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A Review of Marine Growth Protection System (MGPS) Options for the Royal Australian Navy

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Maritime Platforms Division
Defence Science and Technology Organisation

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ABSTRACT

Biofouling of ship's internal seawater systems can have serious implications for performance, continuing operational capability and crew habitability. Internal seawater piping systems and intakes are prone to heavy fouling pressure due to the relative inaccessibility and complexity of these systems. Fouling control in internal systems is optimally maintained by the installation and operation of Marine Growth Protection Systems (MGPS), which prevent fouling by operating within the internal seawater system to deliver antifouling agents. This review of available and emerging MGPS and other fouling control systems provides an overview of the current RAN MGPS experience, other available treatment options and recommendations for ongoing investigation into potential future protocols for fouling management in the RAN fleet.

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A Review of Marine Growth Protection System (MGPS) Options for the Royal Australian Navy

Executive Summary

Internal ship seawater systems, as used for supply to fire suppression and cooling/heat exchangers, are often prone to heavy fouling pressure. Fouling of internal systems can have serious implications for a vessel's short-term operational capability, habitability and survivability and may also have long term impacts on the integrity of internal piping.

The most commonly employed Marine Growth Protection Systems (MGPS) for shipboard internal seawater systems are anodic copper dosing or chlorine based systems; however, other options for fouling prevention and treatment exist, both within 'traditional' biocide chemistry as well as novel non-chemical antifouling strategies. The current RAN fleet employ a variety of strategies for the prevention of internal seawater system fouling, including: sacrificial anodic copper dosing (Cathelco® system), sodium hypochlorite dosing, freshwater flushing and Cu/Ni piping (which has inherent growth protection properties).

Despite the availability of existing technologies for fouling control in internal seawater systems, MGPS have substantial operational limitations and have failed to deliver reliable biofouling control. Peer reviewed scientific literature on shipborne MGPS for internal piping systems is not common, with most documented experiences and trial results derived from power station cooling systems, ship ballast water treatments and industrial water treatment and desalination plants.

It appears that a single MGPS strategy is unlikely to be able to control all fouling pressures experienced by RAN vessels, and a combination of treatments may be necessary. Currently, anodic copper dosing or electrochlorination (or a combination thereof) appears to be the only MGPS technologies mature enough to function effectively in the RAN operating profile and environment. This review examines additional MGPS options available to the RAN and provides recommendations for future trials of potentially suitable emerging technologies.

It is recommended that trials are performed using a field test rig designed to closely simulate conditions encountered in ship board sea chests and piping systems to provide realistic data regarding potential performance in on-board conditions. The review has identified the following options as being suitable for further investigation:

- The testing of carbon dioxide as a pre-treatment to halogen dosing. This technique may be of use as a remediation strategy for control of existing fouling populations (particularly macrofouling species such as bivalves which detect halogen biocides in the water).

- The use of multiple point ozone injection into seawater systems as well as the sea chest as a preventative strategy to protect against initial settlement at seawater intake points as well as throughout internal piping systems

- Trialling of different dosing regimes for biocides in an attempt to reduce overall biocide usage (and therefore discharge). Targeting biocide delivery in response to fouling levels and organism condition may reduce overall required levels of biocide dosing in comparison to continual dosing regimes. Variation of dosing schedules may also increase efficacy of the dosing regime as organisms are less likely to build resistance to a randomised dosing protocol

- The co-dosing of biocides (for example copper and chlorine) may increase the efficacy of the dosing regime

- Thermal treatment is highly desirable for development as a MGPS as both an environmentally benign and potentially sustainable treatment option (particularly if waste heat removed during cooling processes is able to be recirculated for treatment).

Authors

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Clare joined DSTO in 2009 after completing a BEnvSc(Hons) at RMIT University. She is currently undertaking a MSocSc (International Urban and Environmental Management) part-time. Since joining the Environmental Research and Biotechnology Group, she has been involved in research into novel natural chemical biofouling deterrents, characterisation of fouling roughness and topography and Marine Growth Protection Systems for internal seawater systems fouling prevention.

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Lyn joined DSTO in 1985 and has a BSc in Chemistry from RMIT and a MEnvSci from Monash University. Her career at DSTO has involved investigating and providing advice to the Navy on equipment and management options to assist the Navy to respond to emerging environmental issues. Her major areas of involvement include shipboard waste management and pollution control and she was heavily involved in the CFC and Halon replacement programs for the wider ADF. She is currently the Head of Environmental Research and Biotechnology Group.

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Contents

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1. Introduction

Biofouling can impose significant operational, capability and safety penalties on the RAN fleet, as well as posing a distinct threat to Australian (and international) marine biosecurity through the translocation and importation of potential and recognised marine pest species. Internal ship seawater systems, as used to supply water for fire suppression, cooling and heat exchange, are often prone to heavy fouling pressure. This is due to the inaccessibility of many of the areas for maintenance, the complexity of the structures involved (e.g. sea chests which provide niche areas for settlement and growth of a variety of fouling organisms), and the difficulties associated with protecting these areas with conventional anti-fouling coatings [1, 2].

With respect to vessel operability, biofouling not only has the potential to cause blockages of essential pipe work systems, thus reducing effective uptake to essential on-board systems and changing intake flow regimes, but may also degrade the structural integrity of pipework and fittings, leading to corrosion of essential structures and unscheduled maintenance [3]. Operational problems often only become apparent months after colonisation takes place, when the fouling organisms have grown large enough for obstruction to be noticed, or when cooling differentials become critical in tropical waters. From an environmental perspective, vessels are one of the primary vectors for the transfer of non-indigenous and/or pest species in the marine environment [4]. Vessel internal seawater systems in particular have the potential to both transfer non-indigenous organisms between countries across oceanic boundaries and disperse both indigenous and introduced organisms domestically [2].

All RAN bases in Australia are subject to high biofouling levels, and shipboard seawater systems are prone to colonisation and obstruction. The fouling conditions in the home ports of Fleet Base East and Fleet Base West are severe, as both have a warm temperate environment with high abundance of nuisance fouling species including hydroids, barnacles, calcareous tubeworm (whiteworm) and mussels. Many of these species thrive in pipework systems due to warmer flowing water (resulting from engine room heat transfer), the protective environment and the continuous supply of food and oxygenated water. Biofouling problems experienced in RAN ships and submarines have generally occurred when vessels have sat alongside home ports for extended periods with seawater systems running. This enables fouling species, which are more common and abundant in harbour waters, ample opportunity to colonise the seawater cooling system.

The most commonly employed marine growth protection systems (MGPS) for shipboard internal seawater systems are anodic copper and chlorine-based dosing systems; however, other options for fouling prevention and treatment do exist, comprising both 'traditional' biocide chemistry and novel non-chemical antifouling strategies. Depending on the design and purpose of the MGPS, the system can function as a preventative to fouling, or a mitigation and remediation system to reduce and remove existing fouling. Prevention of fouling is the most desirable outcome; however, in practice, complete prevention of all fouling is rarely practical and as such, MGPS are often used in a dual capacity. Remediation of existing fouling can create additional problems, particularly with respect to macrofouling where removal of the organisms from adhesion points may result in the collection of large amounts of debris inside pipework and strainer assemblies and subsequent blockage of the structures.

Peer reviewed scientific literature on shipborne MGPS for internal piping systems is not common, with the literature dominated by results derived from power station cooling systems, ship ballast water treatment systems and industrial water treatment and desalination plant trials.

The RAN currently uses anodic copper dosing MGPS on a number of surface vessels and chlorination MGPS on the Armidale Class Patrol Boats (ACPBs). The Huon Class Mine Hunters are fitted with freshwater dosing systems to control problematic marine fouling species through 'osmotic shock'. Other vessel classes rely solely upon the inherent antifouling properties of the CuNi piping network for the control of biofouling in internal seawater systems.

This review aims to provide: an overview of MGPS currently employed by the RAN, an outline of MGPS options currently available, considerations for current and future fleet, including a critical review of existing MGPS options and makes recommendations as to potential MPGS options for Navy that are suitable for further investigation by DSTO.

1.1 Current MGPS in RAN service

Currently, the RAN employs four different internal fouling control systems:

1. Sacrificial Anodic Copper Dosing (Cathelco® system)
2. Chlorine – as sodium hypochlorite generated on-site (Ecolcell® and Chloropac® hypochlorite generators)
3. Copper/Nickel (CuNi) pipework and
4. Freshwater flushing.

Whilst all have had some limited success, there have been challenges with the application of the systems in practice.

1.1.1 Sacrificial anodic copper dosing

While copper is an important trace element for marine organisms and is found naturally at low concentrations in the aquatic environment, at higher concentrations it is considered one of the three most toxic heavy metals to marine invertebrates of several trophic groups [5]. Copper has been shown to decrease the reproductive success, growth rates and abundance of many species [5], and lead to changes in the structural composition of benthic communities [6, 7]. Early life history stages of marine invertebrates and algae begin to be negatively affected by copper concentrations at least an order of magnitude lower than concentrations that may be toxic to humans [5, 8]. Copper has a very long history of use as an antifoulant in numerous forms. The ancient Phoenicians and Carthaginians are credited with the first documented use of copper sheathing on vessel hulls c. 700 BC [9], though it did not become common practice until the 18th century [10]. In the mid 1800s, the first widespread general-use antifouling coating (named 'McIness') was introduced in the Liverpool dockyards (in the UK), and used

Cu sulphate as the primary toxicant [11]. Cu-based paints remain one of the most effective and practical means of preventing fouling on submerged aquatic structures.

In addition to its use in paints, dissolved copper MGPS are commonly used to prevent the accumulation of biofouling within seawater cooling systems of vessels including the RAN and have been trialled for use in coastal power plants [12]. These systems typically comprise a paired copper anode (for antifouling) and an aluminium or iron anode (for corrosion control) that are strategically placed in-line within the seawater system, as close to the intake point as possible (e.g. in a seachest or strainer box assembly). The anodes are connected to a controller box that directs an electrical current to the anodes, resulting in the controlled release of copper (and aluminium or iron) ions at a desired rate and concentration. Water flow within the system disperses these ions throughout pipe work, with the aim of creating an environment that inhibits the settlement and growth of marine fouling species as well as producing an anti-corrosive layer on internal pipe surfaces. Figure 1 shows a generalised arrangement for a sacrificial anodic copper dosing MGPS.

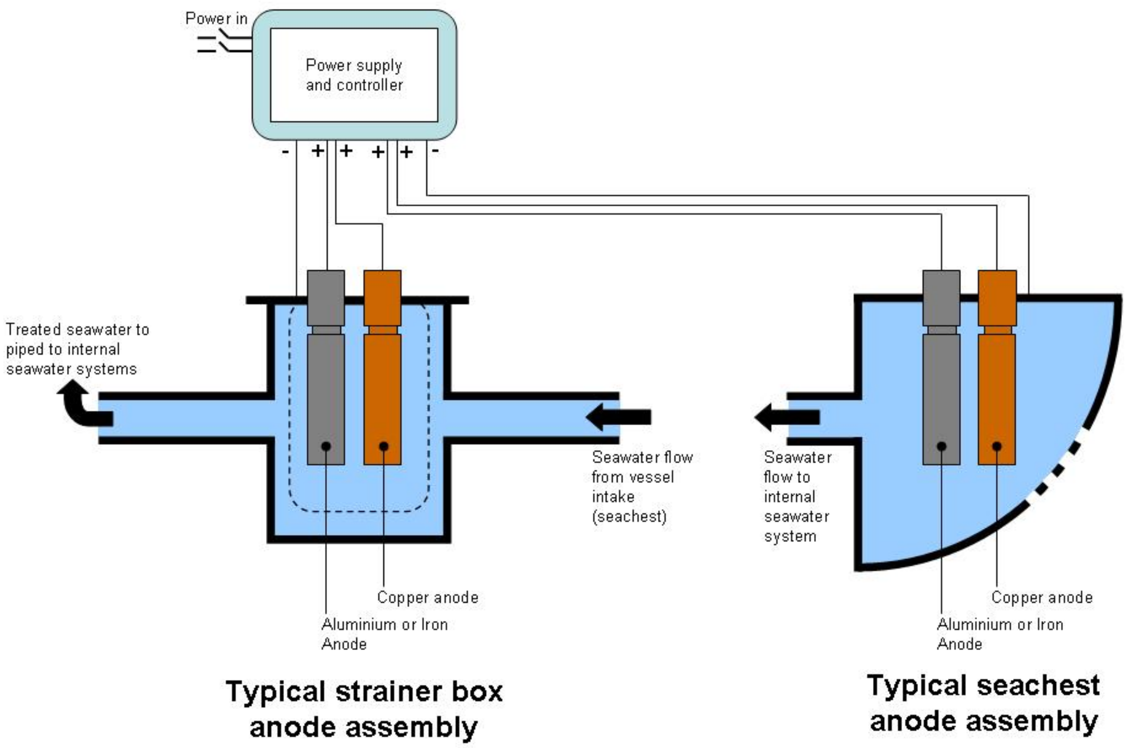

Figure 1 Generalised arrangement of a sacrificial anodic copper dosing MGPS

RAN's success with anodic copper MGPS to treat internal seawater systems has been mixed. While the copper MGPS have generally been effective at preventing fouling, real-world operating conditions dictate that the dosage of dissolved copper being delivered must be increased to levels well above manufacturer's recommendations to be efficacious. For example, levels of dissolved copper up to ten times the manufacturer's recommended concentration (10ppb copper) are reported to be required to prevent tubeworm fouling

(Lewis, unpubl. data). This leads to greater-than-specified running costs due to the more rapid consumption of sacrificial copper anodes (used to generate the dissolved copper) and can also increase the frequency of maintenance regimes due to the increased dosage (and hence wear) required to control hardy organisms. In addition, the efficacy of copper-based antifouling treatments may be reduced by the settlement and growth of copper tolerant species.

Copper tolerance among some marine taxa (including nuisance foulers and known invasives) is a well documented occurrence, resulting in adverse effects to long term diversity within copper-impacted marine habitats [13, 14]. Common copper-tolerant taxa associated with vessel fouling include barnacles, tubeworms, bryozoans and algae [7, 15-17]. Tolerance to copper may even increase as a result of repeated and/or extended exposure to the toxicant [18-21]. Finally, copper is also being subjected to increased global scrutiny as a potential marine pollutant and is already prohibited from use in some European freshwaters, with the possibility of bans extending into marine areas in the future [22].

1.1.2 Chlorine (as sodium hypochlorite generated by electrochlorination)

Chlorine (or sodium hypochlorite) has been proven to provide effective antifouling treatment against a range of fouling organisms, and has been used for many years as a disinfectant and antifoulant [23, 24]. The chemistry of chlorine in seawater is somewhat complex, and strongly influenced by the high concentrations of bromide in seawater. Chlorine reacts readily with bromide to form bromine residuals (in the form of hypobromous acid (HOBr) and the hypobromite ion (OBr^-)) as well as chlorine residuals (in the form of hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-)) [25]. This reaction is very rapid with 99% conversion of chlorine within 10s at full seawater salinity [25]. Bromine species (HOBr and OBr^-) are themselves effective oxidisers, and therefore disinfecting agents. In fact, much of the biocidal effectiveness of seawater chlorination attributed to chlorine residuals (HOCl and OCl^-) are likely largely due to the presence of the bromine residuals instead [26].

Safety concerns regarding the shipboard handling of hazardous liquids or gases (such as chlorine or sodium hypochlorite) have been largely solved by the installation of on-board hypochlorite generators, which produce sodium hypochlorite from seawater. Typical shipboard hypochlorite generators operate by piping sea water (from the vessel in-take) through an electrolyser cell (electrochlorinator) where a low voltage DC current is applied. Chloride in sea water is converted into sodium hypochlorite (NaOCl) by the process of electrolysis and is injected into the system (typically into the seachests) for dispersal throughout the internal seawater system. Dosage of biocide introduced into the system is regulated by adjusting the voltage to the cell (and hence the amount of sodium hypochlorite produced) based on the water flow rate into the system. Chlorine-based antifouling systems currently used by the RAN are based on electrochlorination. Figure 2 shows the general arrangement of an electrochlorination MGPS unit.

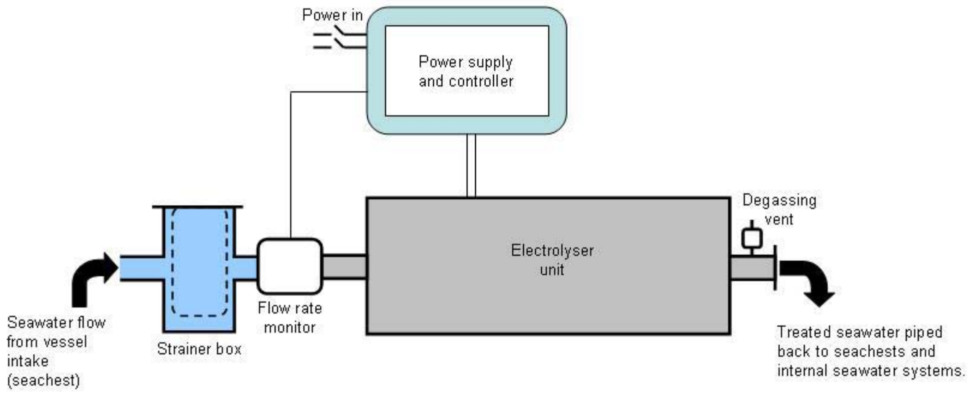

Figure 2 General arrangement of an electrochlorination MGPS unit

One potential problem arising from the use of chlorine antifouling treatments is enhanced corrosion of seawater piping structures as a result of overdosing (if dosage rates are not carefully monitored) [27]. While there is limited data on the effect of chlorination on CuNi alloy corrosion, it is largely concluded that over-chlorination of seawater should be avoided [28]. One study has reported that as little as 0.25 ppm free chlorine increased the corrosion of CuNi 90/10 piping during 30 days of exposure [28 and references therein]. In contrast, numerous studies recommend dosing seawater with chlorine at concentrations of 0.2-0.5 ppm to achieve the benefits of biofouling control while avoiding CuNi corrosion [28 and references therein]. Furthermore, one study has reported that brief chlorination treatments with 0.4-0.8 ppm of residual-free chlorine for 0.5-1 hour several times a day actually promotes the development of the corrosion-protective oxidising layer on the surface of CuNi 70/30 piping; while also reducing the incidence of Microbiologically Influenced Corrosion (MIC) by preventing the formation of biofilms on the internal piping surface [29]. However, different copper-based alloys may behave quite differently with respect to their seawater-chlorine corrosion potential [29, 30]. Numerous environmental and physical factors can further influence the corrosive effect of chlorine on metal and alloy pipework, including: temperature, flow rate, pollution, sedimentation/turbidity and biofouling pressure [28].

To date, the discharge from internal seawater systems remains unregulated. However, a possible future requirement for use of chlorine treatment systems may be the necessity for dechlorination of treated seawater prior to discharge, as residual oxidants can cause adverse effects to the receiving environment [23]. Currently, chlorine residual in a discharge of treated sewage is regulated with a limit of 0.5 mg L^{-1} [31]. Dechlorination treatments themselves can produce a range of undesirable by-products, and end of pipe discharges may require monitoring [32].

1.1.3 CuNi piping

CuNi piping provides some passive fouling control due to the formation of a cuprous oxide degradation layer at the surface of the piping (which also provides corrosion protection) [27, 33, 34]. While the majority of the Navy fleet have been fitted with CuNi internal piping (mostly 90/10 cupro-nickel and some 70/30 alloy), the level of passive protection afforded is generally inadequate under heavy fouling pressure and may not prevent initial formation of biofilms by copper tolerant bacteria [27], which can then lead to microbial induced corrosion (MIC). Such biofilms can comprise a wide range of micro-organisms, ranging from aerobic bacteria at the biofilm-seawater interface, to anaerobic bacteria such as Sulphate-Reducing Bacteria (SRB) at the oxygen-reduced metal surface. These biofilms can induce CuNi pipe corrosion in several ways, including, via the formation of corrosive by-products (e.g. hydrogen sulphide), through the creation of differential aeration cells, and by altering local hydrodynamic conditions (through physical deposition) which can influence corrosion rates [35].

1.1.4 Freshwater flushing/osmotic shock

Freshwater flushing has been used with some success in the Huon Class Minehunters. This treatment involves flooding the internal seawater systems with fresh water, thereby killing any marine species present via the process of osmotic shock (or hyposalinity). However, the consumption of freshwater supplies maybe excessive if the system is run continuously. In particular, the use of freshwater (particularly from potable supplies) may be cost-prohibitive, and generate a poor perception within community within locations/times of low rainfall and water restriction implementation. Furthermore, some organisms (e.g. mussels) can also tolerate freshwater exposure for up to several days [36-38], which reduces the overall efficiency of this treatment.

2. Current MGPS options

2.1 Considerations for Navy for existing and future fleet

For any MGPS to be considered a viable option for application by the RAN there are a number of criteria which must be met by the system. These factors are equally important when considering the viability of new technology for future application on RAN fleet.

If an effective system is developed through research or an effective 'Commercial Off The Shelf (COTS)' system is identified, it must be adaptable to installations on a variety of intake and piping arrangements, compatible with existing plant, or be able to be incorporated into design plans for new acquisitions and builds. The cost of installation on new builds or retrofitting must be acceptable, as should costs associated with ongoing maintenance and operation.

Any MGPS must be able to withstand a variety of fouling pressures found in different marine environments both within Australian and international tropical and temperate waters. Accordingly the MGPS must have broad spectrum efficacy due to the complex nature of fouling communities and the varying pressures faced in port and whilst performing operations. Any antifouling agent used within the MGPS must satisfy local and international regulatory requirements particularly with regard to biocidal discharges.

Finally, any MGPS adopted for use by the RAN must adhere to the highest OH&S standards. The MGPS and any associated precursor chemical feedstock must be able to be safely carried, stored, handled and operated under a variety of local environmental conditions depending on operational duties. The operation and maintenance schedules of the MGPS should have no adverse impact on operational capability or crew and vessel safety.

2.1.1 Prevention or remediation

MGPS are intended to operate as a preventative strategy to reduce the ability of fouling organisms to colonise internal seawater systems. To achieve effective prevention, it is necessary to consider the potential fouling pressures faced by vessels in different marine environments (in port or during operational duties), the type of organisms most prevalent in local fouling communities, regulatory requirements for discharge of any biocidal agents, as well as the design features of the vessel seawater systems. These considerations may influence the final decision on MGPS type.

As previously discussed, experience with currently employed MGPS suggests there is not a failsafe method of deterring all fouling; hence remediation strategies may be required to relieve fouling pressure on colonised areas of the internal systems. Fouling remediation can be achieved through a variety of means, although the removal of fouling organisms from attachment points may cause further difficulties (particularly with hard-bodied macrofoulers such as mussels and barnacles). The remediation technique or agent used is dependant on the type and level of fouling, the area in which it occurs and the availability of remediation agents or staff. Depending on which area of the vessel the fouling is occurring in, removal of fouling may have to be performed by hand. For example the accumulation of mussels in seachest strainer baskets needs to be removed by hand to maintain adequate flow through the seachest.

Biocidal agents used for maintenance of internal seawater systems fall into two main groups: oxidising biocides and non-oxidising biocides. The agents have different modes of action against fouling organisms. Oxidising biocides affect the cellular integrity of the organism, resulting in cell and then organism death, whilst non-oxidising biocides can cause organism death by a variety of means including interfering with cellular transport mechanisms or affecting cellular protein structures.

2.2 Chemical treatment – oxidising biocides

Oxidising biocides are commonly used for the treatment and disinfection of water and associated infrastructure, and describe biocides that control fouling by chemically oxidising (i.e. breaking down) the cellular structure of the organism. Oxidizing biocides are typically cost effective due to their low unit cost, rapid effect on susceptible target organisms and low effectual dosage.

2.2.1 Hydrogen peroxide

Hydrogen peroxide has been shown to cause mortality in a variety of species (including dinoflagellates and their cysts, and zebra mussels) [39]. There are concerns regarding the difficulty in maintaining an effective dose due to rapid degradation of hydrogen peroxide (to oxygen and water) in seawater. This may be particularly relevant for treating large quantities of water [39, 40] or when requiring penetration into convoluted pipe networks with long water-residence times. Conversely, the rapid degradation of hydrogen peroxide is desirable from an environmental point of view, as there is a lower potential for contamination of surrounding waters on discharge [41]. Reported results suggest that treatment with hydrogen peroxide is less successful than treatment with chlorine (particularly for mussel infestations) [40].

2.2.2 Iodine

Iodine is another potential oxidant for fouling control; however, little information is available on its efficacy when used for ship-board applications. One study suggests that iodine was only "modestly effective" for preventing mussel attachment during a field trial of biofouling prevention chemical injection systems [42]. A second investigation [43] suggests that for effective control of mussel settlement by injectable iodine, a higher effective dose was required than either chlorine or copper. Iodine is used commonly in the food and medical industries as an anti-microbial agent, and as a disinfectant in cooling towers, but appears to have limited effectiveness on macro fouling organisms in seawater piping systems [43, 44].

2.2.3 Chlorine dioxide

Chlorine dioxide operates in a similar manner to sodium hypochlorite; however, it is not pH dependent to the same extent. Therefore it is effective over a greater range of water conditions, and has improved biocidal efficacy relative to sodium hypochlorite [45]. ClO_2 is also a stronger oxidant than chlorine, hypochlorite or bromine. Experience suggests that it is more effective than chlorine or hypochlorite for control of mussels and other fouling organisms; however, the relative cost of macrofouling control using ClO_2 is higher than that of sodium hypochlorite or chlorine [45-47]. Co-dosing with hypochlorite solution reduces the necessary dose of ClO_2 and may increase the antifouling action and decrease the time of exposure necessary for control [45].

2.2.4 Ferrate ion (Fe(VI))

The ferrate ion is a stronger oxidant than ozone, bromine or chlorine [48]. Potassium ferrate (K_2FeO_4) is suggested as the formulation of choice for water antifouling treatment, due to ease of production, stability of the compound and the lack of harmful by products [49]. On site generation is now possible using a COTS system known as The Ferrator® however, the system requires chemical feedstock (bleach and ferric chloride) which may be difficult or hazardous to transport and store in an onboard scenario [48]. The technology, although promising, is still relatively new and there appears to be no literature available regarding the efficacy and impacts of the system operating in a shipboard seawater piping environment, though it has been trialled for the onboard treatment of ballast water. Extensive trials would be necessary before any introduction on RAN fleet.

2.2.5 Peracetic acid (CH_3CO_3H)

Peracetic acid (CH_3CO_3H) is commonly used as a disinfectant in wastewater treatment [50], and its commercial formulation is an equilibrium mixture of peracetic acid, hydrogen peroxide, acetic acid and water. It is appealing for use as an antifoulant in seawater systems as it degrades rapidly when released; however, it appears to be less effective in controlling fouling than other compounds such as sodium hypochlorite or chlorine dioxide [44, 51, 52]. Further disadvantages of peracetic acid include its corrosive and unstable nature (making handling a potential concern) and its decomposition to acetic acid [20]. Potential supply issues include the increased cost compared to chlorine dosing [52] and possible problems finding suitable suppliers [20].

2.2.6 Bromine

Bromine has a similar antifouling effectiveness to that of chlorine [40]. It is more effective at higher pH than chlorine; however, it loses efficacy in acidic environments [40, 52, 53]. It is often used in conjunction with chlorine injection and can reduce the overall dosed halogen load due to its greater efficiency at pH 8.00 and above, therefore effectively extending the biocidal 'range' of the dosed oxidants, particularly in mildly alkaline waters [52]. It can form toxic by-products, which are concerning for waste release, but studies suggest that these by-products rapidly degrade, lessening the overall potential for environmental impact [52, 53]. The cost of bromine treatment may be prohibitive for RAN application, as it is predicted to be up to several times more expensive than chlorine, with a similar level of effectiveness [40].

2.2.7 Ozone

Ozone is a stronger oxidant than chlorine, but appears no more effective at treating fouling in marine environments than chlorine [40]. The chemistry of ozone in seawater is complex and differs significantly from that in freshwater because of the presence of bromide ion [54]. In a similar reaction to that observed for chlorine, ozone quickly reacts with bromide ions to form hypobromous acid (HOBr) and hypobromite (OBr^-), which themselves are weaker, but more stable, disinfectants [55-57]. As such, ozone toxicity in seawater is often expressed as a function of total residual oxidants (TRO) rather than as ozone *per se* [58]. In fact, some ballast water treatment studies have shown that bromine ($HOBr/OBr^-$) is actually the primary biocide agent in seawater during ozonation [55, 56]. The residency time of ozone in water treatment situations is much shorter than chlorine, and is influenced by factors such as the amount of bromides in the water, temperature, pH and levels of dissolved matter [12, 57, 59]. While the rapid breakdown of ozone in seawater is a desirable feature from an environmental perspective, it may prove problematic for fouling treatment, as it would be difficult to maintain an effective dosing regime over time and requires multiple dosing injection points throughout a system [40, 60]. There are also concerns about the efficacy of ozone at alkaline pH (levels in excess of pH 8.5), the formation of bromate by-products, its corrosive potential and the high cost of installation and operation (particularly in comparison to chlorine) [41, 44, 52, 55].

2.3 Chemical treatment – non-oxidising biocides

Non-oxidizing biocides control biofouling by interfering with the metabolic processes of the target organism(s). Due to the specificity of many non-oxidising biocides, a single chemical is rarely effective at treating an entire suite of fouling organisms, and those that are immune to a particular non-oxidizing biocide may rapidly replace species that are removed. For the effective control of biofouling, it is often recommended that at least two different non-oxidizing biocides, or an oxidizing and non-oxidizing biocide, be used in an alternating basis. Non-oxidizing biocides can be costly because of the high effective dosage required, long contact times and often high unit cost, however, most do not appear to cause corrosion of system infrastructure.

Non-oxidising biocides are often proprietary formulations. Quaternary ammonium compounds are most commonly utilised; although, other formulations based on various other compounds exist (such as glutaraldehyde, aromatic hydrocarbons and menadione) [39, 50, 61]. Many non-oxidising biocides have shown good fouling control options in overseas applications, but are either not registered for use in Australia, or have limited use permits [39]. Non-oxidising biocides often have to be dosed in very large quantities, making application to RAN vessels impracticable due to the large volumes of chemicals necessary to be transported during operations [60]. It is also reported that microbial resistance to non-oxidising biocides can develop, allowing the formation of an initial biofilm which may provide favourable conditions for secondary and tertiary fouling to occur [62].

2.4 Non-biocidal treatments

2.4.1 Carbon dioxide

Carbon dioxide (CO_2) has potential to be used as a complementary pre-treatment in conjunction with an active bioactive (e.g. chlorine). CO_2 has been shown to induce a narcotic response in macro fouling molluscs (demonstrated in zebra mussels *Dreissena polymorpha*), causing shell gape and facilitating exposure of organisms soft tissues to succeeding biocides [63]. Given that mussels in particular are able to sense oxidants in the environment and are able to close their shells and cease filtering to avoid ingesting the biocide, the addition of CO_2 allows oxidising biocides to remain effective [40, 63]. It must be stressed that CO_2 is not a stand-alone treatment, but rather an oxidant co-treatment for the control of particular macrofouling organisms.

2.4.2 UV radiation

UV radiation is commonly used for sterilisation of treated water, and for the prevention of microfouling and the formation of biofilms [64]. To be effective for larger systems with more complex fouling pressures, co-dosing with a biocide may be necessary. UV radiation is most effective against bacterial and planktonic fouling, and would be suitable as a complementary pre-treatment preventative rather than a complete solution to internal fouling pressures [64]. Comparison of the efficacy of ClO_2 and Cl_2 treatment with and without UV light pre-treatment showed a combination of chlorine dioxide with UV pre-treatment to be the most effective at controlling bacteria [65]. Overall biocide dosages were not reduced by the addition of the pre-treatment, but efficacy was enhanced [65].

2.4.3 Deoxygenation

Deoxygenation of the water in an enclosed system by purging with inert gas (e.g. N_2) results in the creation of a hypoxic environment unable to be tolerated by many fouling species. A multi-organism study on oxygen deprivation in ballast water showed significant mortality for known fouling species larvae after 2-3 days in anoxic water [66]. It was also shown that corrosion was reduced in the ballast holding tank by deoxygenation [66]. This protective effect may extend to seawater piping systems if an effective method of deoxygenation of seawater for internal systems could be developed. However; Lee et al. have shown that corrosion in anaerobic seawater is more aggressive than in aerobic seawater due to the promotion of growth of Sulphate Reducing Bacteria (SRB) which increase corrosion rates in carbon steel [67]. It is important to note that some species are able to tolerate extended periods of low oxygen in the environment (e.g. dinoflagellate cysts; mussels), and some form of co-treatment may be necessary to successfully eradicate all problem species at all life stages [66, 68].

2.4.4 Acoustic energy (ultrasonics)

Acoustic energy (ultrasonics) has also been considered as a means of fouling control. Pulsed acoustic energy (generated by electrical discharge causing an electro hydraulic shock), carried by pipe walls is thought to be able to prevent settlement in seawater systems [69]. Small scale testing conducted on both titanium piping and a heat exchanger with an externally mounted generator (to reduce the formation of cavitation bubbles which can be detrimental to pipe integrity) suggests a level of biofouling inhibition similar to a combination of chlorination/high velocity flushing treatment is achievable [69, 70]. A second study which reported the results of a variety of industrial uses of a COTS ultrasonic water treatment system ('Sonoxide') encourages the formation of 'micro bubbles' by introducing air into the ultrasonic chamber to enhance the performance of the low power, high frequency ultrasonic effect [71]. The inhibition of biofilm formation has also been confirmed by Bott [72], however, it is noted that the initial installation of an ultrasonic treatment system is often cost-prohibitive [72].

2.4.5 Low level Laser

Small scale testing in an experimental flowing water system exposed to low level pulsed laser showed significant mortality in tested diatom and dinoflagellate cells [73]. Laser irradiation was supplied at 532 nm and 0.1 Jcm^{-2} and resulted in mortality rates of between 70 and 90% for the tested marine diatoms and dinoflagellate cells [73]. Previous studies by the same researchers also showed good activity against *Balanus amphitrite* cyprids [74]. The current design of this sterilisation method involves "raw water" passing through an in-line irradiation chamber, before entering the main system. As such, success relies upon all waterborne fouling organisms (e.g. larvae, diatoms) being eradicated first-time at a single point in the system. Any organisms able to survive beyond this treatment point and subsequently establish within the system would require alternative treatment options for removal.

2.4.6 Thermal shock

Thermal shock, by hot water flushing, has been used with some success in the control of zebra mussels in industrial water systems. Temperatures of 32°C with a 48 hour exposure time have been recorded as being lethal to zebra mussels, while a Victorian Parliamentary review of ballast water treatment technologies suggested temperatures of 35 to 45°C were necessary to cause death of dinoflagellate cysts as well as zebra mussels [41]. Other studies on different fouling organisms (colonial hydroid *Cordylophora caspia*) suggest a similar temperature range of 37.7 to 40.5°C causes permanent destruction of the colony [75]. Some organisms such as *Crassostrea gigas* appear to have a greater tolerance for thermal fluctuations [76] and have been shown to require temperatures of greater than 55°C for one hour to achieve 100% mortality (Piola, unpubl. data). It is important to raise the temperature of the treatment water quickly and to maintain temperature for the necessary length of time to avoid any acclimatisation leading to induced thermotolerance of the organisms [41, 75, 77-79]. Microwaves have been tested as a means of rapidly and continuously heating ballast water to induce thermal shock in fouling organisms, and has potential to be applied to sections of internal piping systems [80]. One obvious limitation of this method is the treatment of raw feed water used for system critical cooling.

2.4.7 Engineering and mechanical solutions

In addition to chemical treatments, there is the possibility of applying mechanical or physical solutions to fouling prone areas. Improved filtration mechanisms at intake points could be used to further restrict the intake of smaller fouling organisms and larvae, as well as larger species; however, care would need to be taken not to restrict flow into the seawater system to a degree which adversely impacts its reliability and performance.

Antifouling coatings on internal systems and niche areas may also assist in the protection of internal systems from heavy fouling pressure, although without design changes to niche areas, these may be difficult to apply and maintain.

2.4.8 Design solutions

Some RAN vessels, such as the ANZAC class frigates, have multiple internal seawater systems, some of which can be long and complex. In some cases, these systems provide cooling to mission critical equipment. Design can play an important role in ensuring the operability of these systems. For example, small bore piping, which is particularly susceptible to blockage by even small amounts of fouling, can be reduced or eliminated wherever possible. Mission critical equipment that currently relies on seawater cooling can be isolated from the main seawater system and replaced with a self-contained chilled water system. When installing seawater treatment systems such as copper or chlorine based dosing equipment, consideration should be given to including multiple dosing points throughout the seawater piping network, to ensure that appropriate concentrations of biocide can reach all areas of the system. This is particularly important for vessels that have large and complex seawater systems spanning multiple levels of the vessel.

Another possible strategy is the utilisation of altered flow velocities and turbulence regimes to inhibit the settlement and accumulation of fouling taxa. While theoretically this approach has potential, caution must be taken to maintain flow regimes below maximum recommended flow velocities for the particular Cu/Ni alloy in use in the existing vessel systems, as flow induced 'erosion corrosion' may occur as high velocity flows destroy the passive copper oxide protection layer at the surface of the material [27, 70]. Recommended maximal flow rates for different alloy blends include: <3.5m/s for 90/10 CuNi; <4.0m/s for 70/30 CuNi; and <6.5m/s for 60/30/2/2 CuNiFeMn [81]. Care should also be taken to avoid pockets of turbulent flow. One study [82] suggests that turbulent flow can promote the formation of biofilms that are more resistant to treatment (relative to those formed in laminar flow environments), due to the formation of homogenous and slimy bacterial films which are more difficult to remove than less consistent films.

2.5 Currently available COTS systems/formulations

Please note that the items below are a *selection* of available COTS; this list is NOT exhaustive and there may be other similar formulations and systems available from different suppliers.

2.5.1 Protection

- Various anodic copper protection and electrochlorination systems are available commercially, including Cathelco (copper and electrochlorination systems), Chloropac®, Ecolcell, Tiaano™ ECU 05 (chlorination systems).
  http://cathelco.com/
  http://www.water.siemens.com/
  http://www.howelllabs.com/
  http://www.tiaano.com/

- Chem Free™ Sea Chest Guardian: This system is particularly designed for sea chest protection using ozone, but may provide follow through effects to the rest of the internal piping systems, due to a reduction of settled and viable organisms occurring in the ship's sea chest intakes.
  http://www.deltamarineozone.com/ OR http://www.oceaneering.com/ (in transition)

- The Ferrator® (Ferrate Treatment Technologies) is an on-site generator of liquid ferrate for in stream dosing of ferrate ions for antifouling treatment. The Ferrator ® uses sodium hydroxide, sodium hypochlorite and ferric chloride as feedstock to produce ferrate ions in solution which are then dosed into the water system. The company identifies ballast, waste and industrial water treatments as potential applications, but this could potentially be extended to include shipboard seawater systems [48].
  http://www.ferratetreatment.com/

2.5.2 Protection or remediation

- Mexel® 432 is a "molecular level" filming agent of proprietary formulation which is marketed as having anti-fouling, scale and corrosion properties.
  http://mexel.fr/products-solutions/mexel-432/

- Clog Control™ is an amine based biocide claimed to prevent biofilm formation as well as controlling macrofouling growth. The manufacturers recommended dosage for an industrial sea water cooling system is 0.4 L/hour/100 tons seawater and repeated every 48 hours.
  http://www.marichem-marigases.com/

- Marichem S-Fe is a proprietary blend of filming agents (non-ionic surfactants), inorganic acids and corrosion inhibitors which claims to control micro and macro fouling organisms, whilst reducing corrosion in pipework. Manufacturers dosing recommendations are 0.9 L/hour/100 tons seawater for one hour every two days (depending on fouling load).
  http://www.marichem-marigases.com/

- Pulse Chlorination® (KEMA): The KEMA pulse chlorination system is marketed as the 'optimum chlorination regime for fouling control' utilising sodium hypochlorite. The system was named as a European BAT (Best Available Technology) in 2000. The system takes into consideration the ability of mussels to close their shells and cease filtering periodically in response to chlorine (and other oxidants), and uses short 'pulses' of chlorination to overcome the avoidance response.
  http://www.kema.com

- Clamtrol II/Spectrus CT 1300 is a non-oxidising biocide consisting of 50% N-alkyl dimethyl benzyl ammonium chloride. This biocide has been approved for a limited permit for use in Australia by APVMA (for the Illawarra Blue Scope Steel Steelworks Cogeneration Plant Project). It is marketed as an antifoulant controlling molluscs, algae and bacteria. The product has to be deactivated prior to discharge using bentonite clay and **cannot** be co-dosed with oxidants.
  http://www.gewater.com/

3. Discussion

3.1.1 Issues with current MGPS options

Although there are multiple alternate strategies for fouling control in internal seawater systems, most technologies are untried in under real-world field conditions and often not mature. Trials of available options may result in favourable fouling control results, but application to existing fleet in their current stages of development is considered impractical. In addition, the rationale behind the adoption and development of many existing treatment strategies is based upon antifouling treatment solutions used in coastal power and water treatment plants, which often have different considerations and requirements to those of a vessel. For example, power plants may only be required to maintain fouling below a minimal threshold to ensure effective plant operation and cost-efficiency, while a vessel may need to adopt a 'zero-tolerance' approach to fouling to satisfy biosecurity obligations and integrity of mission-critical systems. Furthermore, land-based treatment strategies may not have the same limitations that are often found aboard vessels (e.g. the storage and use of hazardous liquid chemicals).

When trialling new fouling control options it is important to consider not only the efficacy of the treatment on the fouling community, but also any unintended treatment side effects (such as corrosion or changes to system flow regimes). Impacts on the surrounding environment are also an important consideration in the final selection of MGPS.

Currently, anodic copper dosing and on board chlorination generators appear to be the only viable and mature option for RAN installation in the short term; however, trialling of new techniques may provide suitable options for the future. At present, it appears that a single system is unlikely to be able to control all fouling pressures experience by RAN vessels, and rather a combination approach to treatments may be necessary. To develop an effective solution, it is necessary to consider not only 'single source' solutions, but also combinations of existing and novel treatments. It is also important to identify potential solutions that will be appropriate for the RAN operational profile, and assess the options through a rigorous experimental design both in the laboratory and field. A summary of the characteristics of the options available is presented in Table 1, which outlines the respective treatments, their dosing locations, residence times, relative advantages and disadvantages, whether the agent is employed as an preventative or remediation tool and any potential environmental impacts.

Table 1 . Characteristics matrix of MGPS options

MGPS option	Potential dosing location(s)	Residence time	Advantages	Disadvantages	Preventative	Remediation	Environmental impacts
Sacrificial copper anode	Sea chest Strainer box In-line	Short to medium	Established technology; relatively inexpensive	Large doses required; binds readily to organic matter;	✓		Yes. Considered a heavy metal pollutant. Discharge is regulated (and even banned in some jurisdictions)
Electrochlorination	Sea chest Strainer box In-line	Short to Medium	Established technology; relatively inexpensive; chlorine generated from sea water	May be corrosive to CuNi pipework; efficacy varies with dosing regime; efficacy affected by pH	✓	✓	Discharge may become regulated in the near future; formation and discharge of toxic by-products may be an issue
Cu/Ni piping	N/A	N/A	Exhibit inherent antifouling properties; many vessels already fitted with this technology	Passive treatment system; subject to corrosion; only limited anti biofouling effectiveness; ineffectual against heavy fouling pressure	✓		None
Freshwater flushing/osmotic shock	Sea chest Strainer boxes Discharge outlets	Long (until flushed)	Environmentally benign; proven efficacy (provided sufficient time is given)	Long exposure time; requires access to large volumes of freshwater; may contravene water restriction guidelines	✓	✓	Minimal

MGPS option	Potential dosing location(s)	Residence time	Advantages	Disadvantages	Preventative	Remediation	Environmental impacts
Chlorine dioxide	Sea chest Strainer box In-line	Medium to Long	Established technology; stronger oxidant than chlorine; low corrosion potential; less influence by water chemistry (e.g. pH) than chlorine; may be used in complement with other treatment methods (e.g. chlorine) to increase efficacy	Safety concerns regarding required chemicals; unlike chlorine, cannot be generated from seawater; expensive relative to chlorine	✓	✓	Minimal
Ozone	Sea chest Strainer box In-line	Short	Established technology; no harmful precursor chemicals or by-products; stronger oxidant than chlorine	Minimal penetration into sea water system; influenced by sea water chemistry; may be safety concerns around its generation and use (Exposure limit TWA 0.1 ppm); less effective at alkaline pH levels	✓		Minimal
Ferrate	Sea chest Strainer box In-line	Medium to Long	Stronger oxidant than chlorine, ozone and bromine; easy to generate; stable and long-lasting; no by-products produced	Untried technology on vessels; requires handling and mixing of hazardous chemicals	✓	✓	Minimal

MGPS option	Potential dosing location(s)	Residence time	Advantages	Disadvantages	Preventative	Remediation	Environmental impacts
Hydrogen peroxide	Sea chest Strainer box In-line	Short	Readily available; highly reactive; degrades	Minimal penetration into sea water system; may form heat and/or vapour; breaks down to O_2 and promotes aerobic/oxidising conditions; less effective than chlorine	✓	✓	Minimal
Bromine	Sea chest Strainer box In-line	Short	Wide spectrum of activity; more effective than chlorine at higher pH; may be used in complement with other treatment methods (e.g. chlorine) to increase efficacy	May be consumed quickly; requires high concentration; toxic by-products may be formed; cost prohibitive; very toxic by inhalation (STEL 0.3 ppm)	✓	✓	Formation and discharge of toxic by-products may be an issue
Peracetic acid	Sea chest Strainer box In-line	Short	Non-toxic; penetrates biofilms; only low concentrations required; wide spectrum of activity	Corrosive; unstable; decomposes to acetic acid; requires handling and mixing of hazardous chemicals; less effective than chlorine	✓		Minimal

MGPS option	Potential dosing location(s)	Residence time	Advantages	Disadvantages	Preventative	Remediation	Environmental impacts
Iodine	Sea chest Strainer box In-line	Short to Medium	Comparable performance to chlorine	Limited efficacy against macrofouling; can produce toxic by-products; safety concerns regarding required chemicals; Iodine vapour is toxic	✓		Can produce toxic halogenated by-products
Carbon dioxide	Inline after sea chest	Medium	Used to increase the efficacy of other treatment methods (e.g. chlorination)	Not a stand-alone treatment option	✓	✓	Minimal
Non-oxidising biocides	Sea chest Strainer box In-line	Medium to Long	Highly effective against target organisms; non-corrosive;	High specificity of biocides; multiple biocides often required; long contact times required; large dosages required; expensive; organism resistance may develop;	✓	✓	Minimal
UV radiation	Inline after sea chest	Very Short	Proven technology; low maintenance	Only effective against planktonic organisms and/or life stages (e.g. larvae); cannot treat established fouling; efficacy lowered by turbidity; may require a complementary treatment method	✓		May form bromate by-products

MGPS option	Potential dosing location(s)	Residence time	Advantages	Disadvantages	Preventative	Remediation	Environmental impacts
Deoxygenation	Sea chest Strainer box In-line	Short	Established principal; may have a protective effect on sea water piping	Requires long exposure time (days-weeks); may be difficult to achieve in a uniform manner; may stimulate anaerobic microbial growth		✓	Minimal
Acoustic energy	Throughout sea water system	N/A	No chemicals required; non toxic;	Limited applicability; may be cost-prohibitive	✓		None
Low level laser	Inline after sea chest	N/A	No chemicals required; non toxic;	Only effective against planktonic organisms and/or life stages (e.g. larvae); cannot treat established fouling; may require a complementary treatment method	✓		None

MGPS option	Potential dosing location(s)	Residence time	Advantages	Disadvantages	Preventative	Remediation	Environmental impacts
Thermal shock	Sea chest	Short to medium	Wide efficacy range; heat source may be taken from engines; may be designed as a land-based treatment technology	Energy required to generate desired temperatures may be impractical; uniform exposure to entire system may be problematic; may have structural implications; may form carbonate scale; may stimulate microbial growth if improperly applied	✓	✓	Minimal

4. Recommendations for further investigation

To provide an accurate assessment of the efficacy of any potential treatment regime in conditions relevant to the RAN, it is recommended that promising treatment options such as variations to chlorine dosing regimes and thermal treatment be experimentally evaluated for effectiveness in the RAN context. To increase the relevance of any experimental design, it is suggested that testing be conducted using a 'mock' seachest and seawater piping system (such as that constructed by Defence Research Establishment Atlantic to trial biocides for use on Canadian Patrol Frigates). Such a test system would provide a more realistic indication of potential performance in RAN operation [43].

It is recommended that the following options are viable for further consideration and testing:

1. Further investigation into the efficacy of chlorination for the treatment of onboard biofouling. This should be undertaken under real-world conditions which reflect the actual operating conditions (e.g. water temperatures, fouling pressures, and biofouling species) experienced by the RAN fleet. In addition, such trials should also examine the effects of chlorine on the corrosive potential of CuNi pipework (which is present in many RAN vessels).

2. Trialling of different dosing regimes should be undertaken in an attempt to reduce overall biocide usage (and therefore discharge). For example, pulse, continual, shock, or intermittent dosing [83]. Development of dosage regimes based on organism temporal behaviour and/or site-specific fouling conditions (for example during mussel spatfall in a particular location or at the end of breeding seasons when mussels have reduced physiological condition) [40].

3. Thermal treatment is highly desirable for development as a MGPS as both an environmentally benign and potentially sustainable treatment option (particularly if waste heat removed during cooling processes is able to be recirculated for treatment). Thermal treatment also has good potential for use as a shore-based biosecurity treatment strategy. For example, the sea chests of RAN vessels return to Australia from foreign ports/regions that pose a high biosecurity risk may be treated with hot water and/or steam to minimise the establishment and transfer of unwanted marine species. Such a strategy may form part of a routine maintenance regime.

4. Co-dosing of biocides (for example copper and chlorine), may lead to even greater efficacy of given dose [84, 85].

5. Carbon dioxide pre-treatment to halogen dosing – may be useful for control of existing fouling populations (particularly macrofouling species such as bivalves which detect and respond to halogen biocides in the water). This solution may be particularly suited to treatment of fouling within seachest; however, it may have deleterious effects on cooling within the wider internal seawater system.

6. Ozone injection into seawater systems as well a sea chest protection mechanism.

7. Dosing rates may also be coupled to an in-line biofouling monitoring systems, such as the BIOX or BIOCAF™ systems, to enable a treatment regime tailored to the current level of fouling pressure [45, 51]. In-line biological monitoring systems provide real-time feedback on the level of biological growth occurring in a local area and allow dosing of biocides to be 'tailored' and timed to occur when growth reaches an undesirable level. In this way, targeted biocide delivery increases the efficacy and efficiency of the dosing regime by ensuring that biocides are not dosed when little or no growth is occurring.

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19. ABSTRACT
Biofouling of ship's internal seawater systems can have serious implications for performance, continuing operational capability and crew habitability. Internal seawater piping systems and intakes are prone to heavy fouling pressure due to the relative inaccessibility and complexity of these systems. Fouling control in internal systems is optimally maintained by the installation and operation of Marine Growth Protection Systems (MGPS), which prevent fouling by operating within the internal seawater system to deliver antifouling agents. This review of available and emerging MGPS and other fouling control systems provides an overview of the current RAN MGPS experience, other available treatment options and recommendations for ongoing investigation into potential future protocols for fouling management in the RAN fleet.