PAPER

Review: In-Water Systems to Reactively Manage Biofouling in Sea Chests and Internal Pipework

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ABSTRACT

Sea chests are cavities built into a vessel's hull to aid the efficiency of pumping seawater into internal pipework systems. Sea chests and internal pipework are known hotspots for the accumulation of biofouling, and vessel biofouling is a major pathway for the introduction and spread of nonindigenous marine species. The use of preventive strategies to minimize biofouling within sea chests and internal pipework is difficult due to their structural complexity; therefore, reactive methods to manage the associated biosecurity risk are required. This review examines the efficacy, environmental considerations, and cost of different systems to reactively manage sea chest and internal pipework biofouling within operationally realistic time frames (<3 days) and identifies those that warrant further investigation. Physical removal systems with recapture capability should be developed for accessible areas (e.g., grates), as such systems provide an operational benefit to the vessel. For internal and inaccessible surfaces, the development of thermal systems, particularly steam systems, is encouraged as they offer broad-spectrum efficacy at obtainable temperatures and require relatively short exposure periods. Compared to chemical treatments, thermal treatments are less influenced by environmental variables (e.g., temperature, water chemistry) and regulatory constraints.

Keywords: vessel biofouling, biosecurity, risk management

Introduction

The accumulation of organisms on immersed surfaces is known as biofouling. In the initial stages of biofouling, organic material adheres to a surface and is rapidly colonized by bacteria, microalgae, and cyanobacteria, forming a slime layer. The creation of a slime layer occurs rapidly (i.e., minutes to hours). Aside from continuous cleaning, there is currently no effective technology to prevent slime layer formation (Dobretsov, 2010).

Biofouling is a stochastic process based on the probability of biofouling organisms encountering a surface in a state that is suitable for attachment (Aldred & Clare, 2008). Complex interactions take place between abiotic and biotic factors, and these interactions include the season of first submersion, length of submersion, surface type, presence of biofilm, biofilm type, and light availability (Aldred & Clare, 2008; Terlizzi & Faimali, 2010). Despite the stochastic nature of the biofouling process, "pioneering" macrofoulers typically include green filamentous algae, barnacles, tubeworms, and bryozoans (Hilliard et al., 2006; Lewis & Coutts, 2010).

Biofouling is recognized as a significant pathway for the introduction of nonindigenous marine species (NIMS) into New Zealand (Bell et al., 2011). To reduce the likelihood of entry and establishment of NIMS via the biofouling pathway, New Zealand's Ministry for Primary Industries (MPI) issued the Craft Risk Management Standard for Biofouling on Vessels Arriving to New Zealand (CRMS) on the 14th of May 2014 (MPI, 2014). This standard applies to all types of sea craft entering New Zealand waters and is scheduled to come into force in 2018 to allow industry time to prepare their biofouling management plans (MPI, 2014). The practical difficulties in managing biofouling on different areas of the hull are acknowledged within the CRMS. For example, a greater tolerance of macrofouling has been proposed for vessel niche areas (e.g., sea chests) due to the specific difficulties in preventing biofouling on these areas (Georgiades & Kluza, 2014).

Sea chests are cavities positioned below the water line on the side or bottom of a vessel's hull that houses the openings to the internal pipework system. Sea chests aid the efficiency of pumping seawater on board during vessel operation by providing a motionless reservoir of water for ballast, firefighting, and engine cooling

(Palermo, 1992; Coutts et al., 2003). To prevent the entry of large debris, sea chests are typically protected by grates that are welded or bolted on (Coutts et al., 2003) and may only be accessible when the vessel is drydocked. Sea chest grates do not prevent the entry and settlement of larval stages of sessile species on internal surfaces of sea chests or internal pipework (e.g., Frey et al., 2014; Lewis, 2016).

Consequences of Sea Chest and Internal Pipework Biofouling

Biofouling of sea chests and internal pipework may reduce a vessel's water pumping efficiency, with the economic costs likely dependent on the degree or positioning of biofouling (Pamitran et al., 2016). In extreme cases, the complete blockage of pipes can compromise the use of vital on-board systems (e.g., firefighting systems; Palermo, 1992) and corrode pipes over longer time frames, necessitating unscheduled maintenance (Jones & Little 1990; Grandison et al., 2011).

Biosecurity Risks of Sea Chest and Internal Pipework Biofouling

Ocean-going vessels have been identified as a major vector for the international translocation of NIMS (Bell et al., 2011). It has been estimated that 42–90% of NIMS established in New Zealand, Hawaii, North America, Port Philip Bay Australia, and Japan have likely been introduced via this pathway (Cranfield et al., 1998; Eldredge & Carlton, 2002; Fofonoff et al., 2003; Hewitt et al., 2004; Otani, 2006).

Vessel biofouling is not evenly distributed across the surface of a hull—areas that are protected from a constant or uniform water flow or susceptible to antifouling coating wear or damage tend to accumulate a higher biomass of organisms (Coutts et al., 2003, 2010). These "niche" areas include sea chests and internal pipework (Coutts & Taylor, 2004; Coutts & Dodgshun, 2007; International Maritime Organization [IMO], 2011). Coutts and Dodgshun (2007) surveyed the sea chests of 42 vessels dry docked in New Zealand and identified 150 different taxa, of which 10% were NIMS yet to be established in New Zealand and 35% were cryptogenic. Similarly, Frey et al. (2014) found 299 taxa in sea chests of Canadian domestic and international vessels, with ~15–20% identified as NIMS or cryptogenic.

Sea chest communities are diverse and may consist of bivalves, polychaetes, hydroids, barnacles, bryozoans, crustaceans, ascidians, gastropods, sea stars, anemones, amphipods, and, for areas exposed to sunlight, algae and sea grass (Coutts et al., 2003; Coutts & Dodgshun, 2007; Frey et al., 2014; Lewis, 2016). Sea chests provide a sheltered habitat for mature sessile and mobile organisms that may not be capable of surviving on other more exposed hull locations or in ballast water (Coutts & Dodgshun, 2007; Leach, 2011; Lewis, 2016). The translocation of adult marine organisms to new areas increases the likelihood of establishment because reproductively mature organisms can release propagules into the surrounding environment (Coutts et al., 2003; Godwin, 2003; McDonald, 2012).

Preventive Approaches to Sea Chest and Internal Pipework Biosecurity

Preventive management is the most effective way to minimize biosecurity risk associated with vessel biofouling (Bax et al., 2003; Floerl et al., 2005; IMO, 2011). Reactive management following initial detection of NIMS populations in the marine environment is costly, labor-intensive, and time-consuming, as they are usually well established (Davidson et al., 2008a). In 2011, the International Maritime Organization published guidelines to minimize the transfer of invasive aquatic species via vessel biofouling (IMO, 2011). For sea chests and internal pipework, the guidelines recommend that Marine Growth Prevention Systems (MGPS) be installed to prevent the settlement of biofouling organisms. The application of antifouling coatings to the internal areas of a sea chest and the associated grates was also recommended (IMO, 2011).

The most common MGPS used in vessel sea chests are sacrificial anodic copper systems (e.g., Cathelco®) and chlorine-based dosing systems (e.g., Chloropac® or Ecocell®) (Grandison et al., 2011). MGPS installed within the sea chest should ideally provide protection to both the sea chest and internal pipework; however, those installed within the strainer box only protect the internal pipework (Chris Scianni, personal communication).

Antifouling coatings are often used to prevent or minimize the settlement of biofouling within sea chests (Lewis, 2016). However, as surfaces within sea chests are not exposed to constant or uniform water flows, the ability of antifouling coatings to prevent the settlement and establishment of biofouling can be compromised (Morrisey et al., 2013).

Efficacy of Preventive Measures

Despite the use of MGPS and antifouling coatings within vessel sea chests and internal pipework, recent studies still depict sea chests and internal pipework as "hotspots" for biofouling accumulation (Coutts & Dodgshun, 2007; Lee & Chown, 2007; Grandison et al., 2011; Frey et al., 2014; Lewis, 2016). For example, Lewis et al. (1988) found that the copper dose required to control tubeworm fouling within submarine saltwater cooling systems was at least 10 times greater than the MGPS manufacturer's recommendation.

Although MGPS can reduce the rate at which biofouling accumulates within sea chests and internal pipework, they do not prevent it completely and tend to be less effective against mobile organisms (Coutts & Dodgshun, 2007; Grandison et al., 2011). Development of strategies to prevent the establishment of biofouling in sea chests and internal pipework is ongoing. For strategies that fail or for vessels that do not apply preventive measures, in-water systems that reactively manage the biosecurity risks associated with fouled vessels are required.

Considerations for Reactive In-Water Systems

A number of factors may affect the efficacy of in-water systems for the reactive treatment of sea chests and internal pipework of vessels. Vessel sea chests can be structurally complex; for example, the use of internal baffles or box coolers can make access difficult for inspection and cleaning (Justin McDonald, personal communication). Consultation with the vessel's engineer is therefore necessary to assess any risks to the vessel's structural or operational integrity prior to applying a reactive in-water system.

A number of biotic and abiotic factors can also influence the efficacy of reactive in-water systems: extent and maturity of biofouling communities (Morrisey et al., 2013); organism type (Neil & Stafford, 2005; Rajagopal, 2012), size (Piola & Grandison, 2016), and origin (Piola & Hopkins, 2012); and seawater properties (Rajagopal et al., 1995; Neil & Stafford, 2005). In addition, if calcareous shells and other organism residues are not physically removed, recolonization can be rapid (Claudi & Mackie, 1993) and vessel operational efficiency may not improve (Pamitran et al., 2016).

The effluent from a reactive in-water system can pose a chemical or biological contamination risk to the environment; therefore, any discharge(s) must meet any local regulatory requirements (Grandison et al., 2011; Morrisey et al., 2013; Department of the Environment and the Ministry for Primary Industries, 2015).

Use of reactive in-water systems are likely to be cheaper than vessel dry-docking (Floerl et al., 2010; Piola & Grandison, 2016) and could result in significant savings if used proactively for regular hull maintenance (Pamitran et al., 2016). The duration of in-water system application should be based on required efficacy while taking the vessel's schedule into account. Merchant vessels typically stay in New Zealand for 1–3 days (Inglis et al., 2012).

Lessons Learned From and Adaption of Land-Based Industrial Systems

A number of systems developed to minimize biofouling within land-based industrial water cooling systems are potentially adaptable for in-water treatment of vessel sea chests and internal pipework. Treatments based on chlorine and heat exposure are the most commonly used to manage biofouling within such land-based systems (Venkatesan & Murthy, 2009).

Scope of Review and Evaluation of Reactive In-Water Systems

This review evaluates the potential application of reactive treatment systems to sea chests and internal pipework based on available literature and expert opinion. Although there are recommendations made within this document, the final decisions relating to the implementation of risk management measures under the CRMS will be based on an assessment of risk, New Zealand's obligations under international agreements, the efficacy and cost of risk management measures, technical and operational factors, and any other matters that may be relevant as described in New Zealand's domestic legislation (Biosecurity Act, 1993).

In-water treatment agents or system types used for industrial water cooling systems, vessel sea chests, and internal pipework include chemical oxidizing agents, chemical nonoxidizing agents, and nonchemical methods (Growcott et al., 2016). Agents and system types evaluated within this review are those that are either commercially available or have been experimentally tested on sea chests and internal pipework (Grandison et al., 2011; Atalah et al., 2016).

Chemical Treatments

Chlorine

Chlorine is the most frequently used chemical treatment for aquatic systems and the most extensively studied nonselective biocide, in terms of chemistry, toxicity, and ecotoxicity

(Satpathy et al., 2010; Rajagopal, 2012).

Chlorination of seawater can be achieved via the addition of chlorine gas (Rajagopal, 2012), solid tablets (e.g., granular dichlor; Morrisey et al., 2016), or sodium hypochlorite added as a liquid or generated *in situ* via electrochlorination (Grandison et al., 2011; Rajagopal, 2012). Chlorination chemistry in seawater is complex because of the large number of reactions that occur with organic and inorganic substances (see Khalanski & Jenner, 2012); therefore, not all chlorine is available to act as a biocide. However, some reactions result in the formation of biocidal oxidizing agents (e.g., bromine), which are potentially more effective than chlorine (Khalanski & Jenner, 2012).

Discharged water containing residual chlorine or chlorine by-products can negatively impact upon aquatic ecosystems (Boelman et al., 1997); therefore, discharge limits are imposed by some regulatory agencies (Rajagopal et al., 2012). Neutralization of chlorine-containing effluent prior to environmental discharge can be easily achieved by adding sulphur dioxide or sodium thiosulphate (Chou et al., 1999; Tsolaki & Diamadopoulos, 2010; Morrisey et al., 2016).

The efficacy of chlorine is influenced by a variety of biotic and abiotic factors. Shelled organisms can detect chlorine and close their shell. For example, three mussel species (*Mytilopsis leucophaeata*, *Dreissena polymorpha,* and *Mytilus edulis*) reduced valve openings by more than 90% compared to the control when exposed to 1 mg/L chlorine (Rajagopal et al., 2003). This can be overcome by exposing shelled organisms to chlorine for an extended period of time (up to a few weeks); however, this would be counterproductive within the operational context required and may induce spawning. Alternatively, exposure time can be reduced by using higher chlorine concentrations or by using chlorine in conjunction with a cotreatment (e.g., carbon dioxide or increased temperature—see Miscellaneous Treatments section).

Morrisey et al. (2016) used chlorine to treat Mediterranean fanworm (*Sabella spallanzanii*) fouling on the outer hull of an 8-m-long yacht. Chlorine, in the form of granular dichlor, was applied at an initial concentration of 200 mg/L free available chlorine (FAC), and the vessel was held within an encapsulated dock for 16 h. Thirty *S. spallanzanii* were collected after the experiment, and 28 were judged nonviable; a further 33 individuals collected 6 days post-treatment were also nonviable. This outcome occurred despite the concentration of FAC decreasing within the floating dock from 200 mg/L to 50 mg/L after 2 h and to <10 mg/L after 16 h.

Rajagopal (2012) observed that most shelled organisms succumb to chlorine more rapidly than mussels; therefore, a treatment that induces mortality in mussels may be a good indicator of overall treatment efficacy. The Asian green mussel (*Perna viridis*) was the most resistant among 10 tropical bivalve species exposed to 10 mg/L chlorine at 29°C, with 100% mortality occurring after 48 h (Rajagopal, 2012). However, regardless of the species present, the efficacy of chlorine treatment is influenced by fouling biomass (Mackie & Claudi, 2009a).

The ability of chlorine to be an efficient biocide is affected by abiotic factors such as temperature, pH, and concentration of suspended solids. The doubling of metabolic activity of ectotherms for every 10°C increase in temperature facilitates the increased uptake and, hence, toxicity of chlorine (Chou et al., 1999; Mackie & Claudi, 2009a). By contrast, the biocidal effect of chlorine decreases at pH > 8 as the production of hypochlorite ions are favored compared to the more effective hypochlorous acid (Rajagopal, 2012). Furthermore, it is likely that a higher dose of chlorine will be required when operating in nearshore environments compared to the open ocean, as the higher concentration of suspended organic and inorganic substances will reduce the amount of available chlorine residual (Chou et al., 1999; Morrisey et al., 2016).

The widespread use of chlorine is in part due to its low cost; for example, the 3.6 kg of granular dichlor applied by Morrisey et al. (2016) cost ~NZ$35. However, the efficacy of this treatment against bivalves and assemblages of high biomass is questionable within operational time frames.

Chlorine Dioxide

Chlorine dioxide is considered a more powerful oxidant than chlorine (Rajagopal et al., 2012). Chlorine dioxide is a gas and in solution does not react with bromine or ammonia, resulting in fewer side reactions compared to chlorine. However, chlorine dioxide oxidizes with metals in reduced forms (Fe^{2+}, Mn^{2+}), nitrites (NO_2^-) and sulphites (SO_2^-) and dissolved organic matter (Dore, 1989). In polluted or eutrophic waters, these oxidizing reactions can reduce the amount of freely available chlorine dioxide (Rajagopal et al., 2012). This "demand" must be considered because reactive in-water treatments are most likely to take place in coastal areas (ports) where seawater is more likely to contain organic substances.

The by-products generated by oxidizing reactions of chlorine dioxide in solution mainly consist of sodium chlorite, chlorate, and chloride, which are generally considered acceptable for discharge by regulatory bodies (Mackie & Claudi, 2009b).

Most studies of the effectiveness of chlorine dioxide on industrial cooling systems have focused on preventive treatment via continuous application (Mackie & Claudi, 2009b); thus, few data exist on the efficacy of chlorine dioxide for use as a reactive biofouling treatment.

Chlorine dioxide costs approximately 2.5 times more to use than chlorine (Venkatesan & Murthy, 2009; Grandison et al., 2011).

Bromine

Application of bromine has primarily been as a water treatment for swimming pools (Chou et al., 1999). As a biocide, bromine can be used in different forms (gas, liquid, and solid) including activated bromine, sodium bromide, bromine chloride, and proprietary solutions of bromine with other chemicals (e.g., chlorine) (Mackie & Claudi, 2009b). The biocidal property of bromine is similar to that of chlorine in both action and effectiveness; however, the oxidizing ability of bromine increases at pH > 8 (Mackie & Claudi, 2009b).

Several toxic by-products are formed when bromine is added to seawater, although these may rapidly degrade, potentially limiting environmental concerns (Grandison et al., 2011).

Bromine is often added to chlorine treatments, especially in mildly alkaline waters (Sprecher & Getsinger, 2000; Grandison et al., 2011); however, there is an absence of studies assessing the efficacy of bromine as a sole reactive biofouling treatment.

The cost of bromine may limit its use as it is approximately twice the cost of chlorine (Chou et al., 1999; Venkatesan & Murthy, 2009).

Hydrogen Peroxide

Hydrogen peroxide is used principally as a biocide in small contained systems, such as fuel bays in nuclear power stations (Mackie & Claudi, 2009b). It is difficult to treat large bodies of water with hydrogen peroxide due to its rapid degradation in seawater and inactivation by bacterial enzymes (Rajagopal et al., 2012). In order to be effective, relatively high doses of hydrogen peroxide need to be applied at low temperatures (Jenner et al., 1998; Grandison et al., 2011).

Hydrogen peroxide rapidly degrades to environmentally benign oxygen and water (Grandison et al., 2011); however, there is a paucity of efficacy data regarding the use of hydrogen peroxide for reactive biofouling treatment. In freshwater systems, Petrille and Miller (2000) reported 100% mortality of adult zebra mussels (*Dreissena polymorpha*) when exposed to concentrations of 10, 20, and 40 mg/L of hydrogen peroxide for 7.8, 8.8, and 3 days, respectively. However, the Asian clam (*Corbicula fluminea*) appears to be more resilient.

Hydrogen peroxide is less effective than chlorine treatment, which may lead to increased application costs (Chou et al., 1999) and was not recommended as an in-water treatment by Claudi & Mackie (1993).

Ferrate

Due to its higher redox potential, ferrate is considered a more powerful oxidant than chorine, ozone, or bromine. In the 1970s, ferrate was investigated as a replacement for chlorine, but it was deemed not economically viable at the time (Mackie & Claudi, 2009b).

Potassium ferrate is considered the safest ferrate form for biocidal applications due to its ease of production, stability, and lack of harmful by-products (Sharma, 2002). On-site production of ferrate is now possible through the patented Ferrator® system, which produces ferrate in a liquid form that can be added to water; however, this system requires the addition of hazardous precursor chemicals (sodium hydroxide, sodium hypochlorite, and ferric chloride) (Grandison et al., 2011). The use of the Ferrator system has thus far concentrated on ballast water treatment, and while its use as a reactive biofouling treatment has been considered, there is a paucity of efficacy data (Mackie & Claudi, 2009b).

Ferrate granules cost approximately NZ$12 per kilogram (Yates et al., 2014).

Peracetic Acid

Peracetic acid is used as a disinfectant to eliminate harmful microorganisms from wastewater systems (Cristiani, 2005). The mode of action involves production of oxygen free radicals that break chemical bonds in cell membrane enzymes (Jenner et al., 1998). The recommended dosage in industrial cooling water systems is 1–10 mg/L with a 1–3 h contact time (Jenner et al., 1998).

Peracetic acid is not persistent in seawater and does not produce mutagenic by-products when reacting with organic material (Kitis, 2004; Cristiani, 2005). However, peracetic acid is corrosive, unstable at high concentrations, and may pose health and safety risks if not used in accordance with the manufacturer's instructions (Grandison et al., 2011; Rajagopal et al., 2012).

With respect to biofouling management, peracetic acid appears to be less effective and 10–20% more expensive than chlorine (Venkatesan & Murthy, 2009; Grandison et al., 2011).

Acetic Acid

Acetic acid has been considered for use as a biocide for the reactive treatment of biofouling (Carver et al., 2003; Forrest et al., 2007; Denny, 2008; Piola et al., 2010; Rolheiser et al., 2012; Atalah et al., 2016). It is a weak acid, and its biocidal activity is related to the number of free hydrogen ions present in solution and the anions and undissociated molecules that may act independently of pH (Reid, 1932; Forrest et al., 2007; Cortesia et al., 2014).

Acetic acid is rapidly biodegradable in water (Kitis, 2004), although the use of glacial acetic acid (99% concentration), which is used when a large area is to be treated, has transport and handling risks as it is an irritant and mildly corrosive to metals (Morrisey, 2015).

The use of acetic acid as a biocide has been experimentally tested on biofouling at a small scale (e.g., 20 × 20 cm experimental settlement plates; Piola et al., 2010; Atalah et al., 2016), with 100% mortality of mature fouling assemblages occurring after a 48-h exposure to 5% acetic acid (Atalah et al., 2016). Acetic acid has also been used at the vessel scale to kill *S. spallanzanii* via encapsulation, with complete mortality of this species occurring 3 days after leaks in the encapsulation device were repaired and further glacial acetic acid was added (Javier Atalah, personal communication).

The use of acetic acid (in the form of glacial acetic acid) is not recommended due to costs and safety considerations (Morrisey, 2015); however, the latter considerations can be negated by the use of working concentrations (e.g., <10%) or using sodium diacetate as the starting material. The use of acetic acid as a reactive treatment agent warrants further investigation.

Descalers

Descalers are used to remove accumulated insoluble deposits from the internal surfaces of pipes and to degrade the calcium carbonate shells of fouling organisms. The active substance is usually an acidic compound, such as hydrochloric or phosphoric acid, which reacts with carbonate compounds producing carbon dioxide and soluble salts (Lewis & Dimas, 2007).

The environmental and operator safety concerns associated with the handling and discharge of descalers will depend on the active ingredient of the proprietary product and its concentration.

The use of descalers to kill biofouling has had variable results (Neil & Stafford 2005; Lewis & Dimas 2007), with the effectiveness of all descalers tested found to be dependent on the availability of acid in solution. Recently, Bracken et al. (2016) assessed the ability of seven commercially available descalers to dissolve the calcium carbonate shells of the blue mussel (*Mytilus galloprovincialis*). They found that hydrochloric acid (HCl)-based descalers performed better than those containing phosphoric acid or acid surfactants at 11°C. Interestingly, increasing the concentration of the descaler above 25% had a negligible impact on the rate of shell dissolution, with the majority of dissolution occurring within the first 12 h of exposure. Follow-up experiments achieved 100% mortality after mussels were exposed to a HCL-based descaler in a static system for 12 h (concentration 25%, 11°C).

Lewis and Dimas (2007) concluded that the volume of descaler required to treat heavily fouled internal surfaces is impractical from both an efficacy and economic standpoint. Although the findings of Bracken et al. (2016) may offer a way forward, they concurred that the large volumes required may be prohibitively expensive. This cost should be assessed relative to the key operational benefit of descalers, which is their potential to remove fouling from treated surfaces, thus improving operational efficiencies.

Quaternary Ammonium Compounds

Quaternary ammonium compounds (QACs) are selective biocides that have been used as antibacterial disinfectants (Jenner et al., 1998) and as biofouling treatments in industrial cooling systems (Rajagopal et al., 2012). QACs have been used to reactively treat biofouling of internal surfaces of international yachts arriving in the Northern Territory (Australia) (Neil & Stafford, 2005) as well as Royal Australian Navy vessels (Piola & Grandison, 2016).

QACs are the most commonly used nonoxidizing chemical for biofouling treatment (Grandison et al., 2011), with their biocidal activity related to metabolic disruption.

Two commonly used proprietary formulations for marine applications are *Conquest*® and *Quatsan*®. These commercial-grade disinfectants contain surfactants, alkaline salts, and the QAC benzalkonium chloride. The use of QACs as an in-water treatment has raised concerns about their environmental persistence and adverse effects on aquatic organisms. QACs are not metabolized by aquatic organisms and may accumulate in the edible tissues (Jenner et al., 1998).

QACs are capable of being absorbed on suspended matter in water or on colloids such as humic acids; therefore, neutralization can occur through the addition of clay at 5–40 mg/L (Jenner et al., 1998). *Conquest* at a 1% concentration was found to induce 100% mortality in black-striped mussels (*Mytilopsis sallei*) after 7 h (Bax et al., 2002). Lewis and Dimas (2007) tested the biocidal efficacy of *Conquest* and *Quatsan* on the Australian blue mussel (*Mytilus galloprovincialis planulatus*). For all concentrations tested 100% mortality occurred within 48 and 24 h following a 14-h exposure to *Conquest* and *Quatsan*, respectively. However, a 24-h exposure to *Conquest* TGA® or *Quatsan* within a replica 35-L sea chest and attached piping system did not result in 100% mortality of *M. galloprovincialis planulatus* (Piola & Grandison 2016), and only 10–20% of oysters (*Saccostrea glomerata*) were killed after a 12-h exposure to *Quatsan* (Neil & Stafford, 2005). The effectiveness of QACs is influenced by water temperature, with higher temperatures enhancing physiological activity and biocide uptake (Jenner et al., 1998).

The use of QACs to treat biofouling may be more expensive than other treatment options due to the high doses required and the high cost of the proprietary formulations (Grandison et al., 2011). Efficacy of QACs appears to vary according to the organisms treated.

Physical Treatments

Physical Removal

Physical removal of biofouling encompasses a variety of methods (e.g., hand tools, mechanical rotating brushes; see Morrisey & Woods, 2015). Most physical removal systems are best used on flat or slightly curved external hull surfaces and are likely to be limited in their ability to clean sea chests and internal pipework due to the inaccessibility to all fouled surfaces (Inglis et al., 2012). One of the major constraints with physical removal methods is that all of the biofouling, including mobile organisms, and chemicals released from antifouling coatings need to be contained or treated if they pose an unacceptable contamination risk (Woods et al., 2007; Morrisey et al., 2013; Morrisey & Woods, 2015). The “magic box” treatment system is a physical removal system that may prove suitable. Lewis (2013) reported a successful preliminary trial of this system, which consists of a transparent removable plastic box that can fully isolate the treated area. After the surface is isolated, a high-pressure (5,000 PSI) water lance or hand scraper tool can be inserted through access ports. Effluent is filtered through a two-stage system and then sterilized using ultraviolet light.

It is unlikely that there is a physical removal method capable of treating an entire sea chest and internal pipework system due to limited accessibility. Inglis et al. (2012) has estimated that it would cost ~NZ $4,000 per day to clean the external surface of a vessel’s sea chest grates plus a mobilisation cost of ~NZ $2,000.

Thermal Treatment

Heat has been used extensively to treat biofouling in industrial cooling systems via the recirculation of cooling water (Boelman et al., 1997; Rajagopal et al., 2012). The application of sufficient heat can cause cell and ultimately organism death through the denaturing of proteins (Somero, 2002). Thermal treatment is considered more environmentally benign than biocidal treatments; however, there may be restrictions on the volume of heated effluent that can be discharged (Perepelizin & Boltovskoy, 2011).

The effect of heat treatment on marine species generally follows a pattern consistent with a steep increase in mortality within a narrow temperature range (Rajagopal & Van der Velde, 2012). Bivalves are considered to be more thermally tolerant than other biofouling species; therefore, thermal treatments effective against bivalves should be effective for most other species (Rajagopal & Van der Velde, 2012). Of all bivalve species tested, the oyster *Crassostrea madrasensis* appears to be the most thermally tolerant (Rajagopal et al., 2012). Rajagopal and Van der Velde (2012) state that 100% mortality of all bivalve species can be achieved by raising the temperature to 42°C for approximately 2 h.

Other than taxa-related differences, the time and temperature requirement for mortality of biofouling organisms appears to be dependent on the acclimation temperature (i.e., the difference between the ambient and treatment temperature) (Venkatesan

& Murthy, 2009). For example, mussels acclimatized to higher temperatures are more resilient to heat treatment (see McMahon & Ussery, 1995; Boelman et al., 1997). Organism size can also influence thermal tolerance; however, this is not consistent among bivalve species (Rajagopal et al., 2012).

There are no published data available concerning the time and temperature required to ensure mortality of complex marine biofouling assemblages at the vessel scale, although studies have been completed using replica sea chests (Leach, 2011; Piola & Hopkins, 2012). Leach (2011) achieved 100% mortality of mussels *M. edulis* and *Trichomya hirusta* at 60°C for 10 min. Piola and Hopkins (2012) assessed the efficacy of thermal treatment on species typical to sea chest biofouling. In laboratory experiments, 100% mortality was achieved across all three treatments (37.5°C for 60 min, 40°C for 30 min, and 42.5°C for 20 min) for all species, except the barnacle *Austrominius modestus* and oyster *Crassostrea gigas*. Testing of these thermal treatments within a replica sea chest produced variable results. These two studies highlighted the difficulty in achieving a uniform heat distribution throughout all areas of the replica sea chests.

Results from studies that test the thermal tolerance of organisms in isolation should be viewed with caution, as the biogenic structure of complex biofouling assemblages may provide areas of thermal refuge for some organisms. Sublethal temperature exposure could also cause organisms to spawn (e.g., *Mytilus galloprovincialis*; Apte et al., 2000) or confer thermal tolerance to subsequent treatments and the unintended transport of more resilient individuals (Piola & Hopkins, 2012). For biosecurity purposes, higher temperatures and longer exposure times than those reported effective may be required to provide assurance that a uniform heat distribution across complex structures and assemblages has been achieved.

Maintaining a uniform heat distribution throughout a sea chest and pipework is considered to be predominately an engineering issue. Isolating the sea chest and internal pipework through the application of an external watertight cover could increase heating efficiency and minimize biosecurity risks (Leach, 2011; Piola & Hopkins, 2012).

Thermal treatment through application of steam may represent a viable alternative. In order to apply the treatment, seawater has to be evacuated from the treatment area and should be treated prior to discharge into the marine environment. Steam can then be injected into the sea chest and internal pipework through a hose that is connected to a steam generator (Robert Hilliard, personal communication). Steam treatment could be faster and require less energy than water-based thermal treatments because it avoids heating large volumes of seawater. A further advantage is that propagule release from stressed organisms is unlikely to occur due to the absence of surrounding seawater. Hilliard (personal communication) recommend a temperature of 60°C for 1 h, which, according to the literature reviewed, would be expected to kill all exposed organisms (see Growcott et al., 2016). Temperature measurements of various external steel surfaces throughout the sea chest and internal pipework network could be used as a proxy for internal temperature and thus provide a level of assurance that the heat from the steam is evenly distributed throughout the treated area. To avoid damage to coatings and seals, the external steel temperatures would need to be maintained below 65°C (Robert Hilliard, personal communication).

The cost of applying a thermal sea chest treatment using a commercially available system (Hull Surface Treatment system) on 50, 100, and 200-m vessels has been estimated at ~NZ$5,200, NZ$6,500, and NZ $7,800, respectively (Inglis et al., 2012).

Deoxygenation

The reduction of dissolved oxygen in seawater has previously been achieved through the encapsulation of vessel hulls with impermeable plastic (Inglis et al., 2012). Inglis et al. (2012) concluded that encapsulation techniques were likely to cause significant delays to the schedules of vessels with turnaround times of <4 days, although this is likely to be dependent on the amount of fouling present and water temperature (Artigaud et al., 2014). Bivalves and barnacles are likely to survive for prolonged periods by closing their shells and entering an anaerobic physiological state, reducing the likelihood of achieving 100% mortality (Wang & Widdows, 1993; Inglis et al., 2012).

Potentially any size vessel could be treated via deoxygenation; however, depending on the size and shape of a hull, it can be difficult to wrap a vessel, ensure a watertight seal, and prevent tears (Inglis et al., 2012; Atalah et al., 2016; Justin McDonald, personal communication). Further considerations include the dislodgement of biofouling when installing the containment system (e.g., sea chest covers), the presence of larval stages or spores resistant to anoxic conditions, and potential for treatment prior to discharge of the contained water (i.e., increased biocide concentrations from the antifouling coatings; Inglis et al., 2012).

Freshwater (Osmotic Shock)

Reducing the salinity of seawater can induce osmotic shock in marine organisms, with soft-bodied organisms more likely to be susceptible to changes in salinity compared to bivalves, particularly if they are recruited from intertidal habitats (Chou et al., 1999). Previous studies have shown that mortality of all biofouling species on vessels following immersion in freshwater is difficult and time-consuming (Brock et al., 1999; Davidson et al., 2008b). Inglis et al. (2012) estimated that it may take up to 14 days to achieve 100% mortality. The duration of exposure is influenced by environmental variables (e.g., temperature) and type and level of biofouling present. The use of freshwater as a treatment for vessels with a turnaround time of <4 days would likely cause significant delays and associated economic costs (Inglis et al., 2012). Furthermore, osmotic shock can also cause some organisms to spawn (Apte et al., 2000) potentially increasing the likelihood of establishment.

Miscellaneous Systems

Cotreatments

The application of multiple treatments may improve performance compared to using a treatment in isolation. The use of cotreatments is dependent on cost as well as their ability to accelerate mortality compared to using a single treatment (e.g., Rajagopal et al., 2002; Venhuis & Rajagopal, 2010). Another potential advantage of using this strategy is that biocides may be used at lower concentrations (Mackie & Claudi, 2009b), which lessens the regulatory burden associated with discharge limits (e.g., reduced chlorine concentration when used at higher temperatures), or shorter exposure periods, allowing use on vessels with short dockings intervals.

Venhuis and Rajagopal (2010) tested the ability of carbon dioxide and chlorine to induce mortality in the mussel *M. leucophaeata*. The time required to achieve 100% mortality when using chlorine alone at 1 mg/L was 46 days when acclimatized to 20°C (Rajagopal et al., 2003). With the addition of carbon dioxide (resulting in a reduction of the pH to 5), 100% mortality was achieved in 6 days (Rajagopal et al., 2012). Jenner and Polman (2003) showed similar results when treating *M. edulis*. The use of carbon dioxide as a pretreatment overcomes the valve closing response of bivalves, resulting in exposure of the organism's soft tissue (Venhuis & Rajagopal, 2010).

Harrington et al. (1997) tested the synergistic effect of chlorine and heat on the mortality rate of zebra mussels (*Dreissena polymorpha*). At 30°C and 0.5 mg/L free chlorine, 95% mortality was achieved in 1 day, whereas at 34°C it was achieved in 1 h. These results are similar to those of Rajagopal et al. (2002), who found exposure of *M. leucophaeata* to 0.5 mg/L chlorine at 5°C required 99 days to achieve 95% mortality. The required exposure time was reduced to 47 days at 30°C. Both studies reported that the synergistic effect between heat and chlorine diminishes at 35–36°C, where mortality rates become similar to those obtained for heat alone.

Encapsulation and the creation of anoxic conditions can be accelerated through the addition of oxygen-depleting chemicals such as nitrogen (Tamburri et al., 2002; Morrisey & Woods, 2015). The survival of biofouling when exposed to anoxic conditions is dependent on water temperature, with mortality accelerated at higher temperatures (Claudi & Mackie, 1993; Johnson & McMahon, 1998). Mortality is also enhanced when using descalers at higher temperatures (Bracken et al., 2016).

Although there are benefits to using cotreatments, potential limitations include their cost, effectiveness, and the potential requirement for additional equipment. Costs are likely to be variable and dependent on the cotreatments being applied.

Discussion

All in-water systems identified for the reactive management of biofouling have some limitations (Table 1), and few systems could be applied to vessel sea chests and pipework in an operationally acceptable time frame for commercial vessels (e.g., <3 days).

Management of biofouling in aquatic systems has frequently been achieved by using chemicals because of their ability to reach inaccessible surfaces and relatively low cost, with chlorine being the most commonly used. The efficacy of chemicals to manage biosecurity risk can be limited due to biotic (e.g., type, extent, and level of biofouling) and abiotic (e.g., seawater composition, temperature, pH) variables. Furthermore, chemical-contaminated effluent may not meet regulatory requirements for discharge and may have to be neutralized or disposed of on-shore, increasing operational costs. Some chemicals (e.g., chlorine) may also corrode pipes (e.g., CuNi; Grandison et al., 2011), while

TABLE 1

Advantages and limitations of reactive systems to remove or treat biofouling in sea chests and internal pipework (Forrest et al., 2007; Venkatesan & Murthy, 2009; Grandison et al., 2011; Morrisey, 2015; Bracken et al., 2016).

System Type	Advantages	Limitations
Chlorine	Proven biocide with well-established technology. Relatively inexpensive. Can be generated directly from seawater. Wide spectrum of activity. Rapidly loses toxicity without bioaccumulating.	Efficacy affected by pH, temperature, and suspended solids. Can be corrosive to CuNi pipes. Potential environmental risks associated with discharge. Chlorine discharge is regulated. Forms toxic by-products. Bivalves can detect chlorine and cease aerobic activity that prolongs survival. Biofouling may remain attached to the fouled surface. Worker safety concerns.
Bromine	More effective than chlorine at higher pH. Wide spectrum of activity. Can be used in conjunction with other treatments (e.g., chlorine) to increase efficacy.	Requires a high concentration. Can be consumed quickly. Forms toxic by-products. Approximately twice the cost of chlorine. Potential environmental risks associated with discharge. Biofouling may remain attached to the fouled surface. Worker safety concerns.
Chlorine dioxide	Stronger biocide than chlorine. Technology is well established. Low corrosion rate of pipes. Efficacy not as influenced by water chemistry as chlorine. Potential for use as a cotreatment. Minimal environmental impact.	Approximately twice the cost of chlorine. Cannot be generated from seawater. Biofouling may remain attached to the fouled surface. Worker safety concerns.
Hydrogen peroxide	Highly reactive. Rapid degradation (minimal environmental concern). Readily available.	High concentrations needed due to rapid degradation. May form heat and vapor. Less effective than chlorine. Biofouling may remain attached to the fouled surface.
Ferrate	Stronger oxidant than ozone, chlorine and bromine. No by-products. Easy to produce. Stable.	Unknown efficacy. Requires handling of hazardous precursor chemicals. Worker safety concerns. Biofouling may remain attached to the fouled surface.
Peracetic acid	Only low concentrations required. Wide-spectrum biocide.	Corrosive. Unstable. Requires handling of hazardous chemicals. Worker safety concerns. Less effective than chlorine. Costs more than chlorine. Biofouling may remain attached to the fouled surface. Potential environmental risks associated with discharge.

continued

TABLE 1

Continued

System Type	Advantages	Limitations
Acetic acid	Stable in the presence of organic matter. Easy to produce.	Glacial acetic acid costs more than chlorine. Glacial acetic acid requires handling of hazardous chemicals. Biofouling may remain attached to the fouled surface. Worker safety concerns when using high concentrations.
Descalers	Removes calcareous biofouling through the dissolution of calcium carbonate shells.	Large doses required. Efficacy influenced by biofouling biomass. Requires handling of potentially hazardous chemicals. Expensive compared to chlorine. Potential environmental risks associated with discharge. Can be corrosive to pipework.
Nonoxidizing biocides (quaternary ammonium compounds)	Noncorrosive.	High specificity of biocides. Multiple biocides often required to kill diverse biofouling assemblages. Long contact times required. Large doses required. Expensive compared to chlorine. Organism resistance may develop. Can be less effective than chlorine. Biofouling may remain attached to the fouled surface. Potential environmental risks associated with discharge.
Physical removal	Removal of fouling provides operational advantage to vessel. Reduces the rate of resettlement.	Limited to removing biofouling from exposed hull areas. Difficult to access niche areas and internal pipework. Difficult to contain chemical effluent and dislodged biofouling. Requires recapture of removed biofouling. Environmental release of biocides from cleaned surfaces.
Heat	Reduced environmental impact compared to some chemicals. Broad-spectrum treatment capable of killing all biofouling.	Large energy requirement if heating water. Uniform exposure difficult to achieve. Can facilitate the formation of carbonate scale. Thermal tolerance can occur if sublethal exposure occurs. Biofouling may remain attached to the fouled surface.
Deoxygenation	Environmentally benign when applied without the use of chemicals. Established principle. Conceivably can treat any size vessel.	Long exposure time required (days to weeks). Could promote anaerobic growth of micro-organisms. Can require an oxygen scavenging chemical to accelerate treatment. Requires isolation of the water body. Deoxygenation promotes the growth of corrosion-inducing bacteria. Biofouling may remain attached to the fouled surface.
Freshwater (osmotic shock)	Environmentally benign.	Long exposure time required (days to weeks). Large volume of freshwater needed. Biofouling may remain attached to the fouled surface. Could induce spawning of some organisms.

continued

TABLE 1

Continued

System Type	Advantages	Limitations
Cotreatments	Reduced exposure times. Improved efficacy. Lower temperature and biocide load in bulk water compared with single treatments.	May require additional equipment. Increased cost. Potential environmental risks associated with discharge. Biofouling may remain attached to the fouled surface.

it is likely that biocidal chemicals will have associated health and safety risks.

The efficacy of chlorine is improved at elevated temperatures due to increased aerobic activity of target species. The synergistic effect of temperature also applies to other chemicals (e.g., descalers; Bracken et al., 2016). Despite this, at temperatures >35°C, the mortality rate from a chlorine treatment is similar to that obtained when applying heat alone. Descalers are the only chemical treatment that can remove biofouling that have calcium carbonate shells, conferring an operational benefit to a vessel. However, efficacy data for treating mature biofouling assemblages are lacking, and these chemicals appear to be expensive relative to other biocides. Further information is required to provide greater assurance regarding the use of chemicals for reactive treatment systems; however, there are some that warrant further investigation in an operational context (e.g., chlorine, acetic acid, descalers).

Although deoxygenation and exposure to freshwater are viable options for managing biosecurity risk, they both require extended exposure times to achieve 100% mortality of biofouling assemblages, particularly at low temperatures. Therefore, the practicality of these approaches for vessels with short port residence times remains questionable.

The ability of physical removal systems to manage biosecurity risk is limited to accessible areas (e.g., sea chest grates), but these systems do confer an operational benefit to vessels. These systems may also require recapture technologies, and any effluent could require treatment prior to discharge or on-land disposal.

Thermal treatment is a potentially rapid, reliable, and comparatively environmentally benign reactive treatment method. The development of thermal in-water systems is largely constrained by engineering issues (e.g., ensuring and maintaining an even temperature throughout the treated area); however, the application of heat via steam treatment may overcome these issues. Temperature measurements made on the various external surfaces of the cavities being treated (e.g., internal pipes) can assure the regulator that the minimum temperature has been achieved throughout the treated area for the required period.

Testing frameworks for assessing the biosecurity risk of in-water systems applied to the external hull of a vessel have already been developed (Morrisey et al., 2015), with a similar framework for sea chests and internal pipework underway.

Recommendation

Physical removal systems with effluent recapture will be best suited for managing accessible biofouling (e.g., sea chest grates or sea chests with hinged grates) and provide operational benefits to the vessel if the biofouling is obstructing flow (e.g., improved water pumping efficiency). For internal vessel surfaces and those that are inaccessible, the development of thermal systems, particularly steam systems, is encouraged as they can offer broad-spectrum efficacy at obtainable temperatures with short exposure times. Thermal systems appear to be less affected by biotic and abiotic variables than other treatments and have less regulatory constraints compared to biocide use. Applications of acetic acid, chlorine, and descalers as reactive treatments of biofouling also warrant further investigation in an operational context.

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