

## Review of two decades of progress in the development of management options for reducing or eradicating phytoplankton, zooplankton and bacteria in ship's ballast water

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### Abstract

The worldwide transfer and introduction of non-indigenous invasive aquatic organisms via ships' ballast water has been amply demonstrated to cause significant ecological, economic and human health impacts. Possible solutions to the problem include: 1) treating ballast water to remove or destroy unwanted organisms; 2) re-designing new vessels to eliminate the need to discharge ballast water; and 3) retaining ballast water onboard. Ballast water exchange is currently the only widely acceptable and suggested (sometimes even required) procedure to minimise the risk of ballast water mediated invasions but the variable efficacy and operational limitations of this approach have led to significant financial investment in the last two decades in the research and development of more effective shipboard and shore based ballast water treatment technologies. Specific technologies under consideration include mechanical separation, heat treatment, UV irradiation, cavitation, de-oxygenation and active substances. To date, no single treatment option has proved to be universally effective and increasing attention has focused on multi-component treatment systems. The high flow rates and volumes of ballast water that must be treated pose significant technological challenges, and the presence of sediment in ballast tanks reduces the efficacy of many treatment options as this provides a habitat for resistant organisms such as resting stages of phytoplankton and zooplankton. Mechanical separation devices would best be used as a primary stage of a treatment system comprising multiple technologies because free-living organisms and sediment below a certain size are likely to be largely unaffected. UV treatment systems are unlikely to eliminate all ballast water organisms, as they are not able to deliver a stable lethal dose across a wide range of water quality conditions and many organisms are resistant to UV exposure or can recuperate after treatment. At the current stage of development, cavitation would not be considered appropriate for the shipboard treatment of ballast water due to high capital and operating costs and high power requirements. The heating of ballast water using waste heat from ships' engines has been claimed to be a practical and cost effective treatment options for eliminating ballast water zooplankton and phytoplankton (including resting stages) but concerns have been expressed that attainable temperatures may not eliminate all bacterial pathogens, that this approach does not apply to ships traversing colder seas and may impact on the integrity of vessel structures. Promising research has been conducted on several systems that are able to achieve temperatures capable of eliminating bacteria but these technologies are still under development. De-oxygenation by the addition of glucose or reducing agents are not effective treatment options, however de-oxygenation technologies based on the injection of an inert gas are more promising (notably against larval and adult zooplankton) as they could be cost effective and do not impact on the aquatic environment as ballast water is re-oxygenated prior to discharge. Biocide dosing systems have low capital costs and power requirements but the costs of active substances are significant. Chemical treatment costs and space requirements can be significantly reduced by using onboard chemical generators but the capital cost of these systems is significant and all have biological efficacy, safety, operational and environmental (poor biodegradation) concerns. Treatment systems that produce free hydroxyl radicals would be favourable over other chemical treatments as they are claimed to produce less or no toxic by-products at ballast discharge but these technologies have high power requirements. Each treatment option requires further research on their biological and operational efficacy and safety under full-scale shipboard conditions. As of July 2009, 16 promising systems using active substances had received basic approval and 8 systems final approval from IMO, with 4 systems receiving type approval certification and 2 systems receiving national approval certification. Effectively eliminating the risk of ballast water mediated invasions still remains a monumental technological and economical challenge.

**Key words:** ballast water treatment, invasive species, bacteria, phytoplankton, zooplankton

## Introduction

The introduction in 2004 of the International Convention for the Control and Management of Ships' Ballast Water and Sediments (hereafter referred to as BWM Convention; IMO 2004) has led to significant research and development of ballast water management technologies. At the time of this writing (July 2009) the BWM Convention has been signed by 18 countries representing ca. 15% of world merchant shipping tonnage but the Convention will not enter into force until ratified by 30 states representing 35% of merchant shipping tonnage. Once entered into force, the BWM Convention requires all ships to conduct ballast water exchange (Ballast Water Exchange Standard, regulation D-1) and after a defined phasing-in period, depending on construction date and ballast capacity, ships shall meet the Ballast Water Performance Standard (Regulation D-2) which stipulates that discharged ballast water shall contain:

- less than 10 viable organisms per cubic meter greater than or equal to 50  $\mu\text{m}$  in minimum dimension, and
- less than 10 viable organisms per millilitre less than 50  $\mu\text{m}$  in minimum dimension and greater than or equal to 10  $\mu\text{m}$  in minimum dimension, and
- less than the following concentrations of indicator microbes, as a human health standard:
  - Toxigenic *Vibrio cholerae* (serotypes 01 and 0139) with less than 1 Colony Forming Unit (cfu) per 100 millilitres or less than 1 cfu per 1 gram (wet weight) of zooplankton samples,
  - *Escherichia coli* less than 250 cfu per 100 millilitres, and
  - Intestinal *Enterococci* less than 100 cfu per 100 millilitres.

In response to the adoption of the BWM Convention, a number of shipboard treatment options are under consideration or under commercial development. Many of these options stem from technologies or procedures currently utilised for industrial and drinking water treatment. The shipboard treatment of ballast water may be achieved during ballasting and/or de-ballasting or when the vessel is *en-route*. Either way this involves retrofitting or modifying the existing ships' structures to accommodate appropriate treatment systems. A variety of

mechanical/physical and chemical technologies have been proposed as potential shipboard treatment options. Mechanical treatments include filtration and cyclonic separation and are based on particle-size or specific weight to remove organisms from ballast water (Taylor et al. 2002). When used during ballasting these options have the advantage of returning removed organisms directly to the source water and pose no environmental problem. Physical treatment options are also considered environmentally friendly as they focus on changing the physical properties or hydrodynamic characteristics of the water for organism removal (Taylor et al. 2002). It is the chemical treatment options that pose the greatest environmental threat, since large volumes of treated ballast water will be released into ports around the world. Potential chemical treatment options include deoxygenation, pH and salinity adjustment and the use of chemical biocides or the onboard generation of "active substances". Currently available and prospective treatment options as of July 2009 are reviewed and evaluated. In considering and assessing the various treatment options, it is important to recognise that ballasting and deballasting operations on a proportion of ships takes place at flow rates between <1,000 and 10,000  $\text{m}^3/\text{h}$ , with the higher values applying to dry bulk carriers (5,000-10,000), ore carriers (10,000) or tankers (5,000-20,000  $\text{m}^3/\text{h}$ ) and the lower values to cruise liners, container ships, car carriers etc. (National Research Council 1996). Whilst a variety of potential options have shown promise under laboratory conditions at low flow rates and limited volumetric capacity, it is necessary to evaluate the practicality and cost under realistic conditions when comparing the potential for future large scale use.

## Mechanical/Physical treatment options

### *Ballast water exchange*

Ballast water exchange (BWE) is currently the most widely practised procedure relied upon to minimise the risk of ballast water mediated invasions and will become mandatory for existing vessels following the entry into force of the BWM Convention. After that date Ballast Water Exchange (BWE) methods would continue to be acceptable but only if they can achieve the above D-2 discharge standard.

The BWM Convention (regulation D-1) stipulates that:

“Ships performing Ballast Water Exchange shall do so with an efficacy of 95 per cent volumetric exchange of Ballast Water. For ships exchanging ballast water by the pumping-through method, pumping through three times the volume of each ballast water tank shall be considered to meet the standard described. Pumping through less than three times the volume may be accepted provided the ship can demonstrate that at least 95 percent volumetric exchange is met” (IMO 2004).

Ballast water exchange involves replacing ballast water taken onboard in coastal and port areas, with open oceanic (or otherwise specified) water prior to discharge at subsequent ports of call. Open oceanic water is described by BWM Convention as water from at least 200 nm from the nearest land and at least 200 m in depth (IMO 2004). If this is not possible, 200 nm from land and 50 m depth is acceptable, or designated ballast water exchange zones may be utilised (Gollasch et al. 2007; David and Gollasch 2008). BWE acts to reduce the concentration of coastal organisms and pathogens in the ballast water that may be introduced into a recipient port and replaces them with a lower density of oceanic organisms with a low probability of survival in near-shore waters. BWE may also be beneficial when a ship is sailing between two freshwater ports, as oceanic water would cause an increase in salinity to a point where many freshwater organisms may die (Gray et al. 2007; Perakis and Yang 2003).

There exist two basic methods of conducting BWE: the flow-through method and empty-refill method. Empty-refill involves essentially discharging the ballast water completely and then refilling the tanks. The flow-through method involves ships continually pumping oceanic water into ballast tanks or dedicated cargo holds, allowing it to overflow thus gradually exchanging ballast water.

Both ballast water exchange methods likely offer preventive capabilities; however, it is important to realise several shortcomings. Firstly, the ability to safely conduct BWE depends on weather and sea surface conditions making it not always possible to perform (Rigby and Taylor 2001). Secondly, it is not 100% effective as some sediment and many bacteria, microalgae and zooplankton species have been shown to remain in the ballast tanks following exchange; and finally, if conducted at the wrong time and

location, BWE can result in a greater biological diversity of organisms in the ballast water (Drake et al. 2001; Forbes and Hallegraeff 2001; Drake et al. 2002; Galil and Hülsmann 2002; Mimura et al. 2005; Burkholder et al. 2007; McCollin et al. 2007a).

Rigby et al. (1993) studied the effectiveness of open ocean exchange onboard the bulk carrier MV Iron Whyalla and discovered that 37, 13 and 5% of the original water remained in the ballast tanks after exchanging one, two and three ballast tank volumes respectively. Similar studies have achieved comparable water exchange efficiencies ranging from 93 to 100% (Table 1). However, it must be reinforced that the efficacy of organism removal is a complex issue and is distinct from that of water exchange. Efficiency of BWE will depend on several factors including the nature and behaviour of organisms in the tank, the design and structural configuration of tanks, mixing within the tanks and the type and behaviour of sediments (Rigby and Taylor 2001; Galil and Hülsmann 2002).

**Table 1.** Water exchange efficiency for empty/refill and flow-through ballast water exchange

Mode of Exchange	% Water Exchanged	Reference
Flow-through, 1 tank volume	63.2	Rigby and Hallegraeff (1993)
Flow-through, 2 tank volumes	86.5	Rigby and Hallegraeff (1993)
Flow-through, 3 tank volumes	95	Rigby and Hallegraeff (1993)
Flow-through, 3 tank volumes	90;99	Taylor and Bruce (2000)
Flow-through	86-96	Villac et al. (2001)
Empty/refill, 1 tank volume	93-100	Wonham et al. (2001)
Flow-through, 3 tank volumes	>99	Taylor et al. (2007)
Flow-through, 2 tank volumes	>99	Taylor et al. (2007)
Empty/refill, 1 tank volume	95	Miller (1998)
Empty/refill, 1 tank volume	95-99	Zhang and Dickman (1999)
Empty/refill, 1 tank volume	95-99	Dickman and Zhang (1999)
Empty/refill, 1 tank volume	86	Locke et al. (1993)

Many studies have found that the organism removal efficiency of BWE does not always correspond to the water exchange efficiency. The majority of studies indicate that the effectiveness of BWE at eliminating phytoplankton and zooplankton in ballast tanks ranges widely from 48-100% (Table 2), however, a number of researchers have found increases in the diversity and abundance of some taxa (including toxic phytoplankton species) after the exchange process (Macdonald and Davidson 1998; McCollin et al. 2007a). For example, McCollin et al. (2007a) examined the efficacy of ballast water exchange in the North Sea using both the empty/refill method and the flow through method and found that although there was an overall reduction in the abundance of phytoplankton after exchange, this was not consistent between tanks and voyages and in some cases there were increases in the diversity and abundance of harmful diatom and dinoflagellate species. Zhang and Dickman (1999) and Dickman and Zhang (1999) reported a discrepancy in organism removal efficiency by BWE between two different ships. The older vessel was found to have a removal efficiency of only 48% of diatoms and dinoflagellates compared to an 87% reduction in the modern ship after 95-99% replacement of water following ballast exchange using the empty-refill method (Dickman and Zhang 1999; Zhang and Dickman 1999). This discrepancy in organism removal efficiency was attributed to the age and design of the ships highlighting the complexity of flow patterns and organism behaviour in ballast tanks. A variety of alternative designs incorporating location of pipework and various pumping arrangements have been suggested to improve the relative efficiencies of the different forms of ballast water exchange.

Studies assessing the effects of BWE on the microbial ecology of ships ballast water found no significant difference in the microbial abundance and biomass between exchanged and original ballast water (Drake et al. 2002; Mimura et al. 2005). Nonetheless, BWE remains a valuable interim option and improvements to ships' designs may increase the efficiency of BWE. The operating cost of BWE is approximately US\$0.01-0.02 per tonnes of ballast water but higher costs are involved if a ship requires additional piping for safe or effective exchange (Taylor et al. 2002).

**Table 2.** Organism removal efficiency for empty/refill and flow-through ballast water exchange

Mode of Exchange	% Organism Removal	Reference
Flow-through, 3 tank volumes	75 (original phytoplankton)	Rigby and Hallegraeff (1993)
Flow-through, 3 tank volumes	90-100 (selected taxa)	Taylor and Bruce (2000)
Flow-through	86-96 (phytoplankton)	Villac et al. (2001)
Empty/refill, 1 tank volume	80-100 (coastal organisms)	Wonham et al. (2001)
Flow-through, 3 tank volumes	90-100 (original phyto- and zooplankton taxa)	Taylor et al. (2007)
Flow-through, 2 tank volumes	90-100 (original phyto- and zooplankton taxa)	Taylor et al. (2007)
Empty/refill, 1 tank volume	87 (diatoms and dinoflagellates)	Zhang and Dickman (1999)
Empty/refill, 1 tank volume	48 (diatoms and dinoflagellates)	Dickman and Zhang (1999)
Flow-through	<90 (coastal organisms)	Ruiz and Hines (1997)
Empty/refill, 3 tank volumes	>95 (coastal organisms)	Ruiz and Hines (1997)
Empty/refill, 1 tank volume	67 (plankton)	Locke et al. (1993)

### Filtration

Filtration is an environmentally sound technique for the control of ballast water organisms that works by capturing organisms and particles as water passes through a porous screen, filtration medium or stacks of special grooved disks. It has been proposed as a single treatment option and as the primary treatment component of systems that comprise a combination of technologies (Muntisov et al. 1993; Parsons and Harkins 2000, 2002; Tang et al. 2006; Cangelosi et al. 2007). Filtration systems under consideration for ballast water treatment include self-cleaning backwashing screen filters, disk filters, packed bed and crumb rubber filtration. Potential filters must handle high flow rates, together with

sediment and other material present in the water. Filtration using a filter with a nominal pore size of 50 µm is likely to be effective in removing most zooplankton and significant amounts of microalgae from ballast water, while 20 µm filtration is necessary to remove most dinoflagellate cysts. Membrane filters are needed for the removal of most protozoans, bacteria and viruses. A membrane filter pore size of 0.20 µm is needed for producing bacteria-free filtrates (Gardner and Peel 1991). High capital and operating costs together with the large volumes and high flow rates of water involved in ballasting exclude the use of membrane filters in ballast water treatment. Membrane filtration has been suggested as a valid option in circumstances where cost is not a major issue. For example, membrane filtration plus chlorination has been proposed for the treatment of ballast water on vessel types with small amounts of ballast, such as cruise ships (Oemcke 1999).

Several studies have shown self-cleaning backwashing filtration systems to be effective in the removal of significant amounts of phytoplankton, zooplankton and particulate matter from water bodies (Table 3). Parsons and Harkins (2000, 2002) examined the efficacy of automatic backwash screen filtration with mesh sizes of 25, 40, 50 and 100 µm and an automatic backwash disk filter with a 100 µm mesh. Full-scale trials demonstrated that the 25, 40 and 50 µm filter screens and 100 µm disk filter removed similar quantities of organisms and particles with an overall count efficacy (based upon the total count of all particles above the nominal filter rating) of 88, 88.7, 91.9 and 91.4% respectively. The results for the 100 µm screen filter were somewhat lower with an average overall count efficacy of 61.8%. The consensus of opinion is that the term “minimum dimension” as used in the BWM Convention refers to the organism’s body (excluding spines, antennae etc) and to single specimens in case of colony-forming organisms (Gollasch et al. 2008).

Biological testing has shown that 25 and 50 µm screen filters can significantly change the structure of the planktonic community (Cangelosi et al. 2007). Twenty five micron filtration is significantly more effective than 50 µm at removing zooplankton and microalgae. The 25 µm filter removed almost >99% of macrozooplankton, 99% of dinoflagellates and 81% of microzooplankton and small phytoplankton, whereas the 50 µm filter removed just under 97%

of the macrozooplankton, 91% of dinoflagellates and just over 70% of microzooplankton and small algal species (Cangelosi et al. 2007). Although 25 µm filtration can remove more organisms from the water, it is much less operationally efficient. On a percentage basis, 25 µm filtration exhibited a 60% greater loss of flow than the 50 µm filter screen due to self-cleaning backwash operations (Parsons and Harkins 2000). Disk filters attained the highest net flow rate between 93.3 and 96.1 % (Parsons and Harkins 2002).

Bacteria associated with plankton and other suspended matter are also reduced by 25 and 50 µm filters, however, free-living bacteria or bacteria associated with organisms less than 25 µm are unaffected (Cangelosi et al. 2001). Huq et al. (1996) found significant removal of *Vibrio cholerae* was achieved by filtration of their intermediate zooplankton host. Design improvements may increase the performance of 25 µm filter screens, however the results to date suggest that current 25 µm screen filters are not suitable for shipboard applications. Parsons and Harkins (2000) recommend the 50 µm screen filter for use on ships, however Parsons and Harkins (2002) indicate that disk filters are more attractive than screen filters when evaluated from the perspective of particle removal efficacy, backwash frequency and net ballast flow rate, maintainability and system cost. Filtration is relatively expensive costing an estimated US\$0.06-0.19 per tonne of ballast water (including capital cost) (Taylor et al. 2002; Perakis and Yang 2003).

To date, screen or disk filters have been the favoured filter type for ballast water treatment; however, recently there has also been some interest in the use of crumb rubber, a scrap tyre-derived material, as a filtration medium. Preliminary laboratory experiments conducted at low flow rates indicated that crumb rubber filtration was capable of effectively removing small particles (>2µm), however further experimentation showed effectiveness of this system was found to be considerably lower than screen and disk filters achieving maximum organism removal efficacies of 70% for phytoplankton and 45% for zooplankton and it was only operational at low flow rates (24.4-73.4 m<sup>3</sup>/h) (Table 3).

Clearly, filtration alone cannot prevent the transfer of all ballast water organisms, as free-living organisms below a certain size (25 or 50 µm) are likely to be largely unaffected. This

**Table 3.** Removal efficiency of potential ballast water filtration options

Filter Type	Filter Screen/nominal Pore Size ( $\mu\text{m}$ )	Removal Efficacy (%)	Net Lost Flow Due to Backwash (%)	Reference
Screen Filters	25	94-100 (macrozooplankton)	10.6-21.2	Cangelosi et al. (2007)
		81-85 (microzooplankton)		Cangelosi et al. (2007)
		85-91 (total zooplankton)		Cangelosi et al. (2007)
		99 (dinoflagellates)		Cangelosi et al. (2007)
		37.5 (total phytoplankton)		Cangelosi et al. (2007)
		88 (particles 25 $\mu\text{m}$ or greater)		Parsons and Harkins (2000) Parsons and Harkins (2002)
Screen Filters	40	88.7 (particles 40 $\mu\text{m}$ or greater)	N/A	
Screen Filters	50	94-97 (macrozooplankton)	6.8-13.5	Cangelosi et al. (2007)
		71-81 (microzooplankton)		Cangelosi et al. (2007)
		78-89 (total zooplankton)		Cangelosi et al. (2007)
		91 (dinoflagellates)		Cangelosi et al. (2007)
		8.3 (total phytoplankton)		Cangelosi et al. (2007)
		50-70 (particles greater than 50 $\mu\text{m}$ )		Anderson 2007
		60-95 (bivalve and gastropod larvae)		Waite et al. 2003
		91.9 (particles 50 $\mu\text{m}$ or greater)		Parsons and Harkins (2000)
		ineffective against <i>Phaeocystis globosa</i> (4-6 $\mu\text{m}$ cell diameter; 20-500 $\mu\text{m}$ colony diameter)		Veldhuis et al. (2006)
Ineffective (particles >2-<63 $\mu\text{m}$ )	Veldhuis et al. (2006)			
86 (zooplankton)	Veldhuis et al. (2006)			
Screen Filters	100	83 (macrozooplankton)	N/A	Cangelosi et al. (2007)
		68 (microzooplankton)		Cangelosi et al. (2007)
		79 (total zooplankton)		Cangelosi et al. (2007)
		61.8 (particles 100 $\mu\text{m}$ or greater)		Parsons and Harkins (2000)
Disk Filters	55	80 (organisms >50 $\mu\text{m}$ )	N/A	Wright et al. (2007c)
	100	91.4 (particles 100 $\mu\text{m}$ or greater)	4.9-6.8	Parsons and Harkins (2002)
Crumb Rubber	>500 (media size)	86.8 (particles 10 $\mu\text{m}$ or greater)	N/A	Xie and Chen (2004)
		93.6 (particles 15 $\mu\text{m}$ or greater)		Xie and Chen (2004)
		51.7 (particles 2 $\mu\text{m}$ or greater)		Xie and Chen (2004)
		70 (phytoplankton); 45 (zooplankton)		Tang et al. (2006)

would include most bacteria and viruses, many diatoms, dinoflagellates, other phytoplankton species, microzooplankton and various resting stages. Bacteria associated with crustaceans may be reduced, but filtration acts to primarily remove larger aquatic organisms (>50  $\mu\text{m}$ ) and reduce the sediment load during ballasting. Improvements in filter technology and design may allow the use of smaller pore sizes; however at present 50  $\mu\text{m}$  filtration is operationally feasible. Filtration therefore would best be used as a primary treatment stage of a treatment system comprising multiple technologies. These technologies may include UV, cavitation or dosing with active substances.

#### *Cyclonic separation*

Cyclonic separators or hydrocyclones are simple mechanical devices that operate by centrifugal action causing heavier particles to move to the outside where they are captured by a weir-like feature near the discharge point (Parsons and Harkins 2002). These devices have the advantage of requiring minimal maintenance due to having virtually no moving parts, and pose no environmental risk as collected particles and organisms are returned directly to the source water.

Several studies have evaluated the efficacy of cyclonic separation in removing organisms and sediment from water (Table 4). In most cases,

**Table 4.** Organism and sediment removal efficacy of cyclonic separators

Manufacturer	Flow Rate	Removal Efficiency (%)	Net Flow Loss Due to Discharge Path	Reference
OptiMarin	N/A	15-40 (of particles <50 µm)		Hesse et al. (2004)
Velox Technology Inc.	68-79 m <sup>3</sup> /h	10-30 ( <i>Prorocentrum minimum</i> and <i>Tetraselmis</i> sp.)	10%	Jelmert (1999)
Velox Technology Inc.	68-79 m <sup>3</sup> /h	13.7 ( <i>Artemia</i> sp. cysts)		Jelmert (1999)
Velox Technology Inc.	68-79 m <sup>3</sup> /h	8.3 ( <i>Artemia</i> sp. nauplii)		Jelmert (1999)
Velox Technology Inc.	312-350 m <sup>3</sup> /h	ineffective (phytoplankton)	10%	Sutherland et al. (2001)
Greenship Ltd	N/A	100 (particles >20 µm)		MEPC (2007a)
Greenship Ltd	N/A	80 (particles >10 µm)		MEPC (2007a)
Hamann AG	N/A	>90 (particles >40 µm)		Hamann AG (2007)
Hamann AG	530 m <sup>3</sup> /h	ineffective ( <i>Phaeocystis globosa</i> , particles >2-<63 µm)		Veldhuis et al. (2006)
Krebs Engineers	342 m <sup>3</sup> /h	<15 (zooplankton)		Waite et al. (2003)
Krebs Engineers	342 m <sup>3</sup> /h	no effect (phytoplankton)		Waite et al. (2003)
HydeOptiMarin	340 m <sup>3</sup> /h	33 (particles >100 µm)		Parsons and Harkins (2002)

performance was found to be sub-optimal and significantly inferior to screen and disk filters. Jelmert (1999) tested removal efficacy using dense cultures of the dinoflagellate *Prorocentrum minimum* (10-15 µm), the green alga *Tetraselmis* (10-15 µm) and two isolates of marine bacteria (0.2-1 µm) as model organisms. No significant removal of either *Prorocentrum minimum* or *Tetraselmis* was found with removal efficacies varying between 10 and 30%. As could be expected, no separation effect on bacteria was observed. Parsons and Harkins (2002) found similar removal efficacies. Parsons and Harkins (2002) tested a hydrocyclone on a barge installation which was suggested to be effective in removing particles above the 50-100 µm range. The device removed very little material below about 400 µm resulting in an overall removal efficacy of only 33% of particles above 100 µm. Veldhuis et al. (2006) highlights one advantage of hydrocyclones; although the device was not very effective in reducing total suspended solids, it was capable of altering gelatinous phytoplankton colonies in a manner which greatly reduced the clogging of the secondary self-cleaning filter.

The above results suggest that the cyclonic separation of small organisms, and organisms with a specific gravity close to that of water, is

minimal. This would include many organisms such as viruses, protozoans, bacteria, phytoplankton, chaetognaths and jellyfish. Oemcke (1999) suggests that dinoflagellate cysts should be removable from ballast water using cyclonic separation as they have a specific gravity of greater than 1.05 and typically greater than 1.1. However, given the performance of the systems tested to date, this would prove questionable. The estimated cost of cyclonic separation is US\$0.05-0.26 per tonne of water (including capital cost) (Taylor et al. 2002; Perakis and Yang 2003), which is comparable to filtration. Cyclonic separation does have the advantage of being able to operate continuously under high flow rates (~3000 m<sup>3</sup>/h) and may prove an effective primary treatment option as it acts to improve water clarity prior to secondary treatment (Sutherland et al. 2001). It can also remove large, dense particles thus protecting secondary treatment devices, but current systems are unlikely to remove a significant amount of zooplankton, microalgae and bacteria from water. The particle removal efficacy of some newer designs is suggested to be much greater. For example, Greenship Ltd of the Netherlands has developed a hydrocyclone device that is claimed to be capable of removing 100% of particles 20 µm and larger, and 80% of the particles greater than 10 µm (MEPC 2007a).

### Heat treatment

The use of heat for killing organisms in ballast water has received considerable attention as it is an environmentally attractive option, is potentially cost effective and has been shown to eliminate a wide range of aquatic organisms (Table 5). Several different heat treatment processes have been suggested as potential shipboard ballast water treatment options (Table 6). One proposed method uses waste heat from the ships engine cooling system and exhaust to treat ballast water (Hallegraeff et al. 1997; Rigby et al. 2004). Results from a shipboard trial on the MV *Iron Whyalla* suggest that heating ballast water to 38-45°C is achievable in tropical and subtropical seas and may be an effective way to kill zooplankton and phytoplankton organisms in ballast tanks (Rigby and Hallegraeff 1993; Rigby et al. 1998; 1999). Laboratory experiments have demonstrated: 1) that phytoplankton and dinoflagellate cysts are readily killed when exposed to temperatures in this range, and 2) inactivation time decreases as the temperature is increased (Hallegraeff et al. 1997; Forbes and Hallegraeff 2001). Most vegetative microalgal cells are readily killed at temperatures as low as 35°C with exposure times between 30 min and 5 h. Some resistant species survive such treatments requiring higher temperatures and/or longer exposure times for mortality to occur. The inactivation of the green alga *Dunaliella tertiolecta* and *Nannochloropsis oculata* required temperatures around 42.5°C at longer exposure times of 24 h (Hallegraeff et al. 1997). Dinoflagellate cysts are more resistant to heat treatment than vegetative cells, however can still be killed by temperatures that are considered attainable inside ballast tanks. *Gymnodinium catenatum* dinoflagellate cysts survived a 1 h treatment at 35°C with effective inactivation achieved at exposures ranging from 1 h at 37.5°C, to 2 min at 38-40°C, and 30 s at temperatures of 44.5-46.3°C (Bolch and Hallegraeff 1993; Hallegraeff et al. 1997; Hallegraeff 1998). Similarly, *Alexandrium*, *Protopeperidinium* and *Scrippsiella* cysts have been inactivated in 4.5 h at 38°C and 3 min at 45°C (Montani et al. 1995; Hallegraeff et al. 1997). The heating of ballast water to around 40°C also has the advantage of been able to effectively treat organisms present in ballast sediment (Stocks et al. 2004a), with the exception of bacteria. Rigby and Taylor (2001) indicated that higher temperatures are

experienced at the bottom of tanks as in their system the heated ballast water was pumped in from the bottom.

However, these low temperature strategies (<45°C) will be largely ineffective for controlling most pathogens and concern has been expressed that mild heating of ships' ballast water may stimulate the growth of pathogenic bacteria such as *Vibrio cholerae*. Desmarchelier and Wong (1998) dispelled such concerns on the basis of *V. cholerae* being severely nutrient limited in typical ballast water conditions. Vegetative bacteria, fungi and viruses are generally killed at temperatures in the range of 60-100°C and temperatures exceeding 100°C are usually required to kill bacterial spores, although the level of heat resistance varies widely according to the species (Gardner and Peel 1991). Marine and estuarine bacteria, including *E. coli* and *V. cholerae*, require significantly lower heat treatments of 55-75°C for complete inactivation as compared to enterobacteria associated with warm-blooded animals (Gardner and Peel 1991; Rigby et al. 2004).

A number of studies have tested systems that use additional heat exchangers capable of achieving temperatures of 55-80°C for short periods (Mesbahi et al. 2007a; Quilez-Badia et al. 2008). These short exposure high temperature treatments achieved a reduction in zooplankton of up to 95% and significant reductions of up to 90% for phytoplankton. Most importantly, these treatment systems were capable of causing a 95% reduction of bacteria but there was no significant increase in mortality when the treatment temperature was increased from 55 to 80°C (Mesbahi et al. 2007a; Quilez-Badia et al. 2008). One explanation for the 95% reduction in bacteria was that the vegetative bacterial cells were killed at the lowest treatment temperature (55°C) while the surviving 5% consisted of bacterial spores. As none of the bacterial indicator species listed in the BWB Convention discharge standard are spore forming species it is suggested that they should be relatively easy to kill using heat (Quilez-Badia et al. 2008). Estimated capital costs of this high temperature treatment system are between US\$350,000 and 400,000 for ballast flow rates of 1,000 to 3,500 m<sup>3</sup>/h and estimated operational costs (based on increased fuel consumption) range from over US\$100 for 1,000 m<sup>3</sup>/h to over US\$600 for 3,500 m<sup>3</sup>/h (Mesbahi et al. 2007b).

**Table 5.** Summary of temperatures required for the complete inactivation or mortality of aquatic organisms

Organism Group	Species	Treatment	Reference
Marine bacteria	Marine bacteria including <i>Vibrio cholerae</i> and <i>Escherichia coli</i>	55-75°C	Rigby et al. (2004) Gardner and Peel (1991)
	<i>Vibrio cholerae</i>	73°C, 30 sec	Thornton and Chapman (2004)
	<i>Vibrio cholerae</i>	65°C, 2 min	Thornton and Chapman (2004)
Microalgae	<i>Detonula pumila</i>	35°C, 1 h	Forbes and Hallegraeff (2001)
	<i>Pseudo-nitzschia cuspidata</i>	35°C, 1 h	Forbes and Hallegraeff (2001)
	<i>Skeletonema costatum</i>	35°C, 1 h	Forbes and Hallegraeff (2001)
	<i>Thalassiosira rotula</i>	35°C, 1 h	Forbes and Hallegraeff (2001)
Diatoms	<i>Amphora</i> sp.	35°C, 5 h	Forbes and Hallegraeff (2001)
	<i>Navicula</i> sp.	35°C, 5 h	Forbes and Hallegraeff (2001)
	<i>Navicula jeffreyi</i>	35°C, 5 h	Forbes and Hallegraeff (2001)
Chlorophyte	<i>Dunaliella tertiolecta</i>	42.5°C, 24 h	Hallegraeff et al. (1997)
Raphidophyte	<i>Chattonella</i> sp. cysts	45°C, 3 min	Montani et al. (1995)
Picoplankton	<i>Nannochloropsis oculata</i>	53°C, 100 sec	Boldor et al. (2008)
	<i>Nannochloropsis oculata</i>	42.5°C, 24 h	Hallegraeff et al. (1997)
Dinoflagellates	<i>Gymnodinium catenatum</i>	35°C, 30 min	Hallegraeff et al. (1997)
	<i>Gymnodinium catenatum</i> cysts	38-40°C, 2 min	Bolch and Hallegraeff (1993)
	<i>Gymnodinium catenatum</i> cysts	44.5-46.3°C, 30 sec	Bolch and Hallegraeff (1993)
	<i>Gymnodinium catenatum</i> cysts	37.5°C, 1 h	Bolch and Hallegraeff (1993)
	<i>Alexandrium catenella</i> cysts	42°C, 30 min	Hallegraeff et al. (1997)
	<i>Alexandrium catenella</i> cysts	40°C, 75 min	Hallegraeff et al. (1997)
	<i>Alexandrium catenella</i> cysts	38°C, 4.5 h	Hallegraeff et al. (1997)
	<i>Alexandrium</i> sp. cysts	45°C, 3 min	Montani et al. (1995)
	<i>Scrippsiella</i> sp. cysts	45°C, 3 min	Montani et al. (1995)
	<i>Gymnodinium</i> sp. cysts	45°C, 3 min	Montani et al. (1995)
	<i>Protoperidinium</i> sp. cysts	45°C, 3 min	Montani et al. (1995)
	<i>Gyrodinium</i> sp. cysts	45°C, 3 min	Montani et al. (1995)
Macroalgae	<i>Undaria pinnatifida</i> spores	35-40°C, 0.9-42 min	Mountfort et al. (1999b)
	<i>Undaria pinnatifida</i> gametophyte	55°C, 6 sec	Forrest and Blakemore (2006)
Molluscs	<i>Dreissena polymorpha</i>	36°C, 10 min	Jenner and Janssen-Mommen (1992)
	<i>Crassostrea gigas</i> larvae	40-48°C, 6-97 min	Mountfort et al. (1999b)
	<i>Crassostrea virginica</i>	48.5°C	Sellers and Stanley (1989)
	<i>Corbicula fluminea</i>	44°C	Graney et al. (1983)
	<i>Crassostrea gigas</i> spat	39-45°C, 2-167 min	Rajogopal et al. (2005)
	<i>Brachidontes striatulus</i>	43°C, 135 min	Gunasingh Masilamoni et al. (2002)
	<i>Crassostrea virginica</i>	51°C, 100 sec	Boldor et al. (2008)
	<i>Mytilus edulis</i>	50-60°C, 30-60 sec	Park et al. (1998)
	<i>Ballanus</i> sp.	55-60°C, 10-15 sec	Park et al. (1998)
Echinoderms	<i>Coscinasterias calamaria</i> larvae	39-44°C, 1-35 min	Mountfort et al. (1999b)
	<i>Arachnoides placenta</i>	37°C, 48 h	Chen and Chen (1992)
Crustaceans	<i>Acartia tonsa</i>	30-35°C, 48 h	Heinle (1969)
	<i>Artemia salina</i> nauplii	43°C, 100 sec	Boldor et al. (2008)
	<i>Artemia salina</i> adults	47°C, 100 sec	Boldor et al. (2008)
	<i>Artemia salina</i> cysts	64°C, 100 sec	Balasubramanian et al. (2008)

**Table 6.** Comparison of achievable temperature, biological efficacy and estimated cost of different potential shipboard ballast water heat treatment options

Treatment Process	Attainable Temperature	Biological Efficacy	Estimated Cost (US\$ per tonne)	Reference
Engine waste heat	35-38°C after 24-30 h	100% of zooplankton and phytoplankton	0.056 (including capital costs)	Rigby and Hallegraeff (1993)
	37-38.4°C after 24-30 h	100% of zooplankton and most phytoplankton		Rigby et al. (1998) Rigby et al. (2004)
Heat exchangers	55-80°C for 1-2 sec	95% of zooplankton 63-90% of phytoplankton 95% of bacteria	0.10-0.17 (excluding capital costs)	Quilez-Badia et al. (2008) Mesbahi et al. (2007b)
Microwave heating	69-89°C in 100-200 sec	100% of <i>Artemia salina</i> adults, <i>Artemia salina</i> nauplii, <i>Crassostrea virginica</i> larvae and <i>Nannochloropsis aculata</i>	2.55 (including capital costs)	Boldor et al. (2008)
Microwave heating and additional heat exchanger	73->100°C in several mins	100% of <i>Artemia salina</i> cysts	1.09 (including capital costs)	Boldor et al. (2008) Balasubramanian et al. (2008)

These results indicate that heat treatment using waste heat from ship engines together with additional heat exchangers deserves further investigation as a stand-alone treatment for ballast water as the temperatures able to be reached in onboard situations have been demonstrated to kill zooplankton, phytoplankton (including resting stages) and vegetative marine bacteria. Additionally, the treatment option is considered to be cost effective (US\$0.05-0.17 per tonne excluding capital costs) but some concerns exist over the time and energy required to heat ballast water to the necessary temperature (notably for ships operating in colder seas) and possible environmental impacts following the discharge of large volumes of heated water. It is suggested that heated water should be cooled to less than 10°C above the ambient temperature prior to discharge (ICES WGBOSV 2006). For some ship designs and ballasting/deballasting arrangements, such as on some oil tankers using steam driven deballasting pumps, heat treatment could prove to be very cost effective (Rigby et al. 2004).

Recently, the use of a microwave heating system has been proposed as a ballast water treatment option. Initial laboratory experiments have shown that this system is capable of achieving a maximum temperature of ~89°C very rapidly (100-200 s) and when combined with an additional heat exchanger, temperatures in

excess of 100°C can be reached (Balasubramanian et al. 2008; Boldor et al. 2008). Biological efficacy tests showed that *Artemia* adults, *Artemia* nauplii, *Crassostrea virginica* larvae and the microalga *Nannochloropsis oculata* are completely eliminated at temperatures of 43, 47, 51 and 53°C, respectively, within several minutes using the microwave heating system (Boldor et al. 2008). Slightly higher temperatures of 64°C were required for the complete inactivation of *Artemia* cysts (Balasubramanian et al. 2008). No data are available on bacterial efficacy but it would be expected that marine bacteria would be killed by the temperatures attainable by this device. This technology has higher heating rates compared to conventional heating methods but current systems are only operating at flow rates of 1-2 L/min. The major factors that are likely to negate the use of technology for the large scale shipboard treatment of ballast water are the high energy consumption of the system and high cost. Current cost estimates are about US\$2.55 per tonne of ballast water for a system without a heat exchanger and \$US1.09 for a system that has a heat exchanger (Boldor et al. 2008). Nevertheless, this is a promising technology that is still in its infancy and if costs and energy requirements can be significantly reduced, it may provide an effective treatment option.

### Radiation

The biocidal action of electromagnetic radiation has been known for many years. Three wave-length bands are of interest for the control of organisms: gamma rays, microwaves and ultra-violet rays. The use of gamma and microwave radiation has been suggested as a possible ballast water and residue treatment (Muntisov et al. 1993). However, with current technology, the high energy requirements together with high capital and operational costs are likely to prohibit these technologies for shipboard ballast water treatment. UV irradiation, on the contrary, is considered economically viable and has been demonstrated as a feasible ballast water treatment option.

Ultra-violet (UV) light inactivates organisms by causing photochemical alterations of cell material and has been demonstrated effective against a variety of microorganisms (Chang et al. 1985). UV disinfection is relatively insensitive to temperature changes (Severin et al. 1983) and effectiveness varies with microbe type. Effectiveness depends largely upon the size and morphology of the organism. For example, microalgae require higher inactivation dosages than bacteria and viruses due to their larger size and pigmentation (Rigby and Taylor 2001). However, care must be taken when deciding on lethal UV doses as phytoplankton and bacteria exhibit recovery processes known as photo-reactivation and dark repair. Table 7 summarises the effectiveness of UV irradiation against aquatic organisms.

**Table 7.** Effectiveness of UV irradiation against aquatic organisms

Organism	UV Dosage	Efficacy (%)	Reference
<b>Bacteria and protozoa</b>			
<i>Cryptosporidium parvum</i> oocysts	230 mWs/cm <sup>2</sup>	99	Morita et al. (2002)
<i>Cryptosporidium</i>	330 mWs/cm <sup>2</sup>	99	Buchholz (1998)
<i>Escherichia coli</i>	7-16 mWs/cm <sup>2</sup>	99	Buchholz (1998)
<i>Escherichia coli</i>	25-60 mWs/cm <sup>2</sup>	>99	Waite et al. (2003)
Marine bacteria	96-115 mWs/cm <sup>2</sup>	98.8-99.6	Jelmert (1999)
Marine bacteria	200 mWs/cm <sup>2</sup>	25-90	Cangelosi et al. (2001)
<i>Staphylococcus aureus</i>	7 mWs/cm <sup>2</sup>	99	Buchholz (1998)
Total coliform bacteria	25-60 mWs/cm <sup>2</sup>	>99	Waite et al. (2003)
<i>Vibrio cholerae</i>	7-13 mWs/cm <sup>2</sup>	99	Buchholz (1998)
<i>Vibrio salmonicida</i>	2.7 mWs/cm <sup>2</sup>	99.999	Liltved et al. (1995)
<i>Vibrio anguillarum</i>	2.7 mWs/cm <sup>2</sup>	99.999	Liltved et al. (1995)
<i>Vibrio anguillarum</i>	22 mWs/cm <sup>2</sup>	99.99	Sugita et al. (1992a)
<i>Yersinia ruckeri</i>	2.7 mWs/cm <sup>2</sup>	99.999	Liltved et al. (1995)
<b>Microalgae</b>			
Cyanobacteria	300-600 mWs/cm <sup>2</sup>	90	Buchholz (1998)
<i>Amphidinium</i> sp., <i>Gymnodinium catenatum</i>	<50 mWs/cm <sup>2</sup>	100	Oemcke (1999)
<i>Skeletonema costatum</i>	2.5 KW total output	100	Sutherland et al. (2001)
<i>Tetraselmis</i> sp.	96-115 mWs/cm <sup>2</sup>	87.6	Jelmert (1999)
<i>Prorocentrum minimum</i>	96-115 mWs/cm <sup>2</sup>	84.7	Jelmert (1999)
<i>Gymnodinium catenatum</i> cysts	1,600 mWs/cm <sup>2</sup>	ineffective	Oemcke (1999)
<i>Chattonella</i> sp. cysts	30 lux	94	Montani et al. (1995)
<i>Scrippsiella</i> sp. cysts	30 lux	52	Montani et al. (1995)
phytoplankton	N/A	78	Mesbahi (2004)
<b>Zooplankton</b>			
<i>Artemia</i> sp. nauplii	96-115 mWs/cm <sup>2</sup>	99.5	Jelmert (1999)
<i>Artemia</i> sp. cysts	96-115 mWs/cm <sup>2</sup>	26	Jelmert (1999)
Live organisms	200 mWs/cm <sup>2</sup>	88.7	Wright et al. (2007c)
Nematode eggs	92 mWs/cm <sup>2</sup>	99	Buchholz (1998)
Total zooplankton	N/A	65	Mesbahi (2004)
Total zooplankton	200 mWs/cm <sup>2</sup>	>95	Wright et al. (2004)

Vegetative bacteria are readily inactivated by UV irradiation. Laboratory experiments conducted by Liltved et al. (1995) discovered a dose of 2.7 mWs/cm<sup>2</sup> resulted in more than 5-log (99.999%) reduction of three fish pathogenic bacteria, *Vibrio salmonicida*, *V. anguillarum* and *Yersinia ruckeri*, whilst Sugita et al. (1992a) found a higher dosage of 22 mWs/cm<sup>2</sup> was required to inactivate *Vibrio anguillarum*. This difference in reported UV sensitivity of *Vibrio anguillarum* may possibly be explained by variations in experimental factors such as temperature and water clarity, or different bacterial isolates may respond differently to UV irradiation.

Dinoflagellate cysts have been documented to be resistant to UV irradiation. Oemcke (1999) demonstrated that UV light can effectively control the vegetative dinoflagellate cells of *Amphidinium* sp. and *Gymnodinium catenatum* at a dose of <50 mWs/cm<sup>2</sup>; however cysts of *G. catenatum* were not destroyed at doses of up to 1,600 mWs/cm<sup>2</sup>. Similarly, Montani et al. (1995) reported that UV irradiation is not an effective treatment for the destruction of microalgal cysts as germination of all experimental species was still evident after 2 h exposure.

Several UV treatment systems have reached the shipboard and pilot-scale stage. These systems are comprised of UV-C lamps arranged in circular formations and can treat ballast water during intake and discharge. Jelmert (1999) examined the effectiveness of UV irradiation on *Artemia* nauplii, *Artemia* cysts, the dinoflagellate *Prorocentrum minimum*, the green alga *Tetraselmis* sp. and two isolates of marine bacteria following a primary cyclonic separation treatment. UV doses ranging from 96-115 mWs/cm<sup>2</sup> resulted in 84.7 and 87.6% mortality in the two algal species and a 2.3 and 1.9 log reduction in the marine bacteria. A mortality of 95% was achieved for *Artemia* nauplii and the germination of *Artemia* cysts was reduced by 26% (Jelmert 1999). This system appears inferior to the filtration and UV set-up analysed by Cangelosi et al. (2001), whereby dinoflagellates were reduced in concentration by >95%, highlighting how poor water clarity reduces the effectiveness of UV treatment. The low removal efficacy of particulate matter in the cyclonic separator caused a reduction in UV transmittance resulting in a lower kill rate in the secondary UV

treatment. A UV transmittance of 30-45% resulted in a mean inactivation of 25% for bacteria, while a transmittance of >90% resulted in 90% inactivation (Cangelosi et al. 2001) suggesting that bacteria are shielded from the UV treatment in the presence of high sediment loads (Hess-Erga et al. 2008), thus requiring a physical pre-treatment process such as filtration for effective removal. Conversely, Waite et al. (2003) examined the effectiveness of a pilot-scale treatment system consisting of a hydrocyclone, 50 µm self-cleaning screen filter and a UV system and found that pre-treatment via screens or hydrocyclones is not required to enhance the removal efficiency of *E. coli* with UV treatment. Results also indicated that the dose delivered by the UV system (25-60 mWs/cm<sup>2</sup>) was not efficient or successful at killing phytoplankton in ballast water and the bactericidal effect was short-lived, as regrowth occurred after 18 h.

Onboard testing has been carried out on the USS *Cape May* using a UV disinfection system rated at 200 mWs/cm<sup>2</sup>. Efficacy tests showed that when UV transmittance was in excess of 90%, zooplankton mortalities greater than 95% occurred, phytoplankton growth was reduced but the levels of bacteria were greatly increased (due to the decomposing organic matter) (Wright et al. 2004). One of the latest treatment systems based on UV irradiation has been installed on the cruise ship *Coral Princess* (Wright et al. 2007c). This treatment system consisted of a 50 µm disk filter and a medium-pressure UV disinfection unit also rated at 200 mWs/cm<sup>2</sup>. Efficacy testing of the system revealed an overall reduction in live organisms of 69.7-99.1% (mean 87%) but it did not conform to the BWM Convention's IMO's D-2 discharge standard as >100 individuals per tonne of ballast water larger than 50µm survived the treatment. The UV system was 100% effective against coliform bacteria however no difference was found in colony counts of heterotrophic bacteria in treated water relative to untreated controls.

Acher et al. (1997) propose a different UV system that concentrates UV irradiation on a transparent quartz pipe through which water or effluent is passed. It was suggested that this system is superior to existing shipboard installations as it can operate in waters high in sediment. Preliminary experiments conducted in turbid waters obtained promising results with polio-

virus and several other human pathogens from infested water controlled at doses between 10 and 33 mWs/cm<sup>2</sup> (Acher et al. 1997). However, currently this system can only operate with small water volumes at a low flow rate excluding it as a ballast water treatment option.

In summary, the current UV systems would be unlikely to eliminate all ballast water organisms as they seem unable to deliver a stable lethal dose to the entire ballast flow across a range of water quality conditions. The presence of sediment is likely to drastically reduce the efficacy of UV as small organisms such as bacteria would be shielded from the treatment. Additionally, as many organisms, including dinoflagellate cysts, are resistant to UV irradiation, fine filtration would be necessary for their removal. A primary treatment step may also function to protect the UV source, improve water clarity, thus increasing UV transmittance, and reduce power requirements and maintenance costs. UV treatment systems would best be suited on ships with moderate ballast flow rates (up to approximately 1000 m<sup>3</sup>/h) because once flow rates exceed this rate, these types of systems may require a prohibitively large amount of power. The estimated capital cost for a UV ballast water treatment system ranges from US\$300,000 to \$400,000 depending on the manufacturer with operational costs of approximately US\$0.065-0.26 per tonne of ballast water (Perakis and Yang 2003; Sassi et al. 2005; Lloyd's Register 2008). Although UV is considered an environmentally sound treatment option, possible environmental concerns include the release of ballast water containing genetically mutated organisms, i.e. organisms that manage to survive the UV treatment but have damaged DNA, and propulsion vibrations from ships engines have caused the UV lamps to rupture releasing mercury (Swanson and Perlich 2006). Organism self-repair mechanisms and subsequent regrowth also limit the efficacy of UV treatment (Buma et al. 1995).

#### *Cavitation*

The destruction of microorganisms by acoustic technologies has been of considerable interest for over 80 years. The mechanical effects of ultra-sound on biological systems in a liquid medium are mainly thought to be due to cavitation although pressure wave deflections and possibly the degassing effect may also

contribute to the mortality of aquatic organisms (Mason et al. 2003; Rigby and Taylor 2001).

Cavitation is a relatively new technology for the treatment of ships' ballast water. Data concerning the efficacy of ultrasonic treatment systems in ballast water situations indicate that zooplankton may be effectively controlled, yet the effectiveness against microalgae and bacteria has not been proven. Holm et al. (2008) showed that the survival of zooplankton larger than 100 µm could be reduced by 90%, but phytoplankton and bacteria were largely unaffected. This was confirmed by Mason et al. (2003) and Gavand et al. (2007) who demonstrated that using cavitation alone resulted in the mortality of 19 and 49% of bacteria (Mason et al. 2003) and 5 and 33% of the green alga *Dunaliella tertiolecta* (Gavand et al. 2007) after 5 and 20 min respectively. When using cavitation alone, the decontamination process was shown to be relatively slow using flow-through systems (Mason et al. 2003). Therefore, for effective treatment of ballast water, water would need to be recirculated through the ultrasonic unit or perhaps cavitation needs to be applied in conjunction with another treatment such as heat, UV or active substance.

When sonication is combined with chemical treatments the biocidal action can be significantly improved. For example, after 20 min exposure, *Dunaliella tertiolecta* mortality resulting from the individual treatment of sonication, 100 ppm of ozone and 100 ppm of hydrogen peroxide ranged from 33-40%, while 71-81% mortality was achieved when sonication was combined with ozone or hydrogen peroxide (Gavand et al. 2007). Furthermore, a mortality of 100% was achieved following 5 min exposure with the combined treatments of hydrogen peroxide, ozone and sonication. Likewise, the combination of chlorine (1 ppm) and cavitation reduced bacteria by 86% after 5 min, and 100% after 20 min (Mason et al. 2003), demonstrating that it is possible to combine cavitation with chemical biocides to achieve an increase in organism removal and/or a reduction in the amount of biocide required for effective treatment. Similarly, Sassi et al. (2005) showed that ultrasound treatment alone resulted in the mortality of 80-99% of zooplankton but the combination of cavitation and UV achieved mortality rates of 97-100%.

To date, the majority of studies investigating the effectiveness of ultrasonic treatment against

marine organisms have been conducted using only small volumes of water and low flow rates, typically 5-375 L/min. The up-scaling of cavitation systems for ballast water treatment may prove problematic as flow rates of a single ballast pump may be even higher than 5,000m<sup>3</sup>/h. One potential solution would be to recirculate ballast water through the ultrasound device but this may not be possible on short voyages due to time constraints. In addition, recirculating ballast water may also cause ship stability problems, may resuspend ballast tank sediment thus increasing turbidity, and due to the configuration of ballast tanks, some of the ballast water may not be exposed to the cavitation device (Sassi et al. 2005). Ultrasound decontamination of ballast water has so far not been tested but is likely to require pre-filtration, as cavitation is unlikely to penetrate sediments (Rigby and Taylor 2001; Mason et al. 2003). Pre-filtration may however decrease effectiveness against smaller organisms by removing particulate matter that would increase kills through collision. Overall effectiveness is also influenced by water temperature, water depth and organism concentration. Sassi et al. (2005) estimate the cost of an ultrasound ballast water treatment system for a ship with a ballast capacity of around 50,000 tonnes is in the vicinity of US\$6 million with an operational cost of approximately \$0.56 per tonne of ballast water, but Environmental Technologies Inc. claim to be developing a system costing only US\$500,000 with an operational cost of US\$0.005 (Lloyd's Register 2007). Apart from costs, other aspects that require consideration include health and safety issues, which may arise from noise generated by the ultrasound treatment unit, high energy requirements and hull integrity problems due to repeated exposure to cavitation.

#### *Electrocution*

Electrocution has been considered as a potential treatment of ballast water organisms during ballasting and deballasting and was first proposed by Montani et al. (1995). In their study, germination of dinoflagellate cysts was inhibited using a dosage of 100 V AC for a period of 5 s. Hallegraeff et al. (1997) demonstrated that *A. catenella* cysts were readily killed using a 5 s shock applied to a 4 cm<sup>2</sup> area (>5 V cm<sup>2</sup>); however cysts of *G. catenatum* exhibited a 7% germination success when dosed with a shock of

7.5 V cm<sup>2</sup> for 5 s. No direct comparison can be made between results obtained by these two studies as Montani et al. (1995) provide no detailed description of the apparatus utilised or the precise area that the electric shock was applied. The biocidal action of this electrocution technique was claimed to be the generation of chlorine and heat rather than the electric shock itself (Hallegraeff et al. 1997).

The inactivation of bacteria by generating pulsed electric fields has been demonstrated by Blatchley and Isaac (1992) and Aronsson et al. (2001). The latter authors examined the killing effect of pulsed electric fields on four micro-organisms, including *E. coli*, and found significant reductions do occur (4-to 8-log). Blatchley and Isaac (1992) and Aronsson et al. (2001) suggest the reduction of bacteria can be directly ascribed to the electric treatment, rather to the generation of other chemicals or heat during the process. Treated cells were found to have suffered no membrane damage suggesting that pulsed electric field treatment has profound effects on the intracellular organisation of micro-organisms (Aronsson et al. 2001). However, it is possible that the killing action demonstrated in these experiments is due to other chemical reactions occurring as electrical currents are passed through the liquid medium.

Dosing organisms with an electric shock during ballasting would require the electric shock itself to be biocidal. As the production of chlorine has been demonstrated as the biocidal component of electric shock treatment, this would negate electrocution as a ballast water biocide, however electrolysing seawater has been shown to be an economical way of producing free chlorine (e.g. Dang et al. 2004; Matousek et al. 2006).

#### *Mechanical damage*

The use of high velocity pumps during ballast water intake and discharge may cause lethal damage to some organisms by mechanical abrasion. Taylor et al. (2002) suggest that these systems are hard to install and the cost for installing additional infrastructure to create high velocity jets of water in ballast tanks or pipelines would be prohibitively expensive. Additionally, once water velocity exceeds a certain point (~3 m/s), corrosion problems may become a concern (Taylor et al. 2002). Veldhuis et al. (2006) found that the use of a centrifugal water pump with a

capacity of 530 m<sup>3</sup>/h effectively reduced the total number of living zooplankton, indicating that current ballast water pumps may reduce the survival of larger organisms, but micro-organisms, especially bacteria, would be expected to pass through the pump systems with minimal mortality. Hillman et al. (2004) tested the effectiveness of a prototype high-velocity sonic/shear disintegrator which generates shear and sonic stresses to destroy organisms. Initial results showed that the device was capable of destroying between 97.7 and 100% of *Artemia nauplii* and reduced the hatching rate of *Artemia* cysts by 47%. Promising research has also been conducted on a mechanical treatment device called the ‘Special Pipe System’ which terminates organisms using sheer stress and cavitation produced by the special plate structures of the system. This system is used in conjunction with ozone and is discussed later. The OceanSaver ® Ballast Water System (see later) also includes a cavitation unit.

#### Magnetic treatment

Magnetic treatment has been utilised for the elimination of bacterial growth in diesel fuel. In this process, a magnetic field is pulsed along fuel lines generating very low frequency, non-ionising electromagnetic radiation. This radiation has a much lower frequency than microwave radiation, even lower than radio-waves, yet has a controlling effect on microorganisms (Clear-water Systems Corporation 2004). However, this

technique is considered bacteriostatic rather than bactericidal, as the bacteria are controlled rather than killed. Oemcke (1999) tested a magnetic treatment system on spores of *Bacillus subtilis* and found no effect. No efficacy data are available.

Hitachi have developed an environmentally friendly ballast water treatment system called ‘ClearBallast’, which treats ballast water by removing target organisms and other objects using flocculating agents and magnetic separation. The system operates by the addition of a magnetic powder, a coagulant and a flocculant, which collide with small organisms and aggregate to form magnetic flocs. The flocs are then separated from the ballast water by magnetic separation technology and are removed in a rotating filter drum resulting in the formation of a concentrated sludge that is temporarily stored in part of the treatment system and must be disposed of in landfill (Figure 1).

This coagulation magnetic separation method is suggested to remove not only zooplankton and phytoplankton but also bacteria, sediment and suspended solids in the ballast water (Saho et al. 2004). Land-based tests have been conducted on a pilot-scale system at a flow rate of 50 m<sup>3</sup>/h using water taken directly from Tokyo Bay. Results of the organism removal efficiency of the system revealed that it was able to meet the BWM Convention’s IMO’s D-2 regulation for the discharge of ballast water. The system removed 100% of organisms greater than 10 µm in dimension, reduced the concentration of

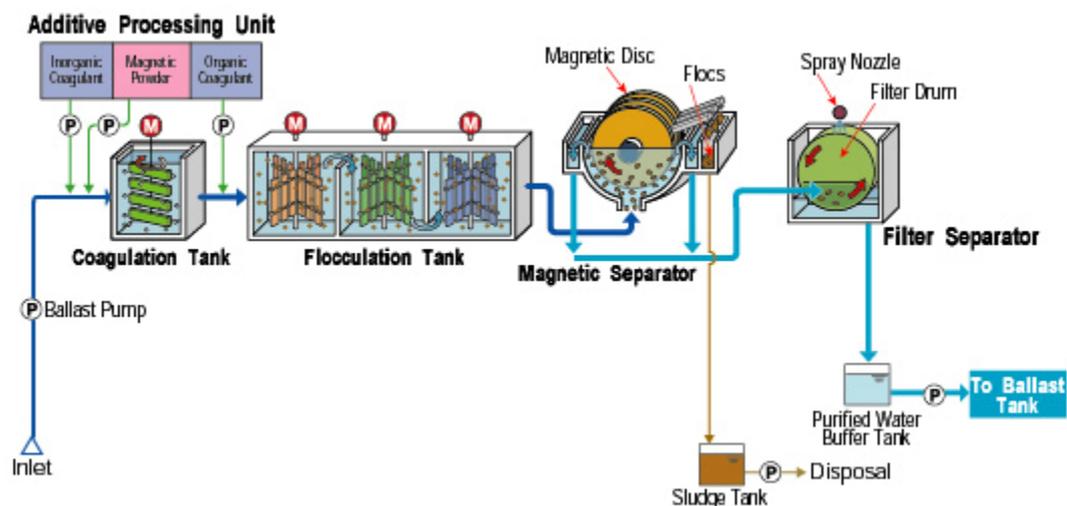


Figure 1. Schematic diagram of the operating processes of the Hitachi ‘Clearballast’ ballast water treatment system  
From: <http://www.hitachi-pt.com>

*E. coli* from 1,100 to 2 cfu/100 ml and reduced the suspended solid concentration to non-detectable levels (MEPC 2007b).

The system is considered to be environmentally friendly since most of the three active substances (Triiron tetraoxide, basic aluminium chloride, acrylamide sodium acrylate copolymer) that are added to the ballast water are collected in the flocs and removed (MEPC 2007b). No volatile organic compounds have been identified in treated ballast water but trace amounts of aluminium (0.08 mg/L) were detected (MEPC 2007b). The use of the 'ClearBallast' system on large ships may be limited by space restrictions. The manufacturer suggests that the system can be scaled up or multiple sets of equipment can be installed allowing a commercial system to treat ballast water at flow rates from 50 to 10,000 m<sup>3</sup>/h, however the volume of the major components of the system increases in proportion to the flow rate. A treatment system capable of handling 200 m<sup>3</sup>/h has a footprint of 20 m<sup>2</sup>, while 100 m<sup>2</sup> is required for a system with a capacity of 2,000 m<sup>3</sup>/h (Lloyd's Register 2007). No installation or operational costs are available at the current stage of development but the system has received Basic Approval from the IMO for the use of active substances.

The above results would suggest that marine microorganisms are not likely to be killed directly by magnetic treatment but the use of systems incorporating magnetic separation and filtration may provide an effective ballast water treatment.

### Active Substances

Many chemical treatment options have been proposed as potential solutions to the problem of ballast-mediated aquatic organism introductions. For a potential chemical treatment option to be effective it must: 1) inactivate all ballast water organisms including resistant resting life stages; 2) not produce toxic by-products; 3) not be hazardous to ships' crew nor corrosive to ships' structures; 4) be cost effective; and 5) degrade at a rate that allows safe discharge of residual chemicals into the aquatic environment. The following section discusses the advantages and limitations of proposed chemical options for the control of ballast water organisms. Table 8 provides a summary of the biological efficacy of potential active substances.

### Chlorine

For the past few decades, chlorine has been used as the disinfectant of choice in water treatment technologies due to its cost-effectiveness. Chlorine can be dosed to water in a variety of forms including liquefied chlorine gas, sodium hypochlorite, calcium hypochlorite, or can be generated electrolytically from seawater. The broad-spectrum biocidal activity of chlorine is mediated by hypochlorous acid, which is formed in aqueous solutions at pH 5-8 (Gardner and Peel 1991). The toxicity of chlorine is a function of several factors including chlorine concentration, pH, exposure time, and type and quantity of chlorine compounds formed.

Chlorination has been shown to eliminate aquatic organisms but the concentration required varies considerably with different organisms. Vegetative algal cells and free-living zooplankton can be killed at concentrations of 1-100 ppm (Laughton et al. 1992; Piyatiratitivorakul et al. 2002; Stocks et al. 2004b; Zhang et al. 2004); however resistant organisms, such as dinoflagellate cysts, zooplankton resting stages and *Bacillus subtilis* spores require considerably higher concentrations (486-2,500 ppm) (Bolch and Hallegraeff 1993; Stocks et al. 2004b; Gray et al. 2006).

Bacterial susceptibility to chlorine varies greatly, with free-living gram-positive and gram-negative bacteria highly susceptible, whereas acid-fast bacteria, bacteria associated with crustaceans and bacterial spores require higher doses. For example, *Bacillus subtilis* spores require a chlorine concentration of 500 ppm for inactivation to occur (Sagripanti and Bonifacino 1996), whereas Zhang et al. (2004) completely eliminated *Vibrio* sp. at 5 ppm. Similarly, Sousa et al. (2001) found doses of 10 ppm were effective in killing free-living *Vibrio cholerae*; however this concentration was insufficient to destroy *Vibrio*'s adhering to crustaceans. It has been suggested that the presence of crustaceans causes an increase in organic matter, reducing the bactericidal properties of chlorine (Sousa et al. 2001). Another study found toxigenic strains of *V. cholerae* required a much higher dose of 100 ppm for the control of free-living cells, with even higher doses (800 ppm) required to achieve satisfactory control of attached *V. cholerae*, yet even at this concentration, regrowth was apparent within 20 min (McCarthy and Miller 1994). Chlorination at 800 ppm was not effective

**Table 8.** Summary of biological efficacy of proposed chemical ballast water treatment options

Treatment Option	Organism	Treatment	Efficacy	Reference	
<b>Chlorine</b>	Marine bacteria (free-living)	1-100 ppm, 5 min-24 h	100% mortality	McCarthy and Miller (1994); Sousa et al. (2001); Stocks et al. (2004b); Zhang et al. (2004)	
	Marine bacteria (attached to crustaceans)	800 ppm, 5 min	below detection	McCarthy and Miller (1994); Sousa et al. (2001); Zhang et al. (2004)	
	Bacterial spores	500 ppm	99.9% inactivation	Sagripani and Bonifacino (1996)	
	Vegetative microalgae	1-100 ppm, 24-72 h	100% mortality	Piyatiratitivorakul et al. (2002); Stocks et al. (2004b); Zhang et al. (2004)	
	Dinoflagellate cysts ( <i>G. catenatum</i> )	>500 ppm, 24 h	100% inactivation	Bolch and Hallegraeff (1993)	
	Zooplankton	2-40 ppm, 24 h	100% mortality	Stocks et al. (2004b); Zhang et al. (2004)	
	Zooplankton resting stages	100-2,500 ppm, 24 h	100% mortality	Stocks et al. (2004b); Gray et al. (2006)	
electrolytic chlorine	Marine bacteria	3-4 ppm	99.99-99.999% mortality	Dang et al. (2004); Matousek et al. (2006)	
	Phytoplankton	3-4 ppm	72%->99% mortality	Dang et al. (2004); Matousek et al. (2006)	
	Zooplankton	4-15 ppm, 12-24 h	95->99% mortality	Dang et al. (2004); Matousek et al. (2006)	
<b>Chlorine dioxide</b>	Marine bacteria	5-20 ppm, 24 h	100% mortality	Ecochlor (2003); Gregg and Hallegraeff (2007)	
	Vegetative microalgae	3-25 ppm, 30-120 min	100% mortality	Junli et al. (1997); Gregg and Hallegraeff (2007)	
	Dinoflagellate cysts	25 ppm, 2 weeks	100% inactivation	Gregg and Hallegraeff (2007)	
	Zooplankton	5 ppm	70-100% mortality	Junli et al. (1997); Oemcke (1999)	
	Zooplankton ( <i>Artemia</i> cysts)	3 ppm, 40 h	97% inactivation	Oemcke (1999)	
	chlorine dioxide generators	Marine bacteria (including <i>V. cholera</i> and <i>E. coli</i> )	5 ppm, 24 h	below detection	Ecochlor (2003); Swanson and Perlich (2006)
		Vegetative microalgae	5 ppm 24 h	99.6% mortality	Ecochlor (2003)
Zooplankton		5 ppm, <24 h	98.4-100 % mortality	Ecochlor (2003); Swanson and Perlich (2006)	
<b>Ozone</b>	Marine bacteria (free-living)	>5 ppm Total Residual Oxidants (TRO), 5-10h	up to 99.99% reduction	Herwig et al. (2006); Perrins et al. (2006a)	
		0.15-0.20 ppm (residual ozone), 180 sec	99.99% inactivation	Liltved et al. (1995)	
	Bacteria ( <i>Bacillus subtilis</i> )	8-14 ppm TRO, 24 h	complete inactivation	Oemcke (1999)	
	Dinoflagellates	>5 ppm TRO, 10 h	>99% reduction	Herwig et al. (2006)	
	Microflagellates	>5 ppm TRO, 10 h	96-99% reduction	Herwig et al. (2006)	
	Diatoms	>5 ppm TRO, 10 h	17-135% of initial concentrations	Herwig et al. (2006)	
	Zooplankton	0.75-7 ppm, 5-48 h	90-100% reduction	Sassi et al. (2005); Jones et al. (2006); Herwig et al. (2006); Perrins et al. (2006a)	

**Table 8.** Summary of biological efficacy of proposed chemical ballast water treatment options (continued)

Treatment Option	Organism	Treatment	Efficacy	Reference
<b>Hydrogen peroxide</b>	Bacterial spores	100,000-140,000ppm	90-99.99% mortality	Sagripanti and Bonifacino (1996)
	Vegetative microalgae	3-100 ppm, 15 min-48 h	100% mortality	Ichikawa et al. (1993); Piyatiratitivorakul et al. (2002);
	Dinoflagellate cysts	100-10,000 ppm, 24-96 h	100% inactivation	Bolch and Hallegraeff (1993); Ichikawa et al. (1993); Montani et al. (1995)
	Zooplankton	10 ppm (increased pH), < 5min	100% mortality	Kurizian et al. (2001)
<b>Peracetic acid</b>	Coliform bacteria	6-8 ppm	>97% reduction	Baldry and French (1989)
	Bacterial spores	300 ppm	99.99% mortality	Sagripanti and Bonifacino (1996)
<b>Glutaraldehyde</b>	Bacteria (free-living)	8-14 ppm	83% inhibition	Sano et al. (2003)
	Bacterial spores	20,000 ppm	99.99% inactivation	Sagripanti and Bonifacino (1996)
	Zooplankton	11-550 ppm, 24-48 h	90% mortality	Sano et al. (2003, 2004)
	Zooplankton ( <i>Artemia salina</i> cysts)	353 ppm, 72 h	90% mortality	Sano et al. (2004)
<b>Peraclean®Ocean</b>	Marine bacteria	125-250 ppm	100% mortality	Gregg and Hallegraeff (2007)
	Vegetative microalgae	50-200 ppm, 48 h	100% mortality	Wright et al. (2004); Fuchs et al. (2001); Gregg and Hallegraeff (2007)
	Dinoflagellate cysts	150-400 ppm, 2 weeks	100% inactivation	Gregg and Hallegraeff (2007)
	Zooplankton	100-400 ppm, <1-72 h	>90-100% mortality	Fuchs and de Wilde (2004); Wright et al. (2004); Veldhuis et al. (2006); de Lafontaine et al. (2008a,b)
	Zooplankton ( <i>Artemia salina</i> cysts)	>350 ppm-700 ppm, 72 h	100% inactivation	Fuchs et al. (2001); Fuchs and de Wilde (2004)
	Freshwater fish species	100-150 ppm, <19 h	100% mortality	de Lafontaine et al. (2008a)
	Fish eggs ( <i>Clupea harengus</i> )	200-400 ppm, 1-16 h	100% mortality	Fuchs and de Wilde (2004)
<b>SeaKleen®</b>	Marine bacteria	1-200 ppm,	100% mortality	Wright and Dawson (2001); Cutler et al. (2004); Gregg and Hallegraeff (2007)
	Vegetative microalgae	0.5-2 ppm, 24-48 h	100% mortality	Wright and Dawson (2001); Cutler et al. (2004); Gregg and Hallegraeff (2007)
	Dinoflagellate temporary cysts	2 ppm, 2 h	100% mortality	Cutler et al. (2004)
	Dinoflagellate resting cysts	6-10 ppm, 2 wk ( <i>Alex. catenella</i> no control at 10 ppm)	100% inactivation	Gregg and Hallegraeff (2007)
	Zooplankton	0.5-2 ppm, 24-48 h	100% mortality	Cutler et al. (2004); Wright et al. (2004)
	Zooplankton resting eggs	2.6-12.7 ppm, 24 h	90% mortality	Raikow et al. (2006)
<b>Acrolein®</b>	Bacteria	3-10 ppm	>99.99->99.999% reduction	Penkala et al. (2004)
	Marine bacteria (onboard trial)	9-15 ppm, 24-72 h	99.99-99.9999% reduction	Penkala et al. (2004)
	Phytoplankton	1 ppm	>99.999 reduction	Penkala et al. (2004)
	Zooplankton	0.18-0.5 ppm, 96 h	50 % mortality	Penkala et al. (2004)

**Table 8.** Summary of biological efficacy of proposed chemical ballast water treatment options (continued)

Treatment Option	Organism	Treatment	Efficacy	Reference
<b>Hydroxyl radicals</b>	unicellular algae, protozoans, bacteria	0.63 mg/L, 2.67-8 sec	100% mortality	Bai et al. (2005); Zhang et al. (2006)
<b>De-oxygenation</b>	Zooplankton ( <i>Coscinasterias calamaria</i> )	>10 mM glucose, 19 d (>5 ppm O <sub>2</sub> )	40% mortality	Mountfort et al. (1999a)
	Macroalgal zoospores ( <i>Undaria pinnatifida</i> )	20 mM glucose, 28 d (always >5 ppm O <sub>2</sub> )	ineffective	Mountfort et al. (1999a)
addition of sulphide	Zooplankton ( <i>Coscinasterias calamaria</i> )	60 µM sulphide, 68h (always >5 ppm O <sub>2</sub> )	100% mortality	Mountfort et al. (1999a)
	Macroalgal zoospores ( <i>Undaria pinnatifida</i> )	200 µM sulphide, 36 d (>5 ppm O <sub>2</sub> )	40% mortality	Mountfort et al. (1999a)
vacuum chambers	Zooplankton >75 µm	< 1 ppm O <sub>2</sub> , <3 d	100% mortality	Browning Jr. et al. (2004)
nitrogen sparging	Zooplankton ( <i>Coscinasterias calamaria</i> )	2.3 ppm, 30 min	99.9% mortality	Mountfort et al. (1999a)
	Macroalgal zoospores ( <i>Undaria pinnatifida</i> )	2.8 ppm O <sub>2</sub> , 10 min	99.9% mortality	Mountfort et al. (1999a)
sparging 86% N <sub>2</sub> , 12% CO <sub>2</sub> , 2% O <sub>2</sub>	Zooplankton	nondetectable O <sub>2</sub> , 15 min-48 h	>95% mortality	Husain et al. (2004)
	Marine Bacteria ( <i>Vibrio cholerae</i> )	nondetectable O <sub>2</sub> , 24 h	>99% mortality	Husain et al. (2004)
Venturi Oxygen Stripping™	Zooplankton	0.27-<1 ppm O <sub>2</sub> , <48-120 h	99-100% mortality	Tamburri et al. (2004); NEI Marine (2007)
	Phytoplankton	<1 ppm O <sub>2</sub> , 120 h	100% mortality	NEI Marine (2007)
	Bacteria ( <i>Enterococci</i> , <i>E. coli</i> )	<1 ppm O <sub>2</sub> , 120 h	99.9% reduction	NEI Marine (2007)
<b>pH adjustment</b>	Dinoflagellate cysts	pH 2-10	no effect	Bolch and Hallegraeff (1993)
	Mixed zooplankton	pH 8.5-10	no effect	Kurizian et al. (2001)
	Ctenophore <i>Mnemiopsis leidyi</i>	pH 8.5-10	no effect	Kurizian et al. (2001)
<b>Salinity</b>	Dinoflagellate cysts	15-50 ‰ salinity	no effect	Bolch and Hallegraeff (1993)
		100 ‰ salinity	No germination	

against *V. cholerae* when applied to 100% or 10% strength ballast water suggesting that attachment to organisms and particulate matter enhanced their survival (McCarthy and Miller 1994).

The biocidal activity of chlorine may be increased if combined with other treatment technologies such as heat or ultrasonic treatment. Mason et al. (2003) found that the lethality of ultrasound on bacterial growth doubled after 20 mins when combined with chlorine at a concentration of 1 ppm. This would also act to drastically reduce the treatment cost.

Chlorine concentrations required for the effective treatment of ballast water are likely to be prohibitively expensive. Bolch and Hallegraeff (1993) indicate that the costs required for

adequate chlorination of 50,000 tonnes of ballast water would be in the vicinity of US\$160,000. Electrolysed seawater may be used to generate chlorine for shipboard ballast water treatment (Dang et al. 2004; Matousek et al. 2006). Matousek et al. (2006) found that a 3 ppm chlorine concentration generated electrolytically from seawater reduced bacteria by more than 99.999% and reduced phytoplankton and mesozooplankton by 99%. Conversely, Dang et al. (2004) found that only 72% of total phytoplankton can be killed if raw seawater is treated by electrolysis with an initial chlorine concentration of 4 ppm. Electrolysing seawater may act to reduce the cost of chlorine treatment; however, several other factors negate the use of chlorination for the control of organisms in

ships' ballast water. Foremost, there is significant concern over the creation of toxic organochlorides and subsequent environmental impacts at the port of ballast discharge. A shipboard assessment of the use of chlorine for ballast water treatment conducted by Vianna da Silva and da Costa Fernandes (2004) found that chlorine concentrations above 3 ppm should not be used due to the formation of high concentrations of toxic by-products such as carcinogenic trihalomethanes (THM) and haloacetic acids (HAA). These products are formed when chlorine reacts with naturally occurring organic and inorganic matter and levels tend to increase with pH, temperature, time and quantity of organic matter. Once discharged in ballast water, these products can persist in the marine environment, bioaccumulate in the food chain and can interfere with or destroy the hormonal systems of marine organisms (Jenner et al. 1997). Additionally, ballast tank sediment is likely to reduce the available free chlorine levels (Bolch and Hallegraeff 1993; Gray et al. 2006); and chlorine treatment has been claimed to increase corrosion of the vessel (Stocks et al. 2004b; Zhang et al. 2004).

#### *Chlorine dioxide*

Chlorine dioxide (ClO<sub>2</sub>) is not used widely in wastewater disinfection due to the high cost involved compared with chlorination. However, the use of ClO<sub>2</sub> in ballast water disinfection is considered advantageous over chlorine for several reasons. Chlorine dioxide treatment is not particularly reactive with organic material, can maintain the bactericidal and inactivation effects within a wider pH range than chlorine and is considered to be more environmentally friendly than chlorine as it does not involve or create free available chlorine or chlorinated by-products. (Muntisov et al. 1993; Junli et al. 1997; Vianna da Silva and da Costa Fernandes 2004). The major by-products resulting from chlorine dioxide disinfection are chlorite, chlorate, and organic, biodegradable by-products such as carbonyl compounds and short chain carboxylic acids (Raczyk-Stanislawiak et al. 2004). Chlorate has been documented to be toxic to marine micro-algae, particularly in nitrate-limited waters (Stauber 1998), however such toxic chlorate concentrations are unlikely to result from the discharge of ballast water.

The majority of ClO<sub>2</sub> work has been conducted on freshwater organisms (e.g. Korich

et al. 1990; Lykins Jr. et al. 1994; Junli et al. 1997), with only few studies available for marine systems (Hillman et al. 2004; Gregg and Hallegraeff 2007). Nonetheless, results indicate that it is an excellent bactericide and sporicide, and is more effective in controlling vegetative bacteria and viruses compared with chlorine. For example, a range of viruses could be controlled at a concentration of 1-7 ppm ClO<sub>2</sub>, whereas a 7 ppm dose of chlorine had no observable effects (Junli et al. 1997). Yet, Junli et al. (1997) also found that there was no significant difference in the inactivation effect on algae between ClO<sub>2</sub> and chlorine, but concludes that ClO<sub>2</sub> is better than or comparable to liquid chlorine in the killing effect on algae.

Efficacy studies conducted in seawater have found that vegetative cells of the dinoflagellates *Alexandrium catenella*, *Gymnodinium catenatum*, *Protoceratium reticulatum* and *Scrippsiella trochoidea* are eliminated at 25 ppm after 2 h; and sexual resting cysts of *G. catenatum* and *P. reticulatum* are inactivated following 2 wk exposure to 50 ppm (Gregg and Hallegraeff 2007). Hillman et al. (2004) tested the effectiveness of a chlorine dioxide generator against *Artemia* cysts and concluded that a 3 ppm concentration can reduce the hatching rate by 97%.

Newer ClO<sub>2</sub> generators are suggested to produce no chlorinated by-products or toxic residual material at discharge. The Ecochlor® Ballast Water Treatment System generates chlorine dioxide using the Eka Chemical Purate® technology, a method that differs from conventional chlorine dioxide generation methods in that it does not involve or create free available chlorine or chlorinated by-products. The treatment system uses Purate® solution (containing 40% sodium chlorate and 8% hydrogen peroxide) and sulphuric acid to produce ClO<sub>2</sub>, which is injected into ballast water during intake.

Laboratory experiments demonstrated that an initial ClO<sub>2</sub> concentration of 5 ppm was effective at eliminating bacterial and planktonic populations to the extent that no regrowth was observed (Swanson and Perlich 2006). Shipboard studies on the biological efficacy of the treatment system as well as degradability and corrosion tests were carried out onboard the MV *Atlantic Compass* in 2005. Results from these experiments showed that the application of 5 ppm of ClO<sub>2</sub> immediately eradicated 100% of zooplankton, reduced the abundance of total coliform bacteria, *Vibrio* colonies and *E. coli* to

non-detectable levels within the first 24 h, and virtually eliminated all phytoplankton biomass (Swanson and Perlich 2006). Some recovery of bacteria and phytoplankton was observed after 5 days indicating that the treatment did not eliminate 100% of organisms. This regrowth was attributed to the presence of a biofilm in the ballast tanks which provided refuge for the organisms that survived (Swanson and Perlich 2006).

Degradability studies conducted during the shipboard trials determined that  $\text{ClO}_2$  remained active in the ballast tanks for several hours but degraded at a rate that resulted in no residual  $\text{ClO}_2$  in the ballast water at the time of discharge. For example, an initial dosage of 5 ppm left no residual  $\text{ClO}_2$  after 20-24 h when the temperature of ballast water was between 10 and 12°C, whilst an initial dosage of 8 ppm in 25-26°C ballast water left no trace after 24-25 h (Swanson and Perlich 2006). Furthermore, corrosion tests conducted in ballast tanks indicated that  $\text{ClO}_2$  had no adverse effect on corrosion, in fact a slight decrease in corrosion was observed in the treated tanks during one experiment (MEPC 2008a). It should be noted that the corrosion tests were only carried out for a period of 28-32 days. Much longer investigations are required to fully understand the effect of the treatment system on corrosion rates.

Advantages of the Ecochlor<sup>®</sup> Ballast Water Treatment System are that it is able to operate effectively under extremely varied water quality conditions at any temperature or salinity. It also has the capacity to treat ballast water at high flow rates. The system does not require the storage of large amounts of active substances onboard but does require the storage of the precursor chemicals (<http://www.ecochlor.com>). According to Carney et al. (2008), the capital cost of the system is between US\$260,000 and US\$400,000 for flow capacities of 200 m<sup>3</sup>/h and 2000 m<sup>3</sup>/h, respectively, with an operating cost of US\$0.06 per tonne of ballast water.

In summary, it appears that  $\text{ClO}_2$  is toxic to a wide range of aquatic organisms and should be considered as a ballast water treatment. Indications are that it is more environmentally friendly than chlorine as degradation products are not expected to persist or bioaccumulate in the marine environment. Further work is required to assess the ability of the biocide to inactivate organisms in ballast tank sediment and possible corrosion impacts.

### *Ozone*

Ozone is a powerful oxidant used to control microorganisms in a variety of applications. It has been demonstrated to be an excellent sterilisation agent in freshwater systems (Korich et al. 1990). However, the biocidal activity of ozonated seawater may differ considerably from that of ozonated freshwater as ozone reacts with bromide and chloride ions to form oxidants in seawater (Sugita et al. 1992b).

Ozone is an unstable gas that decomposes readily to oxygen, therefore must be generated on-site. Ozone can be safely generated from air and could prove beneficial over many other chemical treatment options for the following reasons. Firstly, there is no need to store large amounts of chemicals onboard ships. Secondly, ozone is considered advantageous over other chemical oxidants, as it poses fewer environmental problems. Toxic by-products created during the ozonation of seawater (e.g. brominated organics, bromate, bromamine) can cause environmental impacts at low concentrations, however, concentrations required to impact on most organisms are considerably higher than those generated from ozonation (Stewart et al. 1979).

Ozone reacts with bromide in seawater resulting in a half-life of 5.3 s (Andersen et al. 1995), nonetheless it is possible that molecular ozone will make some contribution to disinfection in seawater regardless of its reactions with bromide and chloride, however, the majority of disinfection is believed to be due to the production of hypobromous acid/hypobromite (Perrins et al. 2006b), which are generally measured as total residual oxidants (TRO's).

The ozonation of seawater has been shown to successfully remove bacterial fish pathogens and viruses at low concentrations with low exposure times (Sugita et al. 1992b; Liltved et al. 1995). Sugita et al. (1992b) propose that ozone treatment at a total residual oxidant (TRO) concentration of more than 1 ppm for several min is able to disinfect seawater, while Liltved et al. (1995) demonstrated that a concentration of 0.10-0.20 ppm of residual ozone inactivated all tested viral and fish pathogens within 3 min. Perrins et al. (2006a) found that although culturable bacteria were initially controlled at TRO concentrations of >1 ppm, once TRO fall below the bacterial inhibition threshold of ~0.5 ppm, heterotrophic bacteria rapidly grow.

Results from laboratory studies suggest that some organisms are resistant to ozone. For example, Andersen et al. (1995) assessed ozone treatment using several planktonic algae and crustaceans as model organisms. All test organisms were effectively controlled by ozonation but dosage required varied between organisms. Dosages required to inactivate crustaceans were found to be 2-5 times greater than those needed to inactivate algal species such as *Amphidinium carterae* and *Karlodinium veneficum* (= *Gymnodinium galatheanum*) (Andersen et al. 1995). Experiments conducted on *Bacillus subtilis* found that much higher TRO dosages of up to 14 ppm are required for adequate inactivation at a pH of 8 with a 24 hr contact time, however reducing the pH to 7 resulted in a reduced dose of 9 ppm required for disinfection (Oemcke 1999). Other organisms that have been demonstrated to be resistant to ozone treatment include dinoflagellate cysts, Cirripeda nauplii, Polychaeta larvae, copepod nauplii, cyclopoid and harpacticoid copepods, mysid shrimp and shore crabs (Deacutis and Ribb 2002; Herwig et al. 2006; Perrins et al. 2006a).

Several companies have produced onboard treatment systems that inject ozone into ships' ballast water during ballast intake; however doubts exist as to whether these systems cost-effectively control all organisms. For example, mesocosm and shipboard testing of the biological efficacy of the Nutech O<sub>3</sub> ozone generator found that the system was capable of significant reductions of up to 99.99% of bacteria, >99% of dinoflagellates, 99% of microflagellates and zooplankton after 5-10 h treatment when the TRO levels exceeded 5 ppm (Herwig et al. 2006; Perrins et al. 2006a). However these reductions varied considerably between experiments and between sampling locations as the distribution of ozone was not homogenous (Herwig et al. 2006). The treatment system was much less effective against diatoms and a number of crustacean species (Herwig et al. 2006; Perrins et al. 2006a). The experiments did not assess treatment effects on resting stages of zooplankton or phytoplankton.

The above results raise doubts to whether ozone treatment can cost-effectively control all ballast water organisms as many organisms, especially bacterial spores, dinoflagellate cysts and many zooplankton species, are likely to survive ozone treatment at the concentrations that are considered environmentally safe and achievable in onboard situations. Ozone may

provide an effective control option for vegetative microalgae, pathogenic bacteria and viruses present in ballast water, though a fine filtration pre-treatment may be necessary to remove resistant organisms. Contact times necessary for bacterial control indicate that ballast tanks would need to be continuously dosed with ozone. Also, steel in vessel structures is likely to be oxidised by ozone and hypobromous acid increasing corrosion (Oemcke and van Leeuwen 1998). Projected costs of an ozone treatment system are in the vicinity of US\$800,000 to \$1.6 million with an operational cost of US\$0.28-0.32 per tonne of ballast water (Sassi et al. 2005; Carney et al. 2008).

#### *Hydrogen peroxide*

Hydrogen peroxide is an oxidative biocide considered attractive for the treatment of ballast water as it is known to be of limited risk to humans and decomposes rapidly resulting in harmless by-products of oxygen and water. It is currently used as a disinfectant in a variety of applications including laboratory and medical applications, and even as a replacement to chlorine for the treatment of swimming pools.

Reported hydrogen peroxide concentrations required for the elimination of marine organisms range from 3 ppm for vegetative dinoflagellate cells of *Karenia mikimotoi* to over 140,000 ppm for *B. subtilis* spores (Ichikawa et al. 1993; Sagripanti and Bonifacino 1996). A large discrepancy exists in the literature in relation to the concentration required to eliminate vegetative algal cells and dinoflagellate cysts. Dinoflagellate cyst inactivation has been achieved with doses between 100 and 10,000 ppm (Bolch and Hallegraeff 1993; Ichikawa et al. 1993; Montani et al. 1995; Hallegraeff et al. 1997). This discrepancy may be due to different resistances of isolates utilised in these experiments, different organic loadings of seawater or different brands of hydrogen peroxide may vary in potency. Similarly, different exposure times used may explain this inconsistency. For example, Piyatiratitivorakul et al. (2002) reported that a concentration of 100 ppm for 24 h resulted in 40 and 66.6% mortality in the raphidophytes *Heterosigma akashiwo* and *Chattonella marina* respectively, whereas 30 ppm (*H. akashiwo*) and 10 ppm (*C. marina*) for 48 h resulted in the complete mortality. This would suggest that the exposure time is a very important aspect of the biocidal action of

hydrogen peroxide. Kuzirian et al. (2001) found that elevating the pH of ballast water reduced the hydrogen peroxide concentrations required (1 ppm) to eliminate a range of invertebrate taxa including the ctenophore *Mnemiopsis leidyi*, the hydrozoan *Pennaria* sp., and a range of polychaetes, crustaceans, chordates and larval bivalves. Similarly, Mesbahi (2004) suggest that the efficacy of hydrogen peroxide can be enhanced by elevated temperature (up to 35°C).

Bacterial spores are the most resistant marine organisms to hydrogen peroxide treatment requiring doses upward of 100,000 ppm for mortality to occur (Sagripanti and Bonifacino 1996). The high concentrations needed for spore and dinoflagellate cyst inactivation would exclude hydrogen peroxide as a ballast water treatment as the cost involved are likely to be substantial. Additional concerns include hazards associated with the distribution, handling and onboard storage of large volumes of hydrogen peroxide. Hydrogen peroxide can however be produced *in-situ* by means of an electrochemical conversion of dissolved oxygen, which is carried out in a specially designed and patented electrochemical reactor. The PeroxEgen™ on-board hydrogen peroxide water treatment system is claimed to be able to control ballast water organisms (including bacteria) by injecting low hydrogen peroxide concentrations (<100 ppm) into ballast water during intake (Eltron Water Systems 2007), however efficacy data are not available. If this method can safely and effectively produce hydrogen peroxide concentrations able to inactivate resistant organisms, it may prove a feasible ballast water treatment.

#### *Glutaraldehyde*

Glutaraldehyde is an organic biocide which has been proposed, either on its own or in combination with surfactant, for the treatment of vessels carrying little or no ballast to control organisms present in ballast tank residues and sediment (Sano et al. 2003, 2004). It has been demonstrated to successfully control the marine bacterium *Vibrio fischeri* at a concentration of 8-14 ppm; however doses of 20,000 ppm are required to inactivate *B. subtilis* spores (Sano et al. 2003; Sagripanti and Bonifacino 1996).

Glutaraldehyde is most active at higher temperatures and above a pH of 7.5 (Sagripanti and Bonifacino 1996). As ballast tank pH generally varies from 4.2 to 8.6, this may limit the appli-

cation of glutaraldehyde, unless the treatment system can account for this strong pH response. Glutaraldehyde is corrosive in its concentrated form, but is not considered to pose any corrosion problems in the diluted form proposed for ballast water treatment.

Observations by Sano et al. (2003) indicate that some ballast water organisms may be resistant to glutaraldehyde treatment; consequently eliminating most organisms may require a concentration of 500 ppm. Pre-treatment of fine filtration may act to reduce this concentration as the amount of sediment and organic carbon present in ballast tanks is likely to impact on the efficacy of glutaraldehyde. In situations where higher amounts of sediment exist in relation to water, the ability of glutaraldehyde to penetrate these sediments and kill any viable organisms is likely to be limited (Sano et al. 2003). In this situation, even higher doses may be required for adequate organism removal.

The high glutaraldehyde concentration required to control ballast water organisms induces three important limitations with respect to ballast water treatment. Firstly, the cost of treatment will be prohibitively expensive; secondly, the potential for detrimental environmental impacts is increased; and finally, occupational health and safety risks increase. Sano et al. (2003) suggest the cost of glutaraldehyde treatment would equate to US\$25 per tonne of ballast water, thus limiting the treatment to vessels with small quantities of ballast water and sediment. The increased risk of environmental impacts will relate to the time required for glutaraldehyde to degrade and the amount of dilution that takes place prior to release into the receiving port (Leung 2001; Sano et al. 2003). The biodegradation of glutaraldehyde relies on its digestion by microbes. As glutaraldehyde is a biocide, the concentration required to remove ballast water organisms is also likely to inhibit bacterial growth and metabolism, however once discharged the concentration will decline as the ballast water is dispersed into the aquatic environment. The biodegradability of glutaraldehyde in seawater has been tested and is a complex issue varying with factors such as initial concentration, nutrient status and microbe concentration. Leung (2001) indicates that glutaraldehyde is considered readily biodegradable in the freshwater environment and has the potential for biodegradation in the marine environment.

### Peracetic acid and Peraclean<sup>®</sup> Ocean

Peracetic acid is another organic biocide suggested as a potential ballast water treatment due to its broad-spectrum activity and lack of undesirable by-products. Very little data exists on the efficacy of peracetic acid in marine systems; however it has been documented to control coliform bacteria in sewage sludge at a concentration of 6-8 ppm, and bacterial spores at 300 ppm (Baldry and French 1989; Sagripanti and Bonifacino 1996). Activity is not affected in the presence of suspended solids and organic matter, however is affected strongly by pH. Sagripanti and Bonifacino (1996) found the biocide to be most active at a pH of less than 3, while activity is lost above a pH of 8. This finding may limit the application of peracetic acid as a ballast water biocide, however Degussa AG of Germany has developed a ballast water treatment product composed of peracetic acid and hydrogen peroxide, with the trade name Peraclean<sup>®</sup> Ocean. It is suggested to be effective against a broad range of microorganisms including bacteria, spores, phytoplankton, aquatic invertebrates and fish eggs at concentrations of 50-400 ppm and exposure times of 2-72 h (Fuchs et al. 2001; Fuchs and de Wilde 2004). Apart from broad toxicity, Peraclean<sup>®</sup> Ocean is claimed to be effective over a wide range of conditions, to be relatively unaffected by organic matter and readily biodegradable and decompose into acetic acid, oxygen and water. The manufacturer indicates that Peraclean<sup>®</sup> Ocean has a half-life of only 4 h in unfiltered seawater and recommends a retention time of 1-2 d in ballast tanks due to its rapid degradation. One of the added advantages over peracetic acid disinfection is that it is most active at pH values of 5-7, but displays good activity up to a pH of 9 (Fuchs et al. 2001).

Peraclean<sup>®</sup> Ocean has been developed as either a stand alone treatment or as the final stage of a treatment system that uses a combination of technologies. Lab-scale testing has shown that the product is capable of eliminating bacteria, vegetative marine microalgae, dinoflagellate cysts and several different development stages of the brine shrimp *Artemia salina*. Gregg and Hallegraeff (2007) eliminated vegetative cells of the marine dinoflagellates *Alexandrium catenella*, *Gymnodinium catenatum*, *Protoceratium reticulatum* and *Scrippsiella trochoidea* at 50 ppm and killed the green flagellate *Tetraselmis suecica* at 100 ppm after

48 h exposure. Fuchs et al. (2001) killed the green alga *Chlorella* within 48 h at 200 ppm, however higher concentrations (up to 1600 ppm) did not result in more rapid mortality (Fuchs et al. 2001). This would suggest, as for hydrogen peroxide, that exposure time is a very important aspect of the biocidal action of Peraclean<sup>®</sup> Ocean for the control of algae. In addition, Peraclean<sup>®</sup> Ocean inhibited bacterial regrowth of *Escherichia coli*, *Staphylococcus aureus*, *Listeria innocua* and *Vibrio alginolyticus* at 125-250 ppm and could completely inactivate *Artemia salina* cysts and resting cysts of the marine dinoflagellates *Gymnodinium catenatum*, *Alexandrium catenella* and *Protoceratium reticulatum* at 350-700 ppm (Fuchs and de Wilde 2004; Gregg and Hallegraeff 2007).

Full-scale shipboard and land-based testing has proved that Peraclean<sup>®</sup> Ocean is an effective biocide for the control of a wide range of planktonic organisms and marine bacteria in both freshwater and seawater (Wright et al. 2004; Veldhuis et al. 2006; de Lafontaine et al. 2008a). Veldhuis et al. (2006) examined the effectiveness of a full-scale land-based ballast water treatment system that used Peraclean<sup>®</sup> Ocean as a final disinfection step. Peraclean<sup>®</sup> Ocean was applied to estuarine water at a concentration of 150 ppm and resulted in the elimination of all zooplankton and phytoplankton but bacterial regrowth was observed after 6 to 10 days indicating that the biocide did not result in full sterilisation (Veldhuis et al. 2006). De Lafontaine et al. (2008a) treated freshwater ballast onboard the MV *Canadian Prospector* using a Peraclean<sup>®</sup> Ocean concentration of ~100-150 ppm and observed a >90% reduction in free-floating microorganisms and phytoplankton after 5 d. The treatment also showed a lethal effect on fish with 100% mortality achieved in less than 19 h for a range of cold water fish species, however the treatment was found to be ineffective against adult zebra mussels and some organisms buried in ballast sediments were not affected by a 5 d exposure to ~100-150 ppm of Peraclean<sup>®</sup> Ocean (de Lafontaine et al. 2008a).

Although the manufacturer indicates that Peraclean<sup>®</sup> Ocean-treated ballast water may be safely discharged after 1-2 d, degradability studies have shown that this biocide may degrade at a slow rate resulting in the discharge of potentially toxic ballast water into the marine environment. Results from the shipboard trials conducted by de Lafontaine et al. (2008a) suggest a retention time of 15-29 d is required

prior to discharge when using Peraclean<sup>®</sup> Ocean at a concentration of 100-150 ppm for treating freshwater ballast due to the presence of toxic residues, and studies conducted in marine harbour water recommend a retention time of >6 d (Veldhuis et al. 2006). Biodegradability studies by Gregg and Hallegraeff (2007) found that 200 ppm Peraclean<sup>®</sup> Ocean concentrations degraded to a level non-toxic to marine microalgae in 2-6 wk. Degradation occurred more rapidly when exposed to light and ballast tanks sediments, whereas filtered seawater, humus-rich seawater, relatively clear freshwater and a lack of light appear to be the worst conditions for the degradation of Peraclean<sup>®</sup> Ocean (Gregg and Hallegraeff 2007; de Lafontaine et al. 2008b).

The cost for this type of treatment is suggested to be in the vicinity of US\$0.20-0.30 per tonne of ballast water (Rigby and Taylor 2001). Apart from being expensive for use onboard ships with large ballast capacities, some concerns still exist on the routine use of Peraclean<sup>®</sup> Ocean with regard to potential residual toxicity of treated ballast water (e.g. when the holding time for degradation onboard is shorter than recommended), reduced effectiveness in the presence of sediments, the need to store chemicals onboard and possible ship corrosion.

#### SeaKleen<sup>®</sup>

SeaKleen<sup>®</sup> is a patented biocide developed by Garnett, Inc. Atlanta and manufactured by Vitamar Inc. Memphis. It consists primarily of menadione (a water-soluble form of Vitamin K3), which belongs to the chemical class of naphthoquinones, and has been shown to be toxic to a wide range of freshwater and marine organisms. Apart from its broad toxicity, the manufacturer suggests that SeaKleen<sup>®</sup> is an attractive ballast water biocide because it is apparently of low toxicity to mammals, birds and species of fish, it has a short half-life causing it to degrade to harmless products within days, it has no known corrosive properties, and it is relatively cost-effective (Wright and Dawson 2001). Laboratory testing has proved SeaKleen<sup>®</sup> to be toxic to aquatic algal species (*Chlorella* sp., *Isochrysis galbana*, *Neochloris* sp., *Tetraselmis suecica*), vegetative dinoflagellates (*Alexandrium catenella*, *A. tamarense*, *Gymnodinium catenatum*, *Karenia brevis*, *K. brevisulcata*, *Karlodinium veneficum*, *Prorocentrum minimum*, *Protoceratium reticulatum*, *Scrippsi-*

*ella trochoidea*), dinoflagellate temporary cysts (*Glenodinium foliaceum*), raphidophytes (*Chattonella marina*) and zooplankton (*Crassostrea virginica* larvae, *Cyprinodon variegates*, *Dreissena polymorpha* larvae, *Leptocheirus plumulosus*, *Mytilus galloprovincialis*) at concentrations ranging from 0.5 to 2 ppm (Wright and Dawson 2001; Cutler et al. 2004; Gregg and Hallegraeff 2007).

Full-scale shipboard trials of SeaKleen<sup>®</sup> were conducted onboard the USS Cape May in Baltimore Harbour in 2001. Results from the tests indicate that dosing ballast tanks with a concentration of 2 ppm SeaKleen<sup>®</sup> resulted in overall zooplankton mortalities of 99 and 100% after 24 and 48 h (Wright et al. 2004). Phytoplankton were controlled with SeaKleen<sup>®</sup> concentrations as low as 1 ppm after 24 h, however the effectiveness on bacteria was not clear (Wright et al. 2004, 2007a). Some disagreement exists regarding the bactericidal properties of the product. Wright and Dawson (2001) and Cutler et al. (2004) suggest that SeaKleen<sup>®</sup> is extremely effective against bacteria and can eliminate *Escherichia coli* and *Vibrio fisheri* at a concentration of 1 ppm. Conversely, mesocosm experiments conducted at the University of Washington claimed that SeaKleen<sup>®</sup> at 2 ppm had no observable effect on culturable bacteria (Herwig and Cordell 2004) and Gregg and Hallegraeff (2007) required concentrations of 50-200 ppm to inhibit regrowth of *E. coli*, *Listeria innocua*, *Staphylococcus aureus* and *Vibrio alginolyticus*.

Inconsistencies also exist in the literature concerning the degradability of SeaKleen<sup>®</sup>. Herwig and Cordell (2004) and Wright et al. (2007a) reported a half life of 18-30 h for SeaKleen<sup>®</sup>, yet Cutler et al. (2004) found that SeaKleen<sup>®</sup> degraded to only 21% of the initial concentration in darkness in seawater without any organisms after 28 d. The latter authors suggest that degradability is faster under light conditions and in the presence of biological material; however, Gregg and Hallegraeff (2007) found that the degradation of 4 ppm SeaKleen<sup>®</sup> was minimal after 15 wk and was not influenced by the presence of ballast tank sediment, biological matter or light conditions. Faimali et al. (2006) also report that exposure to light failed to accelerate the degradation rate of SeaKleen<sup>®</sup>. These authors indicate that a 10 ppm concentration of menadione in drinking water has a half life of 1,500 h under both light and

dark conditions and takes >5,000 h to totally degrade.

It has been suggested that the use of SeaKleen<sup>®</sup> may be advantageous in situations where water turbidity is high or to treat residual ballast tank sediments due to a low binding affinity to particulate matter (Wright et al. 2007a). Several studies indicate that SeaKleen<sup>®</sup> does retain its activity in the presence of sediment but it is less effective against resistant resting stages and sediment dwelling organisms. For example, Gregg and Hallegraef (2007) found that the biocidal effect of SeaKleen<sup>®</sup> was not influenced by the presence of sediment but the product failed to kill resistant resting cysts of the toxic dinoflagellate *Alexandrium catenella* at 5 times the recommended dose (10 ppm) in sediment-free trials. Additionally, Sano et al. (2004) controlled the amphipod *Hyalella azteca* at comparable SeaKleen<sup>®</sup> concentrations in both sediment-free samples (2.5 ppm) and samples containing a 1:4 sediment to water ratio (3.5 ppm), but 88 ppm was required to control the burrowing oligochaete *Lumbriculus variegatus* in the 1:4 sediment to water ratio compared to 1.8 ppm required in the water-only exposures. These findings indicate that SeaKleen<sup>®</sup> may provide an effective treatment against organisms in the water column when ballast water contains a high suspended sediment load. While effective control of resistant resting stages and sediment-dwelling organisms might be possible, the required concentrations would be likely to make the treatment prohibitively expensive and may pose environmental problems due to the discharge of toxic ballast water and residual sediment.

The estimated cost of SeaKleen<sup>®</sup> is approximately US\$0.20 per tonne when applied at a concentration of 2 ppm, which may limit the use of this biocide to vessels with small or moderate ballast capacities. Additional concerns that may limit the use SeaKleen<sup>®</sup> as a routine ballast water treatment option include the possible discharge of toxic ballast water due to low degradability of the biocide and the limited effectiveness against bacteria (Gregg and Hallegraef 2007).

Several other naphthoquinone compounds are currently being investigated as potential ballast water biocides. These include juglone, plumbagin and menadione nicotinamide bisulphite (Faimali et al. 2006; Wright et al. 2007b). Like menadione, juglone and plumbagin are natural plant products, with juglone isolated from the black walnut tree *Juglans nigra*, and plumbagin, a compound found in members of the sea

lavender family, Plumbaginaceae (Wright et al. 2007b). Both products have been shown to exhibit greater bactericidal activity and overall toxicity to aquatic organisms compared to menadione (SeaKleen<sup>®</sup>), however menadione was considered to be favourable biocide for ballast water treatment as the production cost of menadione is less than 2% the cost of either juglone or plumbagin (Wright et al. 2007a). Nonetheless, further work should assess the degradability of juglone and plumbagin and their ability to inactivate resistant marine organisms, such as dinoflagellate resting cysts.

Menadione nicotinamide bisulphite is a synthetic derivative of menadione (Faimali et al. 2006). Preliminary screening of its efficacy against marine organisms found that it can effectively eliminate a variety of ballast water organisms in the absence of light. Zooplankton larvae, including *Artemia salina* nauplii, *Balanus amphitrite* nauplii, *Mytilus galloprovincialis* larvae and *Tigriopus fulvus* larvae were completely eliminated at concentrations of 0.5 to 5 ppm, growth of the green alga *Chlorella minutissima* was inhibited at 0.5 ppm and germination of dinoflagellate cysts (*Scrippsiella trochoidea*) was reduced to 30% (compared to 90% in controls) after exposure to 5 ppm (Faimali et al. 2006). The product displayed a variable effectiveness against bacteria (1 to >64 ppm required to inhibit regrowth) and was not as effective against *Alexandrium catenella* (EC 50=32 ppm) (Faimali et al. 2006). The major advantage this compound has over its parent molecule (menadione) is that it is highly biodegradable. Faimali et al. (2006) imply that menadione nicotinamide bisulphite has a half life of 48 h under dark conditions and <6 h under light conditions compared to 1,500 h for menadione when prepared in drinking water.

#### *Acrolein*<sup>®</sup>

*Acrolein*<sup>®</sup> is a broad-spectrum biocide produced by the Baker Petrolite Corporation. It is used extensively in the petroleum industry as a biocide to mitigate bacteria in produced fluids and is sold as an aquatic herbicide to control submerged plants and algae in irrigation canals. It is claimed to be toxic to a range of microorganisms including bacteria and algae, as well as macroorganisms such as molluscs, crustaceans, fish, and aquatic plants (Penkala et al. 2004). Lab-scale experiments on marine organisms indicate that vegetative dino-

flagellates and both Gram-negative and Gram-positive spore-forming and non-sporulating marine bacteria can be controlled at concentrations of 1-6 ppm after contact times of 24 and 72 h (Penkala et al. 2004). After 24 h exposure, a concentration of 6 ppm caused a >99.99% reduction in bacterial strains of *Pseudomonas fluorescens*, *Bacillus cereus*, *B. subtilis* and *Staphylococcus epidermidis*, while 10 ppm achieved a >99.999% reduction. No viable motile cells of the marine dinoflagellate *Akashiwo sanguinea* (= *Gymnodinium sanguineum*) were observed at 1 ppm (Penkala et al. 2004). Results from a 5 d shipboard trial found that ballast tanks treated with 9 ppm effectively reduced bacteria by 99.99% for a period of 2 d; and 15 ppm inhibited bacterial regrowth for 3 days, whereas 1 and 3 ppm of Acrolein<sup>®</sup> was ineffective (Penkala et al. 2004). This would indicate that the demand for Acrolein<sup>®</sup> in ballast tanks is much higher than what was predicted from laboratory experiments, nonetheless it is estimated that microorganism regrowth can be inhibited by maintaining >2 ppm residue in ballast tanks (Penkala et al. 2004). Acrolein<sup>®</sup> is claimed to react with water and particulate matter within the ballast tanks resulting in a discharge concentration of zero ppm, thus allowing its safe discharge over board. Laboratory studies conducted by Penkala et al. (2004) determined that the product has a half-life of 20-25 h for concentrations of 1, 5 and 10 ppm when prepared in natural port water; however, results from the shipboard trials found that the rate of degradation was much faster. For example, tanks that were treated with 9 ppm had substantially decreased concentrations of <2.5 ppm within 24 h (Penkala et al. 2004) suggesting that the physical and chemical conditions inside the ballast tank increase the degradability of Acrolein<sup>®</sup>. Acrolein<sup>®</sup> may also be deactivated by sodium sulphite before discharge, however this would act to increase the treatment cost. The current estimated cost of Acrolein<sup>®</sup> for treating ballast water is between US\$0.16 and 0.19 per tonne. We suggest that future research should assess 1) the ability of Acrolein<sup>®</sup> to inactivate resistant ballast water organisms such as dinoflagellate cysts; and 2) the capacity of the product to inactivate organisms in ballast tank sediment (cf. Gregg and Hallegraeff 2007). Concerns about the routine treatment of ballast water with Acrolein are similar to those expressed for the active substance Peraclean.

#### *Hydroxyl radical treatment*

One of the more recent treatment options proposed for the control of ballast water organisms involves the onboard generation of hydroxyl- and oxygen radicals. These free radicals are aggressive and can break down almost any organic compound to carbon dioxide and water (Taylor et al. 2002). It is recommended as a tool for controlling ballast water organisms during ballasting and/or deballasting. The hydroxyl radicals are predominantly produced from the positive ions  $O_2^+$  and  $N_2^+$  reacting with water, and the concentration required to kill microorganisms is reportedly only 0.63 mg/L (Bai et al. 2005). At this concentration, unicellular algae, protozoans and bacteria are killed within 2.67-8 s (Bai et al. 2005; Qiong et al. 2009; Zhang et al. 2005). The main reasons of cell death are lipid peroxidation, destruction of cell DNA and RNA, and damage to the antioxidant enzyme system (Zhang et al. 2006). No efficacy data exist for resistant life stages such as cysts and spores.

This method also has the following advantages: 1) ballast water quality is improved, as turbidity has shown to be decreased to 50% following the 2.67s treatment; 2) the radicals are reported to be short-lived (nanoseconds), decomposing into water, oxygen and carbon dioxide, making it an environmentally sound technique; and 3) the equipment is small in size, operationally simple and cost effective. Bai et al. (2005) implies that the running cost of hydroxyl radical treatment is 1/30<sup>th</sup> the cost of ballast water exchange; however the initial cost and power requirements would be expected to be considerable. Taylor et al. (2002) indicates that corrosion problems may be a concern, unless the reactor is kept well separated from the main ballast piping system, however this technology should still be pursued for ballast water applications, as it may provide a cost effective, safe, environmentally friendly ballast water treatment. Several companies have developed treatment systems that use a combination of mechanical separation and free radical generation. The effectiveness of several of these systems is discussed later.

#### *De-oxygenation*

De-oxygenation has been suggested to be a cost effective technique to prevent aquatic introductions while reducing ship corrosion. De-

oxygenation can be achieved by the addition of nutrients, glucose or a reducing agent such as a sulphide, by the use of a vacuum chamber, or oxygen can be purged out of the ballast tanks with a continual flow of an inert gas from an onboard generator (Mountfort et al. 1999a; Tamburri et al. 2002, Browning Jr. et al. 2004; Tamburri et al. 2004, McCollin et al. 2007b).

Initial results indicated that the addition of glucose or sulphide had minimal effects on living organisms, however the other techniques have been shown to effectively kill many zooplankton species (including larval stages) and aerobic bacteria but results against phytoplankton have been inconclusive (Table 8). This approach is considered unlikely to remove taxa adapted to low oxygen environments or with resistant stages such as cysts and spores. For example, Anderson et al. (1987) reported that the viability of dinoflagellate cysts of *Alexandrium tamarense* was not reduced when stored in an oxygen-deprived environment.

Mountfort et al. (1999a) tested the effectiveness of de-oxygenation by the addition of glucose or sulphide. The addition of glucose did not significantly reduce the oxygen concentration and was ineffective in killing *Coscinasterias calamaria* starfish larvae or *Undaria pinnatifida* seaweed zoospores over a 28 d period, and sulphide addition was capable of eliminating *C. calamaria* larvae but it did not completely kill *U. pinnatifida* zoospores (Mountfort et al. 1999a). Conversely, studies conducted by McCollin et al. (2007b) found that the addition of nutrients to ballast water stimulated the growth of bacteria resulting in an anoxic environment, which caused a reduction in the abundance and viability of zooplankton but the results for phytoplankton showed no effect. Similarly, experimental trials using vacuum chambers to suffocate aquatic organisms have been demonstrated to be able to remove dissolved oxygen from ballast water to levels below 1 ppm resulting in the elimination of many zooplankton species (Browning Jr. et al. 2004) but the effect on phytoplankton was not clear.

Recently, preliminary experiments indicate that the combination of low oxygen (2%) and high carbon dioxide (12%) is capable of eliminating of >95% of zooplankton and invertebrates within several hours, and can kill >99% of *Vibrio cholerae* in 24 h, however experimental data is unavailable on the effects on phytoplankton, cysts and spores (Husain et al. 2004). Cost estimates for this type of treatment system

range from US\$135,000 to in excess of US\$3 million depending on ballast capacity and operating costs are approximately US\$0.06 per tonne of ballast water (Lloyd's Register 2007).

NEI Treatment Systems, LLC of Los Angeles, California has developed the Venturi Oxygen Stripping™ system- de-oxygenation technology that rapidly removes 95% of dissolved oxygen from ballast tanks. The system removes oxygen from ballast water by the introduction of an inert gas into the water as it is being pumped into ballast tanks. Initial laboratory experiments conducted under a range of environmental conditions demonstrated that dissolved oxygen levels dropped to 0.27-0.87 ppm leading to greater than 99% mortality of zooplankton (copepods, barnacle larvae, polychaete larvae, cladocerans, crustacean nauplii, bivalve larvae and nematodes) in less than 48 h, however, the system was less effective against phytoplankton and no obvious difference in bacterial abundances were observed (Tamburri et al. 2004). Further testing at the Chesapeake Biological Laboratory showed promising results. The system was capable of eliminating 100% of zooplankton and phytoplankton after 120 h of treatment, and reduced the levels of *Enterococci* and *E. coli* bacteria by more than 99.9% (NEI Marine 2007). In addition, biological trials from a shipboard installation onboard the bulk BWM Convention carrier the *TECO Ocean* suggest that the treatment system is capable of meeting the D-2 discharge standard when operating at a flow rate of 1000m<sup>3</sup>/h, however experimental data are not available. The cost of the Venturi Oxygen Stripping™ system ranges from US\$150,000 to \$400,000 depending on the flow capacity of the ship and operating costs are approximately US\$0.05 per tonne of ballast water (Lloyd's Register 2007).

The above results indicate that de-oxygenation may eliminate zooplankton but it is unlikely to be an effective ballast water treatment, as a many organisms such as seaweeds, phytoplankton, cysts and spores, anaerobic bacteria and many viruses are likely to survive such conditions. Although a number of authors indicate that using de-oxygenation techniques may provide ship owners with a significant economic saving (approximately US\$80,000-100,000 per year) due to a reduction in ballast tank corrosion (Deacutis and Ribb 2002; Browning Jr. et al. 2004), it is suggested that alternating back and forth from anoxic conditions to air as well as the stimulation of anaerobic bacteria may act to

enhance corrosion rates (Oemcke 1999; Tamburri et al. 2004).

#### *pH adjustment*

Many organisms cannot survive large variations in pH (Muntisov et al. 1993). Raising or lowering pH level in ballast tanks can be achieved by the addition of alkali or basic chemicals and may effectively kill many organisms. However, this technique has several drawbacks. Firstly, lowering the pH may have significant negative effects in terms of corrosion, while elevating the pH may result in chemically unstable water (Oemcke 1999). Secondly, altering the pH involves the addition of chemicals during ballast water intake or to the ballast tanks, consequently requiring a large storage space and increasing safety risks. Thirdly, this treatment would result in production of vast quantities of residues that would need to be kept onboard and disposed of safely in landfills, and ballast water pH may need to be restored prior to discharge by the addition of neutralising agents (Muntisov et al. 1993). Finally, pH adjustment may not render all ballast water organisms inactive, especially cysts, spores and other resistant physiological resting stages. For example, Bolch and Hallegraeff (1993) showed that the germination of dinoflagellate cysts of *G. catenatum* was not affected after 24 h exposures to pH values ranging from 2 to 10 and Kurizian et al. (2001) found no difference in mortality of mixed zooplankton species between control and elevated pH (8.5 to 10) samples. Bacteria are also capable of surviving wide variations in pH. The optimal pH for rapid multiplication of *V. cholera* on copepods is around 8-9, with a decline in multiplication evident at an acidic pH (6-6.5) (Huq et al. 1984). However, this decline in abundance may be explained by the death of the copepods, rather than the mortality of the bacterium.

#### *Salinity adjustment*

Salinity adjustment is aimed to inactivate or osmotically destroy marine organisms present in ballast water by increasing or decreasing the salinity of the water, as it is believed that freshwater organisms cannot survive oceanic and estuarine conditions. Conversely, survival of oceanic and estuarine species is likely to be

reduced when challenged by freshwater conditions. As not all ships will travel between freshwater and oceanic conditions this procedure could be achieved by the addition of salts to ballast tanks or by the use of an onboard desalination unit. The latter is considered to be expensive, time consuming and would require an enormous amount of energy.

Another factor limiting the use of salinity adjustment for the treatment of ballast water is that many pathogens and resting stages of organisms are likely to survive such treatments. For example, the survival and viability of non-culturable estuarine *E. coli* and *V. cholerae* was unaffected over a range of salinities from 5 to 33 g/L (Xu et al. 1982; Huq et al. 1984; Munro and Cowell 1996). Similarly, *G. catenatum* cysts exposed to freshwater and salinities between 15 and 50 g/L were unaffected; however, extreme salinities of 100 g/L prevented their successful germination (Bolch and Hallegraeff 1993). Salinities in this extreme range are not considered economically or practically achievable in onboard situations.

#### **Multi-Component Treatment Systems**

Many ballast water treatment systems use a combination of treatment options (Table 9). A selected number of such systems that are currently under commercial development and in various stages of testing and/or IMO approval are discussed below. The BWM Convention requires that systems used to comply with the Convention must be approved by the Administration and need to be tested in a land-based facility and on board ships to prove that they meet the performance standard D-2 of the BWM Convention. Successful fulfillment of the provisions should lead to the issuance of a Type Approval Certificate. Systems which make use of Active Substances to comply with the Convention shall be approved by IMO in a two-tier process - to ensure that the ballast water management system does not pose unreasonable risk to the environment, human health, property or resources.

#### *Mechanical treatment and ozone disinfection*

Mitsui Engineering and Shipbuilding Co., Ltd in conjunction with the Japanese Association of Marine Safety (JAMS) have developed the *Special Pipe Ballast Water Management System*

**Table 9.** Summary of processes and key system data of selected multi-component ballast water treatment technologies in advanced stages of approval (from Lloyd's Register 2008; Carney et al. 2008)

System Name	Manufacturer	Treatment Process	Active Substance Basic Approval	Active Substance Final Approval	Type Approval IMO	National Approval	Capacity ('000's m <sup>3</sup> /h)	Footprint (m <sup>3</sup> ) capacity 200 vs 2000 m <sup>3</sup> /h		Efficacy
<i>AquaTriCom</i>	Aquaworx, Germany	Filtration/ UV-C radiation+ultra-sound	Yes	No	No		0.25-4	NA	NA	NA
<i>Blue Ocean Shield</i>	COSCO, China	Hydrocyclone/ filtration/UV	Yes	No	No		0.25	NA	NA	NA
<i>Clearballast</i>	Hitachi, Japan	Flocculation + magnetic separation + filtration	Yes	Yes	No		>10	20	100	100% > 10 µm; >99.8% <i>E. coli</i> ; Exceeded D2
<i>EcoBallast</i>	Hyundai, Korea	Filtration? UV radiation	Yes	No	No		NA	NA	NA	NA
<i>Ecochlor</i>	Ecochlor, Germany, USA	Chlorine dioxide	Yes	No	No		10	6.75	9.5	NA
<i>EctoSys</i>	Permasand, RWO, Sweden, Germany	Filtration + electrochemical treatment	Yes	Yes	No		>10	3	20	removed 100% of <i>Artemia</i> cysts; exceeded D2 standard
<i>Electro-Cleen</i>	Techcross and KORDI, Korea	Electrolysis/Electro chlorination	Yes	Yes	Yes		>10	2	6.5	NA
<i>GloEn-Patrol</i>	GloEn-Patrol, Korea	Filtration+UV+ electric decomposition	Yes	No	No		4	1.8	14.8	NA
<i>Greenship, Sedinox</i>	Greenship Ltd, Netherlands	Cyclonic separation + electrochlorination	Yes	Yes	No		>10	4	20	99-100% bacteria; 100% >50 µm; 98-100% 10-50 µm 87 % organisms; 100% coliform bacteria
<i>Hyde Guardian</i>	Hyde Marine Inc, UK	Filtration + UV	Yes	No	No	Yes	>10	7	35	
<i>Nei Treatment System</i>	Nei Treatment Systems LLC, US	Venturi Oxygen Stripping (VOS)	Yes	No	No	Yes	0.5-10	5.25	NA	NA
<i>NK-03, BlueBallast</i>	NK Ballast Water Treatment System, Korea	Ozone	Yes	Yes	No		0.2-3	22	40	NA
<i>Oceansaver®</i>	Metafil, Oceansaver AS, Norway	Filtration + cavitation electrolysis + deoxygenation	Yes	Yes	Yes		>10	NA	NA	NA
<i>Optimarin</i>	Optimarin, Norway/US	Filtration + UV	Not applicable	Not applicable	No		>10	3	6-11	NA
<i>Pure ballast</i>	Alfa Laval Tumba AB, Sweden	Filtration + advanced oxidation	Yes	Yes	Yes		5	3	12	99.99999% <i>E. coli</i> 99.9999% >10 µm
<i>Resource Ballast Technology System</i>	Resource Ballast Technology, South Africa	Filtration + electro chlorination + cavitation	Yes	No	No		>10	12	4	NA
<i>SEDNA</i>	Hamann AG/Degussa AG, Germany	Cyclonic separation +filtration +active substance	Yes	Yes	Yes		2	4.3	9	Exceeded D2; 100% phyto + zooplankton
<i>Special Pipe</i>	Mitsui Engin. Shipbuilding JAMS, Japan	Mechanical treatment , cavitation+ ozone (1 ppm)	Yes	No	No		NA	15	NA	99% phytoplankton; 89% zooplankton
<i>TGBallast cleaner and TGEnvironmental guard</i>	Toagosei grp; Tsurumi Soda Japan	Filtration + sodium hypochlorite+ sodium sulfite	Yes	No	No		NA	NA	NA	NA

(combined with ozone treatment). The system consists of four treatment processes; a pre-treatment unit, the disinfection unit, a gas/liquid separation unit and discharge unit. The disinfection unit terminates organisms using sheer stress and cavitation produced by the special plate structures of the 'Special Pipe' and the ozone treatment enhances the killing effect. The pre-treatment unit prevents the blockage of the disinfection unit, the gas/liquid separation unit prevents gaseous ozone entering the ballast tanks and the discharge unit decomposes any remaining oxidant in the ballast water to safeguard against chemical discharge during de-ballasting. The system has been granted basic approval from the IMO for the use of active substances (GESAMP 2008).

Land-based tests of a prototype system using a flow rate of 20 m<sup>3</sup>/h showed that a single passage through the pipe resulted in the termination of 54.8% of all phytoplankton and of 65.1% of zooplankton and mortality was increased to 99 and 89%, respectively, by injecting 1mg/L of ozone into the seawater (Kikuchi et al. 2004). Further experimentation on an up-scaled model found that the system was capable of eliminating 69.6% of phytoplankton and 94.3% of zooplankton after a single passage through the system without the addition of ozone when operating at a flow rate of 115 m<sup>3</sup>/h and mortality was increased to 80% and 100% of phytoplankton and zooplankton, respectively, by a two-time passage through the system (Kikuchi et al. 2004). Furthermore, 85% of phytoplankton and 100% of zooplankton were eliminated at a flow rate of 150 m<sup>3</sup>/h following a single passage through the system (Kikuchi et al. 2004). This indicates that the effectiveness of the 'Special Pipe' component of the treatment system is increased with an increase in flow rate. Efficacy data on the removal of bacteria are not available; however, the secondary ozone treatment is likely to inhibit bacterial growth if TRO concentrations are maintained at around 1 ppm. Advantages of the system are that it is easily retro-fitted to existing ships and it does not require the storage of large amounts of chemicals onboard. Disadvantages include potential health and safety issues for crew and possible increased corrosion of ballast tanks due to the application of ozone, and it may not be economically feasible for ships with high ballast pump flow rates. The system costs approximately US\$ 1 million for installation on an existing container ship with an

estimated operating cost of US\$0.15 per tonnes of ballast water (MEPC 2006).

#### *Filtration, cavitation, electrochemical disinfection and de-oxygenation*

The Oceansaver<sup>®</sup> is a Norwegian-made multi-component treatment system consisting of a mechanical filtration unit, a hydrodynamic cavitation chamber, an electrochemical disinfection unit and a nitrogen super-saturation generator. The mechanical filtration unit used is an automatic self-cleaning 50 µm wedge wire filter that operates during ballast intake returning trapped organisms and sediment back to the source location. Efficacy tests have shown that the filter effectively removes only 50-70% of material over 50 µm (Andersen 2007).

The hydrodynamic cavitation unit involves the formation and implosion of cavitation bubbles which generate forces and shockwaves that affect particles and organisms larger than 10 µm. Land-based experimental testing has shown that the cavitation unit allows the other treatment components in the system to act more effectively (MEPC 2007e).

The electrochemical disinfection unit produces active substances electrochemically from seawater *in-situ* in a side stream of the main ballast water without the addition of any active substances to the water. The active substance formed is primarily hypochlorous acid with small concentrations of chlorine gas, ozone, hydrogen peroxide, chlorine dioxide and hypochlorite. The treated water is then re-injected back into the ballast water. This component of the system would not be effective when operating in freshwater; however, it may be possible to generate active substances using an external source of brine or seawater (MEPC 2007e).

The nitrogen super-saturation unit injects nitrogen into the ballast water to reduce the dissolved oxygen concentration to levels of 2-3 mg/L (Andersen 2007). This leads to hypoxic conditions in the ballast water preventing the re-growth of organisms that require oxygen for their survival. The treated water is then aerated during ballast discharge to avoid the discharge of hypoxic water.

The system has been in operation on several vessels including the MV *Federal Welland* and *Hual Trooper* since 2005 and received basic, final and type approval from IMO. The manu-

facturer suggests that an advantage of this system is that it may be run in several configurations depending on the level of treatment required. For example, following the primary filtration step, any combination of the three secondary treatments may be used depending on the particular properties of the ballast water.

Disadvantages include potential human-health impacts on crew members due to the production of active substances, including chlorine gas and carcinogenic trihalomethanes (THM's). Initial acute toxicity tests carried out following the electrochemical treatment step found that samples taken immediately after treatment and 5 d after treatment showed aquatic toxicity (MEPC 2008b). Although no total residual oxidants were detectable after 24 h, measurements of the formation of disinfection by-products and other chemicals showed a significant increase in the level of several THM products (trichloromethane/bromoform, dibromochloromethane and tribromomethane) directly after treatment and after 5 d of storage (MEPC 2008b). To reduce the production of these disinfection by-products a neutralization step was introduced, while the deoxygenation step has been shown to reduce corrosion.

It is suggested that the Oceansaver<sup>®</sup> system is capable of treating in excess of 10,000 m<sup>3</sup> of ballast water per hour, however several treatment systems will be required to operate at this level. The technology is expected to cost approximately US\$800,000 per unit with an operating cost of \$0.06 per tonne of ballast water (Lloyd's Register 2007).

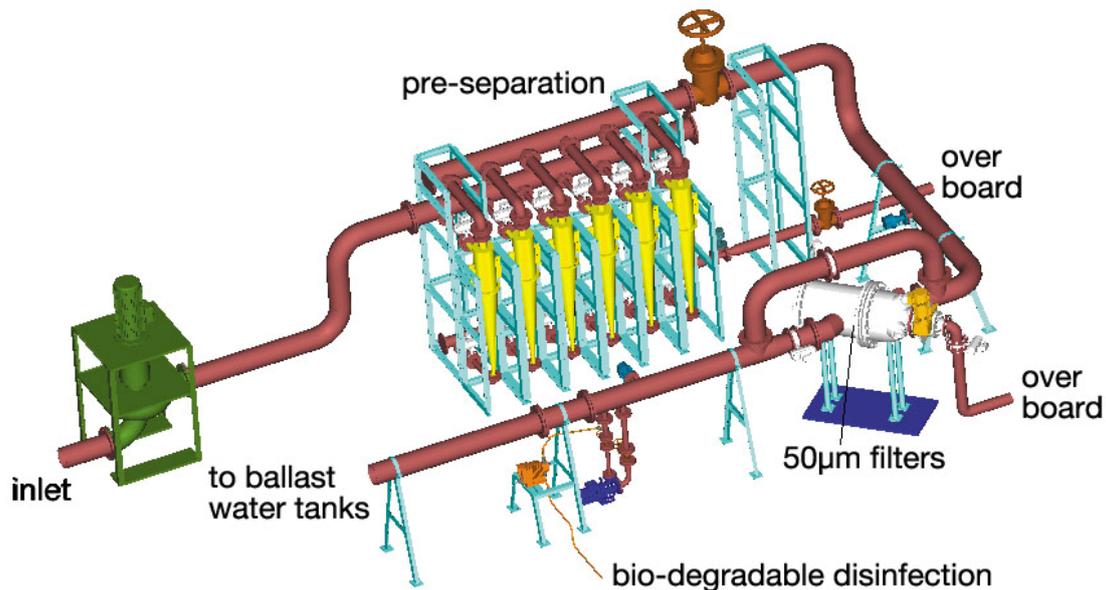
#### *Cyclonic separation, filtration and chemical biocide treatment*

Hamann AG and Degussa AG of Germany have produced the SEDNA<sup>®</sup> (Safe, Effective Deactivation of Non-indigenous Aliens) - a modular ballast water treatment system which consists of a two-step physical separation and a secondary biocide treatment that operates during ballast intake only (Figure 2). Physical separation is conducted by a number of hydrocyclone devices and a self-cleaning 50 µm filter that function to reduce the sediment load of the ballast water and remove organisms greater than 50 µm. These devices increase the stress on organisms present in the ballast water, resulting in physical damage to the organisms as well as an increased

sensitivity towards the secondary chemical treatment (HSB 2006). The secondary treatment uses the oxidative biocide Peraclean<sup>®</sup> Ocean to provide complete disinfection of small organisms (<50 µm) and bacteria. The manufacturer suggests that the SEDNA<sup>®</sup> system is superior to other ballast water treatment systems as it is not limited with regard to water sediment load, salinity and temperature or voyage length; it is fully automated and maintenance can be carried out by trained ship personnel; it can be customised for ballast pump capacities ranging from 50 to 2000 m<sup>3</sup>/h; and the chemical is fully biodegradable and only requires a retention time of 24 h in ballast tanks before it can be safely discharged overboard (HSB 2006; Lloyd's Register 2007).

Results of sediment removal efficacy tests conducted by the manufacturer suggest that the system is capable of removing up to 40% of particles >10 µm and >95% of the suspended solids >30 µm and biological efficacy tests have shown that the system is capable of exceeding the BWM Convention D-2 standard (HSB 2006). Independent tests carried out by Veldhuis et al. (2006) on a SEDNA<sup>®</sup> system capable of treating 530 m<sup>3</sup>/h found that the physical separation components of the treatment system did not remove the sediment component of the natural harbour water, which consisted of mainly clay (<2 µm) and silt (<63 µm) particles, or *Phaeocystis globosa* cells but did reduce the abundance of some zooplankton species. Although the hydrocyclone did not effectively reduce the total suspended solids of the incoming water, it did act to alter the structure of gelatinous phytoplankton colonies of *P. globosa* in a manner that the self cleaning filters were not clogged as often. For example, when the hydrocyclone devices were not operating, the filter was clogged within 10 min, whereas under full operation the filter self-cleaned every 60 to 90 min (Veldhuis et al. 2006). Lastly, the Peraclean<sup>®</sup> Ocean disinfection step effectively eliminated all zooplankton species, all phytoplankton species examined (*Chaetoceros muellerii*, *Chlorella autotrophica*, *P. globosa*) as well as bacteria at a concentration of 150 ppm (Veldhuis et al. 2006). At this concentration (150 ppm), bacterial regrowth was inhibited for a period of 6-10 days indicating that Peraclean<sup>®</sup> Ocean did not achieve a full disinfection of the incoming water (Veldhuis et al. 2006).

Potential disadvantages of the system include the cost effectiveness of Peraclean<sup>®</sup> Ocean



**Figure 2.** Schematic diagram of the three treatment stages of the SEDNA® ballast water treatment system  
 From: [http://www.hamannasia.com/web/ballastwater\\_korea.html](http://www.hamannasia.com/web/ballastwater_korea.html)

(approximately US\$0.30 per tonne of ballast water), possible increased corrosion due to the use of an oxidative biocide, the reduced effectiveness of Peraclean® Ocean against resistant organisms and in the presence of sediments, health and safety issues and space requirements relating to the need to store large amounts of noxious chemicals onboard and possible residual toxicity of treated ballast water, as several studies have found that the biocide degrades at a much slower rate than claimed by the manufacturer (e.g. Gregg and Hallegraeff 2007; de Lafontaine et al. 2008a).

Nonetheless, the SEDNA® ballast water treatment system using Peraclean® Ocean was the first operational system that has received both Basic and Final Approval by the IMO for its use of an active substance as well as for the whole system and Type Approval by the relevant national regulatory authority, the Federal Maritime and Hydrographic Agency, Hamburg (MEPC 2007d).

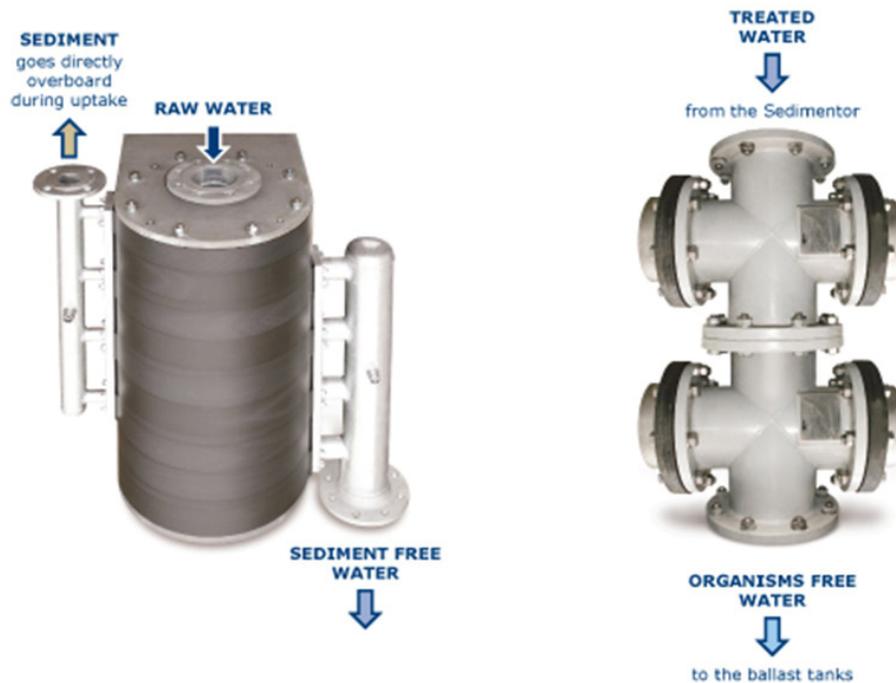
#### *Cavitation and filtration*

Environmental Technologies Inc. and Qwater Corporation of the United States are developing treatment systems that combine filtration and cavitation. Although, no efficacy data are avail-

able for either system, it is believed that pre-filtration may decrease the effectiveness of cavitation by removing particulate matter that acts to kill smaller organisms through collisions. An alternative approach that deserves investigation is the combination of cavitation with chemical biocides and/or UV treatment. Mason et al. (2003) and Gavand et al. (2007) have demonstrated that the efficacy of cavitation is increased by the addition of chemicals including chlorine, ozone and hydrogen peroxide; and similarly, Sassi et al. (2005) showed that the efficacy of ultrasound treatment can be significantly improved when combined with UV irradiation. At the current stage of development, however, ultrasound technologies would not be considered appropriate for the shipboard treatment of ballast water due to high capital and operating costs and high power requirements (Rigby and Taylor 2001).

#### *Mechanical separation and electrochlorination*

Several companies have produced two-stage ballast water treatment systems that combine primary separation devices followed by disinfection by electrochlorination. *Greenship Ltd* of the Netherlands has designed a shipboard ballast water treatment system that includes the



**Figure 3.** Main components of the Greenship ballast water treatment system. (left) the ‘Sedimentor’- a hydrocyclone device ; and (right) the ‘Terminox’- a sodium hypochlorite generator. From: <http://www.greenship.nl/insidecontent/news16.html>

‘Sedimentor’- a hydrocyclone for removing sediment and biota during uptake, and the ‘Terminox’- an electrolytic cell that produces sodium hypochlorite for disinfection (Figure 3).

Efficacy experiments conducted on a laboratory test unit with a capacity of 50 m<sup>3</sup>/h suggest that the ‘Sedimentor’ is capable of removing 100% of particles 20 µm and larger, and 80% of the particles greater than 10 µm (MEPC 2007a). This would act to remove most phytoplankton and zooplankton species from the ballast water and would significantly minimise the sediment load increasing the killing effect of the sodium hypochlorite. Tests on the effect of the electrolytic cell showed a killing efficacy of >99.99% of heterotrophic bacteria (including *E. coli*) after 2 min when performed with 10 ppm sodium chlorite (MEPC 2007a); indicating that the system is capable of meeting the bacterial component of the BWM Convention. In addition to the laboratory test, supplemental land-based tests were conducted on natural seawater using a system with a capacity of 100 m<sup>3</sup>/h. Results showed that the system removed 100% of organisms >50 µm, 98-100% of organisms 10-50 µm and eliminated 99.9-100% of aerobic heterotrophic bacteria including *E. coli* and

Enterococcae (MEPC 2007a). For best results a free chlorine concentration of at least 2.6 ppm is recommended. The system is capable of producing higher levels of chlorine; however concentrations above 3 ppm should not be used as they pose environmental problems due to the formation of toxic by-products. Residual measurements of sodium hypochlorite found that no trace of free chlorine was found in treated ballast water after 90 min, however, several trihalomethane and haloacetic acid products were detected (MEPC 2007a). Other drawbacks of the system include potential increases in ballast tank corrosion and concerns regarding the toxicity of treated ballast water at discharge. Toxicity tests have shown that treated ballast water caused no negative effects on larvae of the brine shrimp (*Artemia franciscana*) or freshly fertilised eggs and yolk-sac larvae of the sole (*Solea solea*) after 24 h, but the diatom *Skeletonema costatum* did not survive exposure to treated ballast water even in tests conducted 96 h after treatment (MEPC 2007a). Preliminary shipboard testing has shown that the system operates effectively in salinities of >3 ‰ meaning that the system can operate in 96% of all situations worldwide (MEPC 2007a). In order to operate in freshwater, seawater or

brine needs to be injected into the system. The estimated cost for full installation of Greenship's Ballast Water Management System is US\$2,300,000 for a system capable of treating a flow of 2000 m<sup>3</sup>/h (Carney et al. 2008). This system achieved basic approval from IMO in 2008.

Severn Trent De Nora builds a similar treatment system, the BalPure® Ballast Water Treatment System, but this differs in that filtration is used prior to electrochlorination. The capital cost of this system is considerably less than the Greenship system (\$US500,000 for 2000 m<sup>3</sup>/h flow capacity) and has an operational cost of US\$0.02 per tonne of ballast water (Lloyd's Register 2007).

#### *Filtration and free radical treatment*

RWO GmbH Marine Water Technology and Veolia Water Solutions and Technologies have developed 'CleanBallast!'- a two-stage ballast water treatment system that consists of a mechanical separation step and an electrochemical treatment step (Figure 4). The mechanical filtration step uses self-cleaning disc filters to remove suspended solids, sediment and larger organisms and prevent the accumulation of

sediment in ballast tanks. The filtration system consists of an array filter housings that operate in parallel and are self-cleaned one at a time allowing filtration to operate without reducing the ballast water flow rate. The electrochemical treatment step produces active substances in-situ by the Ectosys® electrochemical treatment cell. This unit produces several different disinfectants (free hydroxyl- and oxygen radicals and a small amount of hypochlorous acid) directly from seawater. The treatment system operates during ballast intake, however land-based tests showed that re-growth of organisms does sometimes occur, therefore, during ballast discharge the filter unit is by-passed and the ballast water is treated again with the electrochemical treatment cell (MEPC 2007c).

Only a very limited amount of efficacy data is available on the 'CleanBallast!' system. The filter component has been shown to remove 100% of *Artemia salina* cysts (NAG Marine 2007) and biological efficacy tests conducted in river, brackish and seawater at four different locations indicate the system is capable of exceeding the D-2 standard of the BWM Convention for the three size classes of organisms (MEPC 2006), however experimental data are not available.



**Figure 4.** The RWO GmbH Marine Water Technology 'CleanBallast!' ballast water treatment system.  
From: <http://www.nagmarine.com/environmental.html>

Two advantages Ectosys<sup>®</sup> electrolysis has over conventional electrolytic chlorine generators is that it can operate effectively in freshwater without the need to add brine or seawater and produces less chlorine and therefore less chlorine disinfection by-products. Results from acute toxicity studies on treated effluent have shown no significant effects caused by treatment with the 'CleanBallast!' system. The system does produce small amounts of hydrogen and chlorine gas but these are not regarded as a problem if the system is adequately vented during operation. Low concentrations of several THM and HAA by-products as well as bromate are also formed, especially in waters with high salinity (MEPC 2007c). No corrosion data are available for the 'CleanBallast!' system. The system has a capacity of 500 m<sup>3</sup>/h and due to its modular design can be adapted to all flow rates by the joining of numerous units.

Alfa Laval Tumba AB of Norway in partnership with global shipping firm Wallenius has also developed a chemical-free treatment system that uses filtration and chemical disinfection with free radicals produced in the patented AOT (Advanced Oxidation Technology) unit. During ballasting, water passes through a 50 µm filter to remove any large particles and organisms. Water then continues to the AOT unit, which contains titanium dioxide catalysts that generate free radicals when hit by UV light. During deballasting, water is passed again through the AOT unit to eliminate any organisms that may have re-grown during transit. The treatment system uses no chemicals or additives and has no toxic residuals. Laboratory pilot-scale tests conducted at a flow rate of 25 m<sup>3</sup>/h have shown that 'PureBallast' system eliminates over 99.999% of organisms >10 µm and can achieve a 99.999% reduction in the concentration of *E. coli* bacteria (Alfa Larval 2008). The system has undergone full-scale testing onboard the Wallenius car carrier, the MV *Don Quijote*. Wallenius also plans to install 'PureBallast' on all newly built car carrier vessels. The 'PureBallast' system has received full approval from the IMO for the use of active substances and has recently been granted full Ballast Water Type Approval from the relevant Norwegian authorities. Due to the modular design, the system can be adapted for different vessel types and can cover a flow range of 25-5000 m<sup>3</sup>/h. The operational cost of the system is approximately US\$0.06 per tonnes of ballast water (MEPC 2006).

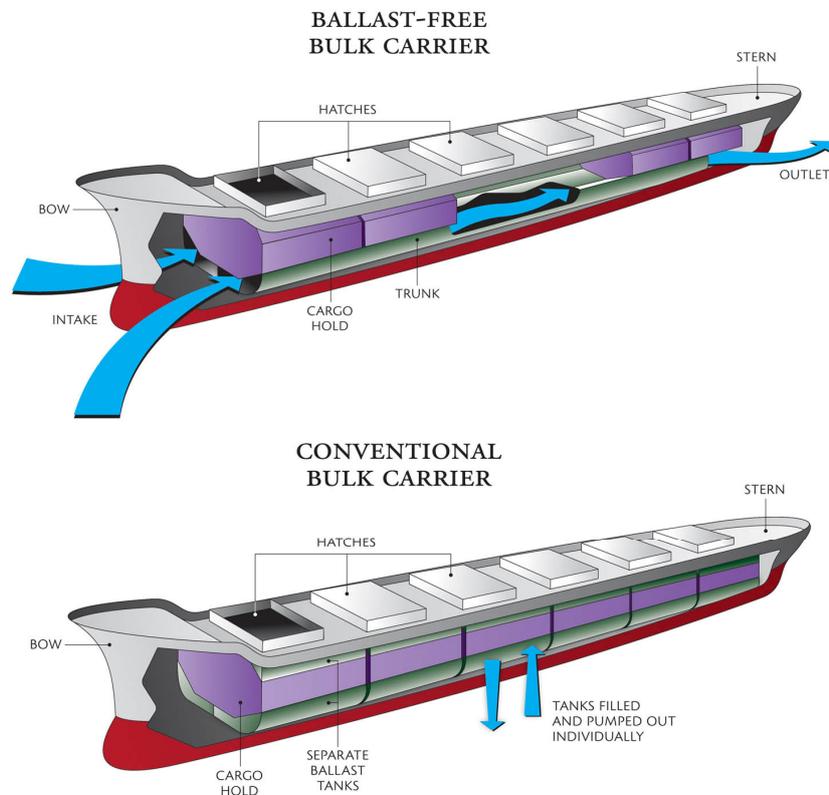
### The 'ballast-free ship' concept

Another technology that could reduce the ballast-mediated transfer of non-indigenous organisms is the 'ballast-free ship' concept. This concept was patented in 2004 and is intended for new-vessel construction only. It involves redesigning the ballast system of ships so that a constant flow of water runs through the entire length of the ship essentially eliminating the transport of ballast water (Figure 5). The concept involves replacing traditional ballast tanks with longitudinal, structural ballast trunks that extend beneath the cargo region of the ship below the ballast draft (Parsons and Kotonis 2007). These trunks are flooded with seawater to reduce the buoyancy of the vessel and due to the motion of the ship through the water, a slow, continuous flow of 'local seawater' moves through these open ballast trunks (Parsons and Kotonis 2007). When a ship is required to take on cargo, the ballast trunks can be isolated from the ocean by valves, then the water is pumped out using conventional ballast pumps.

Computer modelling and scale model tests have shown that the idea is technically and economically feasible with vessels operating at normal speed (Parsons and Kotonis 2006, 2007), however the entire vessel design needs to be redeveloped to support the proposed concept and it may only be suitable for certain ship types. If successful, this design would eliminate the need for costly ballast water treatment equipment or active substances and is even suggested to result in as much as a 7.3% reduction in the power needed to propel the ship (Erickson 2008). The researchers suggest that the new design would result in a net capital-cost saving of around US\$540,000 per ship and combined with the expected fuel savings, total transport costs would be cut by \$US2.55 per tonne of cargo (Erickson 2008).

### Conclusions and recommendations

The variable efficacy and operational limitations of ballast water exchange (BWE) have led to significant financial investment in the research and development of ballast water treatment technologies. Each of the shipboard treatment options discussed here have their own advantages and disadvantages with regard to factors such as biological efficacy, cost, ship and crew safety, power and space requirements,



**Figure 5.** Operating principle of the ‘ballast-free ship’ concept compared to traditional ballast tanks.  
From: <http://www.umich.edu/Releases/2008/Mar08/ballast>

operational efficacy and environmental soundness.

Mechanical separation technologies may reduce the concentration of organisms and sediment taken in during ballasting but they are unlikely to satisfy the BWM Convention’s D-2 discharge standard. These devices (together with cavitation) may act to improve water clarity thus improving the performance of secondary treatments. Many of the ballast water treatment technologies employ a combination of either filtration and/or cyclonic separation followed by chemical biocide dosing, electrolytic treatment or UV irradiation.

Treatment systems that combine mechanical separation and UV irradiation have the advantage of being environmentally sound and relatively cost effective. These systems are intended for ships with ballast water flow rates up to ~1000 m<sup>3</sup>/h. The treatment of larger flow rates is possible, but the systems would consume

a prohibitive amount of power and may be subject to space limitations. Another disadvantage is that they are unlikely to eliminate all ballast water organisms, as they are not able to deliver a stable lethal dose across a wide range of water quality conditions and many organisms have been demonstrated to be resistant to UV treatment. In addition, the presence of sediment in ballast water is likely to shield small organisms, such as bacteria, from UV irradiation. Further research should aim to enhance the efficacy of systems using UV by either improving water clarity or by combining with another treatment such as heat, ultrasound or chemical reagents.

Cavitation is also considered to be an environmentally safe option but at the current stage of development, it would not be considered appropriate for the shipboard treatment of ballast water due to high capital and operating costs and high power requirements. This technology is

also likely to be limited by the high flow rates of ballast pumps. This problem may be overcome by recirculating ballast water through the treatment device. This approach may also increase the efficacy of UV irradiation but it may not be possible on short voyages due to time constraints and may cause ship stability problems. Further research is required on the biological efficacy of ultrasound in a wide range of water conditions as well as potential health and safety issues and hull integrity problems due to repeated exposure to ultrasound.

The heating of ballast water using waste heat from ships' engines has been claimed to be a practical and cost effective treatment option for eliminating ballast water zooplankton and phytoplankton (including resting stages) but concerns exist that the attainable temperatures will not eliminate bacterial pathogens or that heating may impact on the structural integrity of vessels. Promising research has been conducted on several systems that are able to achieve temperatures capable of eliminating bacteria. One system uses additional heat exchangers to reach temperatures of  $>55^{\circ}\text{C}$  for short periods but it is not known whether this temperature can be achieved for the entire ballast capacity. The other treatment system uses microwaves to heat water to temperatures in excess of  $100^{\circ}\text{C}$  but at the present stage of development, high energy requirements and costs would eliminate the use of this technology in shipboard situations. Nonetheless, heat treatment deserves further investigation for ballast water treatment as it is an environmentally sound option that can potentially eliminate all ballast water biota including sediment-dwelling organisms.

De-oxygenation by the addition of glucose or reducing agents are not effective ballast water treatment options, however de-oxygenation technologies that are based on the injection of an inert gas are more promising as they are cost effective and do not impact on the aquatic environment as ballast water is re-oxygenated prior to discharge. Disadvantages of de-oxygenation are that it is unlikely to eliminate ballast water organisms adapted to low oxygen environments, such as resting stages, and the process takes several days to asphyxiate organisms and thus may not be appropriate when the voyage length is short.

Systems that use flocculating agents and magnetic separation to remove ballast water organisms is a promising technology but it may be limited by space restrictions as the treatment

system is large and the recovered material must be stored onboard and disposed of in landfill.

Biocide dosing systems that use proprietary active substances would have low capital costs and power requirements but chemical costs are significant. Dosing ballast tanks with chemical biocides requires onboard chemical storage areas and the chemicals would need to be available in ports worldwide. Treatment costs and space requirements can be significantly reduced by using onboard chemical generators. The onboard generation of ozone, chlorine, chlorine dioxide and hydrogen peroxide is possible but the capital cost of these systems is significant and all have biological efficacy, safety, operational and environmental concerns. Most chemical treatment systems use mechanical separation and/or cavitation to enhance the killing effect of the biocides while other treatment systems use no mechanical pre-treatment ahead of the chemical disinfection. For all these treatment systems, it needs to be determined whether resistant organisms that reside in ballast tank sediment can be effectively eliminated. The major concern regarding the use of chemical biocides or active substances is the potential environment impacts from the release of toxic ballast water or disinfection by-products. The treatment systems that produce free hydroxyl radicals by either electrolysis or advanced oxidation would be favourable over the other chemical treatments as they are suggested to produce less or no toxic by-products at ballast discharge and, unlike electrochlorination systems, they can operate in both freshwater and seawater. The major limiting factor for these technologies is high power requirements and it is unlikely that the power available onboard ships will be sufficient for the operation of these systems at high flow rates.

At the time of writing this review (July 2009) 16 promising systems using active substances had received basic approval and 8 systems final approval from IMO, with 4 systems receiving type approval certification and 2 systems receiving national approval certification. The still limited production capacity for ballast water treatment systems may not be sufficient to equip all vessels by 2011 when the D-2 discharge standards are planned to apply to the first group of vessels.

In summary, reducing the risk of ballast water mediated invasions represents a significant technological challenge. Ideally, a treatment option that is 100% effective is required. At the

present time, no treatment option or multi-component treatment system has proved to be completely effective as each are limited by one or more factors including cost effectiveness, space and energy requirements, environmental soundness, safety and biological efficacy. Many of these limitations relate to the high flow rates and volumes of water that must be treated. Although many of the treatment options are suggested to be able to meet the BWM Convention D-2 discharge standard, further research is required to increase their biological and operational efficacy and safety under full-scale shipboard conditions, in particular, their ability to inactivate resistant organisms such as dinoflagellate cysts.

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