require a concentration of 500 ppm. Risk of detrimental environmental impacts is increased(Sano <i>et al.</i> 2003).
SeaKleen® a.i. menidione (vitK)	Found to be effective against some freshwater organisms (TenEyck & Mays 2009) and marine organisms (Wright <i>et al.</i> 2009).	Adversely influenced by low water temperatures (6°C compared to 17°C) (Gregg & Hallegraeff 2007)	Adversely influenced by the presence of humus-rich seawater and ballast water sediments (Gregg & Hallegraeff 2007)	Residual toxicity to even the most sensitive organisms would be eliminated once the discharge had dispersed beyond 100 feet from the vessel (Wright <i>et al.</i> , 2009). Minimally effective on some bacteria and green algae species. Degraded readily under high light/high transmittance conditions. However, if either light or light transmittance of the water was reduced, degradation was slow and incomplete (TenEyck & Mays, 2009).
Peraclean® Ocean a.i. Peracetic acid	Toxic response of treated waters was higher in fresh water than in salt water (Lafontaine <i>et al.</i> 2008)	Adversely influenced by low water temperatures (6°C compared to 17°C) (Gregg & Hallegraeff 2007)	Activity is not affected in the presence of suspended solids and organic matter (Gregg <i>et al.</i> 2009). The rate of decay of	Most active at a pH of less than 3, activity lost pH > 8 (Sagripanti & Bonifacino, 1996). Discharge of treated fresh water may pose toxicological risk to fresh water

Treatment	Salinity	Temperature	Turbidity	Other
			<p>peracetic acid and hydrogen peroxide in water accelerated in the presence of sediments (Lafontaine <i>et al.</i> 2008). Adversely influenced by the presence of humus-rich seawater and ballast water sediments (Gregg &amp; Hallegraeff 2007)</p>	<p>receiving environments and to cold waters in particular (Lafontaine <i>et al.</i>, 2008). Degrades considerably slower in the dark compared to samples kept under 12 h light/12 h dark (Gregg &amp; Hallegraeff, 2007).</p>

## ***Justification***

Rapport C148/13

Project Number: 4305111601

The scientific quality of this report has been peer reviewed by the a colleague scientist and the head of the department of IMARES.

Approved:

E.M. Foekema  
Researcher



Signature:

Date:

30 September 2013

Approved:

M. de Wit  
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Signature:

Date:

30 September 2013