



# Treatment agents for biofouling in internal pipework of recreational vessels

A review of pipework configurations, biofouling risk, and operational considerations

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## **Executive Summary**

The availability of reactive treatment tools to treat or clean vessels of unwanted marine biofouling is an important requirement for effectively managing marine biosecurity risks at the New Zealand border. Standardised treatments for the external planar surfaces of vessel hulls are available but vessel 'niche areas'—prone to accelerated biofouling development—are comparatively less well explored. The Ministry for Primary Industries (MPI) has identified a gap associated with the lack of proven treatment tools for vessels' internal pipework systems, particularly those of recreational vessels.

This report used literature searches, interviews with industry experts, and vessel inspections to gain insights into the types of pipework systems likely to be encountered on board recreational vessels, and the associated biofouling risks. Three main types of pipework systems that come into direct contact with seawater were identified: (1) engine cooling systems, (2) ancillary seawater supply systems, and (3) below-water discharge systems.

Engine cooling systems supply a steady flow of seawater when a vessel's engine is in operation. Ancillary seawater supply systems can service a range of on-board features, including deck wash-down, toilets, refrigeration condensers, and desalination plants. Belowwater discharge systems are primarily limited to blackwater discharge and deck-draining scuppers; most other on-board systems discharge above the waterline. Each of these three main classes of pipework system can develop biofouling but systems with open exchange of seawater with the ocean, or those with a continual flow of seawater, pose the highest risk. A diverse range of biofouling taxa are able to foul internal pipework but the taxa most commonly reported were barnacles, hydroids, mussels, oysters, and tubeworms. Conversations with industry experts and real-world sampling experience indicate that biofouling is most likely to be encountered near pipework inlets or outlets. The presence of biofouling also depends on patterns of operation of a given pipework system (e.g., sporadic vs continual use of engine cooling systems). It is generally expected that biofouling loads in pipework systems will be low to moderate because high fouling loads will impair or prevent the operation of a vessel. Regardless, even low biofouling loads within pipework systems will pose potential biosecurity risks if biofouling is able to be dislodged or if reproductivelymature individuals are present. This risk is particularly apparent for international yachts whose previous destinations may include locations with known high-risk pest populations.

Building on the review of recreational vessel pipework and associated biofouling, a decision framework was developed to assess the operational feasibility of prospective treatment agents for biofouling in internal pipework, as identified by Growcott *et al.* (2016). These treatment agents were assessed based on the following criteria:

- **effective** against adults and juveniles of relevant biofouling taxa at realistic working concentrations or intensities and within 48 h;
- **safe** for the environment and operators at relevant concentrations or intensities;
- **biosecure** and will not exacerbate risk of release and establishment of marine non-indigenous species;
- **consented** for use, or some existing precedent for use, in the New Zealand marine environment;
- **compatible** with pipework and other vessel components;
- feasible to apply, with realistic resource, cost, and infrastructure requirements; and
- **quality control** methods are available to confirm that treatment thresholds (e.g., biocide concentration or temperature) have been exceeded.

Two main classes of treatment agent were assessed: chemical and non-chemical.

Chemical treatment agents included the oxidising agents chlorine, chlorine dioxide, bromine, hydrogen peroxide, ferrate, peracetic acid, and acetic acid. A range of commercially available descaler formulations and quaternary ammonium-based disinfectants were also considered. For most of the chemical treatment agents, insufficient information was available to accurately gauge efficacy against all relevant biofouling taxa. The exceptions were acetic acid and some commercial descaler formulations, such as Rvdlvme<sup>®</sup>. Published reports were available demonstrating that both acetic acid and relevant descaler formulations can be effective against intact fouling assemblages within 48 h. Chlorine is known to be effective against some biofouling taxa but it is unclear whether this treatment agent will render resilient (able to withstand or recover quickly) taxa nonviable inside the stipulated maximum treatment timeframe of 48 h. Although insufficient information was available to accurately gauge the spectrum of activity of bromine, it should be noted that this treatment agent is generally considered a more potent and stable alternative to chlorine. With the exception of chlorine dioxide, some descaler formulations, and quaternary ammonium compounds, chemical treatment agents were deemed safe for operators and the environment. Likewise, few specific risks to biosecurity or vessel components were identified. Chlorine, bromine, and the acid-based biocides (acetic acid and descaler formulations) can be neutralised post treatment, thus reducing their environmental risk. However, only chlorine and acetic acid have existing precedent for consented use in the New Zealand marine environment. Chlorine has recently been granted approval by the Environmental Protection Authority and some regional councils for marine biosecurity purposes, while acetic acid has been applied in biosecurity incursion scenarios in the past.

Non-chemical treatment agents assessed were physical removal, thermal stress, deoxygenation, and osmotic shock. Of these, only thermal stress could feasibly be applied to pipework and likely be effective within 48 h. Physically removing biofouling from inside complex pipework is not currently realistic and poses an elevated risk for accidental release of biofouling organisms into the environment, while deoxygenation and osmotic shock can take several weeks to kill resilient taxa. By contrast, heating water to approximately 50–60°C renders biofouling organisms, including resilient taxa, nonviable in 2 h or less. Thermal stress also poses few risks to operators and the environment, is unlikely to harm vessel components at or below 60°C, and heated water is a common discharge to the New Zealand marine environment.

Although bromine and the descaler formulation Rydlyme<sup>®</sup> could warrant further consideration, the decision framework favours three prospective treatment agents as being potentially suitable for application to the internal pipework of recreational vessels:

- chlorine;
- acetic acid; and
- thermal stress.

Chlorine and acetic acid satisfy all safety and compatibility considerations for an internal pipework treatment but there is some uncertainty regarding their effectiveness against resilient taxa within the allotted maximum treatment timeframe of 48 h. It may prove that chlorine or acetic acid is an effective treatment agent in this scenario but further preliminary laboratory testing is required to determine this outcome. By contrast, thermal stress has been demonstrated in several independent studies to be rapidly effective against a broad range of biofouling taxa, including resilient taxa. Thermal stress is well suited for application to internal pipework given the confined spaces and relatively small total volumes to be treated,

and the discharge of tens of litres of heated water into the environment is unlikely to present serious consenting hurdles.

Because thermal stress presents fewer unknowns for developing an operational treatment protocol compared to chlorine or acetic acid, it is considered that thermal stress is the overall 'best' treatment option for further exploration in the context of this project. While systems to raise and maintain the temperature inside vessel pipework are not readily available, devices that could form the basis of an active (e.g., domestic hot water califont heaters) or passive (e.g., flexible heating elements) heat treatment system are available. Constructing and characterising a purpose-built heat treatment system in a controlled setting is the next step in developing an operational treatment protocol.

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# 1 Introduction

## 1.1 BIOSECURITY RISKS POSED BY BIOFOULING

Biofouling on the submerged surfaces of vessels is a well-documented pathway for the introduction of marine non-indigenous species (NIS; Hewitt and Campbell, 2010). In New Zealand, the Ministry for Primary Industries (MPI) has recently issued the Craft Risk Management Standard (CRMS) for vessel biofouling to minimise the risk of further NIS introduction and establishment. The CRMS will come into force on May 15<sup>th</sup> 2018; from then, all vessels arriving in New Zealand must comply with the standard's 'clean hull' requirements (Ministry for Primary Industries, 2014). Key to implementing the CRMS is the availability of methods to inspect and, where necessary, treat vessels for unwanted biofouling.

Inspecting the planar external surfaces of a vessel's hull is relatively straightforward – divers or remotely operated vehicles can readily access these areas and visually determine the extent of biofouling (Floerl and Coutts, 2013). Modern antifouling formulations are at least partly effective in preventing marine growth on external planar hull surfaces (Chambers et al., 2006; Inglis et al., 2010), and mechanical or chemical treatments are available for removing unwanted biofouling from the hull (Hopkins and Forrest, 2008; Floerl et al., 2010a). Inspecting and treating 'niche areas' is challenging by comparison. Niche areas are portions of the vessel that tend to accumulate biofouling more readily because they are not antifouled, rapidly lose antifouling protection, or do not provide the hydrodynamics required for antifouling paint protection. Examples of niche areas include sea chests, dry-docking support strips, bow thrusters, rudders, and propeller shafts (Davidson et al., 2009a; Inglis et al., 2010; Morrisey and Woods, 2015). Although they typically comprise a small percentage of the total submerged surface area of a vessel, niche areas often contain the majority of total biofouling biomass and diversity on a vessel (Hopkins and Forrest, 2010; Inglis et al., 2010). Not only are niche areas highly prone to accumulating biofouling, they are often hidden from normal view and are difficult to inspect and treat. One niche area that has received little attention by most sampling programmes to date is the internal pipework of vessels (Bracken et al., 2016).

## 1.2 INTERNAL PIPEWORK – THE NEED FOR REACTIVE TREATMENTS

Internal pipework is a prime example of a niche area that is 'out of sight – out of mind'. The risks associated with internal pipework have not been well characterised but there are examples of NIS being detected in pipework systems. For example, a recreational vessel that entered Northern Australia with a visibly clean hull was subsequently found to harbour over 200 non-indigenous mussels in internal pipework systems (Neil and Stafford, 2005). MPI has identified a gap associated with treating pipework biofouling of vessels entering New Zealand, particularly recreational vessels.

Recreational vessels entering New Zealand originate from a wide range of locations around the world. More than 600 recreational vessels arrive in New Zealand each year, the majority of which are yachts of less than 20 m in length (Inglis *et al.*, 2012). The biosecurity risk to New Zealand posed by the internal pipework systems of these vessels is poorly understood, and there are currently no treatments available to manage 'risky' vessels. Treatments for internal pipework have been explored overseas, with some being implemented operationally. For example, the Northern Territory Department of Primary Industries and Resources (Australia) treats the internal pipework of all recreational vessels entering Darwin using the disinfectant Conquest<sup>®</sup> (Lewis and Dimas, 2007).

## 1.3 PROSPECTIVE TREATMENT AGENTS FOR INTERNAL PIPEWORK

Growcott *et al.* (2016) reviewed treatments for biofouling in sea chests and internal pipework, comprehensively summarising the literature to identify prospective treatment agents. Treatment agents were separated into two broad classes: chemical and non-chemical.

#### 1.3.1 Chemical treatment agents

Chemical treatment agents are biocides that can be grouped into two main categories: oxidising and non-oxidising. There is a degree of overlap between these two classes because some oxidising chemicals also have other biological activities. Regardless, separating treatment agents into these two broad categories is useful for the purposes of this review.

Oxidising chemicals act to remove electrons from susceptible chemical groups (Finnegan *et al.*, 2010). At sufficient concentrations, this oxidative process overwhelms the natural defence mechanisms of cells and disrupts cellular integrity. Because oxidative chemical treatment agents are non-specific, they tend to have broad spectra of activity and are potentially effective against diverse biofouling assemblages (Grandison *et al.*, 2011). The following oxidising chemical treatment agents were identified by Growcott *et al.* (2016)<sup>1</sup>:

- chlorine;
- chlorine dioxide;
- bromine;
- hydrogen peroxide;
- ferrate;
- peracetic acid; and
- acetic acid.

Descalers are commonly used to remove metal carbonates (scale) from seawater cooling systems (Growcott *et al.*, 2016). Descalers encompass an array of proprietary commercial formulations containing various acids either in isolation or combination with corrosion inhibiters, surfactants, colour indicators, organic acids, and salts. Some commonly available formulations spanning the basic types of descaler (i.e., blended acids, phosphoric acid, sulphamic acid, and hydrogen chloride) will be considered in this report:

- Triple7 Enviroscale Plus<sup>®</sup> (citric acid: 30–60%; lactic acid: 30–60%);
- TermoRens<sup>®</sup> Liquid 104 (citric acid: 5–15%; phosphoric acid: <10%);
- Barnacle Buster Concentrate<sup>®</sup> (phosphoric acid: 85%);
- Descalex<sup>®</sup> (sulphamic acid: 60–100%);
- NALCO<sup>®</sup> 79125 Safe Acid (sulphamic acid: 60–100%); and
- Rydlyme<sup>®</sup> (hydrogen chloride: < 10%).

Non-oxidising treatment agents encompass a vast array of potential biocidal activities. Indeed, all biocidal activities other than oxidative cellular damage fall within this class. Compared to oxidising treatment agents, non-oxidising chemical treatment agents can be more specific if they target set biochemical pathways. Such specificity may allow for better management of potential negative side effects but there is a higher likelihood that some biofouling taxa are (or may become) resilient to the agent (Chapman, 2003). Growcott *et al.* (2016) identified only a single non-oxidising chemical treatment agent—quaternary ammonium compounds (QACs). There are no doubt a number of other non-oxidising chemicals that could be used for biofouling control but, to our knowledge, none have been previously applied in scenarios related to reactive treatment of vessel pipework. Because the current review aims to build on

<sup>&</sup>lt;sup>1</sup> The authors of Growcott et al. (2016) have since acknowledged that acetic acid and some acids used as active ingredients of descalers are non-oxidising.

<sup>2 •</sup> Treating biofouling in internal pipework of recreational vessels

existing knowledge and research in the area of marine biofouling management, non-oxidising chemicals considered as treatment agents for vessel pipework will be limited to QACs.

#### 1.3.2 Non-chemical treatment agents

Non-chemical treatments aim to exceed the tolerance of biofouling organisms to a given environmental parameter. Compared to chemical treatment agents, fewer toxicological and environmental risks exist for non-chemical treatment agents. Growcott *et al.* (2016) identified four non-chemical treatment agents that could be applied to vessel pipework:

- physical removal;
- thermal stress;
- deoxygenation; and
- osmotic shock.

## 1.4 SCOPE AND OBJECTIVES OF THIS DOCUMENT

The objective of this report is to assess the operational suitability of the prospective treatment agents introduced in Section 1.3 for treating biofouling in internal pipework of recreational vessels. The report begins with a summary of the literature and interviews with experts in the fields of marine biosecurity, vessel maintenance, and legislation to gain insights into pipework systems found on board recreational vessels and the associated biofouling risks. A decision framework is then presented for selecting operationally feasible treatment agents, taking into account:

- relative effectiveness against biofouling;
- ecotoxicological and operator safety;
- potential to exacerbate biosecurity risks;
- consenting requirements;
- compatibility with pipework materials;
- operational feasibility, including delivery of treatment agents, infrastructure requirements, and expense; and
- quality control considerations relating to the need to field monitor the treatment for the duration of the required exposure period.

Each of the prospective treatment agents is assessed against this framework to identify the 'most suitable' treatment agent to use as the basis for developing a protocol for treating biofouling in internal pipework of recreational vessels at the New Zealand border.

# 2 Configuration of pipework on board recreational vessels

Developing an effective treatment protocol requires an understanding of pipework configurations typically encountered on board recreational vessels, and their relative biosecurity risk. Treatment agents must be compatible with all pipework materials, and protocols must be designed to reach all parts of pipework likely (or able) to harbour biofouling. Design of effective treatments thus requires knowledge of pipework configurations, diameters, and total volumes, plus an understanding of where biofouling tends to accumulate in pipework systems and which taxa are likely to be present.

Peer-reviewed databases were searched (Google Scholar, Web of Science) but detailed descriptions of vessels' pipework systems and their associated biofouling are largely outside of the scope of the scientific primary literature. As such, non-peer-reviewed literature databases (Google) were searched and a range of industry experts were contacted. In the case of non-peer-reviewed information, all citations have been verified by, or directly build upon information provided by, industry experts.

- **Murray Barton**, Biosecurity Manager, Northern Territory Department of Primary Industries and Resources, Darwin, Australia. Leads a team that treats the internal pipework of all international recreational vessels entering Darwin.
- John Baudier, Director, Yacht Services New Zealand, Nelson, New Zealand. Owns and operates a company that manages the refit and maintenance of a range of recreational vessels and provides logistical support to super yachts visiting New Zealand.
- **Grant Hopkins**, Senior Scientist, Cawthron Institute, Nelson, New Zealand. Extensive background in marine biosecurity, including the design of sea chest treatments.
- John Lewis, Senior Associate, ES Link Services Pty Ltd, Melbourne, Australia. More than 30 years of experience with marine biofouling management, including the development of treatments for internal pipework systems.
- **Bruce Lines**, Director, Diving Services NZ Ltd, Nelson, New Zealand. Owns and operates a commercial diving service, and has implemented biosecurity incursion responses for government.
- **Richard Piola**, Marine Scientist, Australian Department of Defence, Defence Science and Technology Group, Melbourne, Australia. Manages biofouling research and development for the Australian Navy, and has developed treatments for internal pipework of naval vessels.

Regional body staff members were contacted regarding consenting requirements for pipework treatment (Section 3.3) and to provide council perspectives on the various treatment approaches.

- Mandy Bishop, Manager Consents and Compliance, Nelson City Council.
- Dean Evans, Manager Environmental Programmes, Nelson City Council.
- Matt Spiro, Planner, Auckland City Council.

Domiciled and international recreational vessels moored in the Nelson Marina (Nelson, New Zealand) were also inspected as part of this report. Of particular note was a 23 m-long, US-flagged cruising yacht that has an extensive international itinerary, having recently voyaged from North America. This vessel was undergoing maintenance that allowed easy access to, and inspection of, all pipework features. The owner of the vessel, who works in the boatbuilding industry, detailed the pipework systems on board the vessel, how these systems can vary between vessels, and their own experience of pipework biofouling.

Sections 2.1 and 2.2 of this report present a synthesis of the findings from: peer-reviewed and non-peer-reviewed literature searches; interviews with industry and regional body experts; and vessel inspections. Personal communications have not been cited throughout the text – rather, the information presented is a consensus of all information gathered.

## 2.1 PIPEWORK CONFIGURATIONS

A range of pipework systems are found on board recreational vessels and a comprehensive overview of pipework configurations and construction can be found in 'Boatowner's mechanical and electrical manual: how to repair, maintain and improve your boat's essential systems' by Calder (2015). This instructional book is well recognised by boat owners as the 'go-to manual' for vessel maintenance and repair.

The current review is constrained to pipework systems that have direct contact with the sea and are accordingly at risk of accumulating marine biofouling. Systems that transmit freshwater or discharge above the waterline, such as freshwater reticulation systems and most greywater discharge systems, are not considered. There are three main classes of pipework systems on recreational vessels that come into direct contact with the sea:

- engine cooling systems;
- ancillary seawater supply systems; and
- below-water discharge systems.

#### 2.1.1 Engine cooling systems

Engine cooling systems supply a steady flow of seawater to cool a vessel's engine(s). Seawater is drawn through a skin fitting (a flush-mounted, through-hull fitting) or fittings (vessels > 20 m often have two intake skin fittings), on the underside of the vessel. An intake grate is sometimes incorporated over the skin fitting to prevent large debris being drawn into the system. Water that is drawn through the skin fitting passes through a gate or ball valve and a strainer basket before entering a cooling manifold (Figure 1). The gate or ball valve allows the vessel to be isolated from the surrounding seawater while undergoing maintenance. The strainer basket prevents debris entering the cooling systems, and typically incorporates a removable inspection port to allow access to the strainer basket and easy identification of obstructions or biofouling (Dickens, 2015). It is common practice to close the gate or ball valve when the engine is not in operation to reduce the risk of flooding and to prevent biofouling of heat exchangers.

There are two types of engine cooling manifold system: open cooling and closed cooling. With open cooling (also known as raw water cooling), seawater passes directly through galleries in the head of the engine. With closed cooling, antifreeze circulates through the head of the engine and seawater cools an associated heat exchanger (BoatSafe, 2012). Regardless of whether the cooling system is open or closed, water is driven through the system using a positive displacement impeller pump, exits into the engine exhaust, and is discharged from the vessel above or at the waterline.

The size of the pipework fittings and the total volume of an engine cooling system are proportional to the size of the vessel—larger vessels require larger engines that in turn necessitate a pipework system capable of handling greater volumes of cooling water. The cruising yacht inspected as part of this report is larger than the average recreational vessel entering New Zealand (approximately 90% of recreational vessels entering New Zealand are < 20 m long; Inglis *et al.*, 2012). This vessel had twin intake skin fittings and inspection ports of 150 mm in diameter. The total volume of the engine cooling system was estimated to be

approximately 40 L. Smaller vessels may have intake skin fittings as small as 25 mm in diameter, and the total volume of the engine cooling system could be as little as 10 L.



Figure 1. The engine cooling system on board a 23 m long cruising yacht. The system incorporates twin intake skin fittings (not visible) and inspection ports (only left had side is visible). Note the tubeworm and barnacle biofouling on the window of the inspection port. A gate or ball valve acts to isolate the vessel from the sea (another gate or ball valve is located below the inspection port). Seawater is distributed to the engine via a manifold system. This system does not incorporate a strainer basket and the seafloor can be seen when looking down through the inspection port window (i.e., view down through the intake skin fitting).

#### 2.1.2 Ancillary seawater supply systems

Some vessels will have multiple independent ancillary seawater supplies but it is most common for a vessel to have a single intake skin fitting, with or without an intake grate, dedicated to ancillary seawater systems. Ancillary seawater systems can include:

- deck washdown;
- toilet, galley, and shower supply (note: many shower and galley systems use freshwater);
- refrigeration (Burton, 2013);
- air conditioning (MyBoatsGear, 2012); and
- desalination plants (Brett, 2015).

A right-angle bend may be installed directly after the skin fitting to allow the pipework system to fit below the floorboards of the vessel (Figure 2). A gate or ball valve to isolate the system for maintenance is a ubiquitous feature, and a strainer basket or inspection port is often incorporated. Proportional in size to the number of dependent ancillary systems, the inspection port is typically followed by a manifold system to distribute seawater to appropriate locations throughout the vessel. Pipework used for ancillary systems is often smaller than for engine cooling systems, with 25 mm diameter pipework and fittings being

most common. Given the smaller diameter piping used, it would be uncommon for the total volume of an ancillary seawater system to exceed 20 L.

A range of pump types are used with ancillary seawater supply systems, including variablevolume impeller, centrifugal, and positive-displacement pumps. Variable-volume impeller pumps use changes in displaced volume from one side of the pump to the other to create suction and compression. Impellers are usually made of flexible rubber or synthetic materials (often polyether ether ketone). Centrifugal pumps use a rapidly rotating impeller (plastic or metal) to accelerate water outwards, and thus create a vacuum (Machinery Spaces, 2010). Positive-displacement pumps, including hand-operated diaphragm pumps, use reciprocating pistons or diaphragms to successively create suction and discharge (The Engineering Toolbox, 2014). As a practical consideration for applying pipework treatments, variablevolume impeller and positive-displacement pumps can prevent the flow of water through a system when not in operation but centrifugal pumps allow for free passage of water.

Even when not in use, deck washdown, toilet, and shower seawater supplies can be filled with seawater throughout their entire length, and refrigeration and air-conditioning systems that use seawater to cool the condenser are often in continual use. In contrast, desalination plants are only filled with seawater sporadically (i.e., when in use at sea) and are regularly flushed with freshwater. Desalination plants are also filled with a 'pickling' agent when not in use for extended periods to protect the reverse osmosis membranes (Smith, 2014).

#### 2.1.3 Below-water discharge systems

Although many systems on board vessels discharge above the waterline, there are examples of systems that discharge below the waterline and are vulnerable to marine biofouling. Two common below-water discharge systems are:

- blackwater discharge; and
- deck-draining scuppers.



Figure 2. Intake for the ancillary seawater systems on board a 23 m long cruising yacht. Seawater is drawn in via a through-hull skin fitting, passes through a gate valve and inspection port, and is

# distributed via a manifold system. Note the older brass and glass inspection port with associated barnacle biofouling, and newer plastic fittings.

Blackwater, or sewage, is typically discharged below the waterline to minimise odour. On smaller (< 20 m) or older vessels, blackwater can be discharged directly from the toilet, with a vented loop incorporated in the system to prevent seawater flowing back into the vessel (MyBoatsGear, 2013). The piping downstream of the vented loop is in open contact with the ocean. Larger (> 20 m) or newer vessels have blackwater holding tanks, from which sewage is pumped overboard while at sea (Ministry for the Environment, 1999). Only pipework that is located past the vented loop or holding tank and below the water line is in open contact with the ocean. Pipework diameters and total volumes of blackwater discharge systems are comparable to, or slightly larger than, those seen for ancillary seawater supply systems. Of interest, some vessel owners fill toilet systems with freshwater and household vinegar when in port for extended periods of time to prevent calcification of toilet pipework (Calder, 2015) but it is unlikely that this procedure treats pipework downstream of the flushing mechanism.

Some vessels have deck-draining scuppers that discharge below the waterline. Skin fittings on the deck of the vessel are piped to skin fittings below the waterline, allowing entrained seawater to passively drain back to the ocean. Again, the diameter and number of scuppers is proportional to the size of the vessel. The cruising yacht inspected as part of this report has eight individual scuppers of approximately 75 mm in diameter. Only the portion of the scupper pipework below the waterline is filled with seawater during normal operation.

#### 2.1.4 Materials used in construction of pipework

Materials used in the construction of vessel pipework vary with the age of the vessel. Modern vessels or vessels that have recently been refitted use plastic fittings and pipework wherever possible. High density polyethylene (HDPE) and polyvinyl chloride (PVC) are the most commonly used materials. Plastic presents an adaptable, affordable, and corrosion-resistant construction material. Engine cooling systems predominantly comprise metal piping, typically marine grade stainless steel (Figure 1). Engine heads can be made of aluminium or cast steel, while closed cooling heat exchangers can incorporate marine grade stainless steel, copper, brass, and aluminium. O-rings and fibre gaskets are also found in engine cooling systems, and the engines' seawater pumps have stainless, bronze, rubber, or synthetic impellers (Daniello, 2009). Rubber or synthetic polymer seals are incorporated around inspection ports (often glass or Perspex<sup>®</sup>), and similar seals could conceivably be found at other locations within a vessel's pipework. Older vessels often have fittings and pipework made of rubber, copper, brass, bronze, or related metal alloys. Some vessels will have pipework of varying ages, with a mixture of modern plastic fittings and older alloyed metal fittings (Figure 2). It should be noted that vessel owners, especially those on tight budgets or travelling to remote locations where professional maintenance services are unavailable, often undertake vessel repairs and maintenance themselves. Pipework systems on board such vessels can be 'jury-rigged' using a range of material types and configurations. Refrigeration systems and desalination plants incorporate various metals, plastics, and seals. Of particular note are the reverse osmosis membranes used for desalination, which are highly sensitive to chemical and biological agents (Brett, 2015).

#### 2.1.5 Opportunities and barriers to treatment application

The primary features that may assist with the application of biofouling treatments are the strainer baskets, inspection ports, and isolation valves found as part of most engine cooling and ancillary seawater supply systems. Strainer baskets or inspection ports, where they are present, could provide convenient locations to apply a treatment once corresponding skin fittings have been plugged. Inspection ports are utilised in this way for a pipework treatment

implemented in Australia's Northern Territory. However, this approach relies on closing the gate or ball valve immediately adjacent to the skin fitting; the skin fitting, intake grate (where present), and pipework leading up to the gate or ball valve would remain untreated. These sections of the pipework system pose high likelihood of biofouling (Section 2.2.3), thus applying treatments externally using divers presents a more robust approach.

Convoluted pipework systems, such as those with multiple skin fittings, bends, or manifolds could be challenging to treat and inspect. Complex systems may contain 'dead spots' that limit the dispersion of a treatment and provide refuges for biofouling organisms. Systems with right-angle bends immediately after a skin fitting could limit access to pipework, and will need to be considered to ensure that appropriate protocols are developed. Intake grates could interfere with sealing pipework from the external environment or recirculation of a treatment. The impellers used to circulate water through engine heat exchangers could also hamper recirculation of treatments. Because they operate via positive displacement, the impellers or run the boat's engine during treatment application.

Desalination plants may be extremely difficult to treat as they contain fragile membranes that are likely to be harmed by a range of treatment agents (excluding perhaps freshwater). However, the configuration and sporadic use of desalination plants mean that they are unlikely to contain marine biofouling (Section 2.1.2, Section 2.2.3).

## 2.2 PIPEWORK BIOFOULING

The taxonomic identity of biofouling organisms, their location within a given pipework system, and their relative abundance or biomass will directly influence the effectiveness of a treatment.

#### 2.2.1 Identity of biofouling organisms encountered in pipework

The experts consulted as part of this review have observed a range of different biofouling taxa within vessel pipework systems. Taxonomic identity and relative abundance vary not only between vessel types but also between the pipework systems within a single vessel. Ports or harbours from particular geographic locations tend to result in 'signature' biofouling assemblages within pipework systems. In Nelson Marina (Nelson, New Zealand), the authors of this report were able to see tubeworms and barnacles within the pipework systems of resident vessels (Figure 1), and the alga *Colpomenia* spp. was seen at the outlet of an engine exhaust system that had not been operated in several months (Figure 3). A local vessel owner reported that mussels (taxonomy unknown) regularly foul engine cooling, ancillary seawater, and scupper systems of his vessel. In Port Melbourne (Melbourne, Australia), blue mussels are the dominant biofouling taxon in the pipework of naval vessels. Hydroids are also commonly encountered, particularly in high-flow pipework systems. Oysters are occasionally observed, while barnacles are almost never encountered. By contrast, barnacles and tubeworms (Hydroides spp.) are ubiquitously abundant in the pipework of commercial dredge vessels, with mussels typically forming minor components of biofouling communities in these vessels. Submarines in Sydney Harbour (Sydney, Australia) have experienced issues with hydroids (*Ectopleura* spp.) and tubeworms fouling their pipework. Inspections conducted by Biofouling Solutions on over 300 commercial vessels, and similar inspections conducted by Canadian authorities (Frey et al., 2014), have demonstrated that biofouling in the seawater systems of commercial vessels is typically composed of secondary biofouling<sup>2</sup> (barnacles, hydroids, and tubeworms), though in some instances tertiary<sup>3</sup> biofouling including mussels, ascidians, and oysters can occur (Biofouling Solutions, unpublished data).

<sup>&</sup>lt;sup>2</sup> Sessile macrofouling attached directly to the paint or hull surface, or its adherent biofilm.

<sup>&</sup>lt;sup>3</sup> Larger sessile macrofouling that builds up on and amongst the secondary biofouling layer.



Figure 3. *Colpomenia* spp. in the outlet of an engine exhaust of a vessel that has been berthed for several months at Nelson Marina.

Published literature on vessel pipework biofouling is limited but there are documented reports of NIS being encountered in the pipework of recreational vessels. For example, Asian bag mussels (Neil and Stafford, 2005) and black-stripped mussels (Ferguson, 1999) have been sampled from the pipework of yachts entering Australia. Because information on pipework biofouling in recreational vessels is scarce, it should be assumed that pipework could feature a diverse range of sessile marine taxa. Mobile species could conceivably be encountered in internal pipework, although no documented reports were found. Algal species are only likely to be present near inlets and outlets (Figure 3) where sunlight levels are sufficient for photosynthesis. Nevertheless, the main classes of pipework biofouling organisms that were reported or observed as part of this report were:

- barnacles;
- hydroids;
- mussels;
- oysters; and
- tubeworms.

#### 2.2.2 Extent of biofouling encountered in pipework

There are few documented reports of the biofouling loads encountered in internal pipework of vessels. Because biofouling reduces flow rates in critical pipework systems, vessel operation will be impaired or prevented above certain threshold biofouling loads (Grandison *et al.*, 2011). There is an associated impetus for vessel owners to treat or remove biofouling before it reaches such thresholds (John Baudier pers. comm.), although it should be noted that pipeline maintenance behaviour for recreational vessels has not been formally described nor biofouling thresholds quantified. Regardless, it makes intuitive sense that biofouling thresholds for pipework systems will be proportional to:

- the diameter of pipework;
- the complexity of the system; and

• the relative volumes of water that need to be drawn through the system.

Because recreational vessels use relatively small diameter pipework and most of their pipework systems incorporate multiple bends, valves, and manifolds (Section 2.1), it is expected that the majority of recreational vessels arriving to New Zealand will feature a 'low' to 'moderate' biomass of biofouling organisms within their pipework systems. This expectation matches the experience of the industry experts interviewed as part of this review, who agreed that pipework systems of recreational vessels generally features 'low' biofouling loads. It is difficult to quantify these anticipated biofouling loads using established metrics developed for external hull surfaces of vessels but, broadly speaking and based on the literature reviewed and expert surveys, it is anticipated that most pipework systems on board recreational vessels will correspond to Level of Fouling (LOF; Floerl, 2004) scores of  $1^4$  or  $2^5$ . Some larger diameter systems may regularly rank up to an LOF score of  $3^6$ .

While pipework biofouling loads are generally expected to be low or moderate, it is anticipated that some poorly maintained vessels will pose exceptions and feature higher levels of biofouling. Granting the relationship between the amount of pipework biofouling and biosecurity risk is not understood, it should be assumed that any adult biofouling organisms present in pipework have potential to be dislodged or to release reproductive propagules while a vessel resides in New Zealand. Approximately 97% of recreational vessels entering New Zealand are classified as long-stay vessels (> 20 days) under the CRMS for vessel biofouling. The majority of recreational vessels reside in New Zealand for several months, which could allow immature fouling to become reproductively viable during their stay, and visit multiple coastal centres and natural locations around the country (Floerl *et al.*, 2009; Inglis *et al.*, 2012; Georgiades and Kluza, 2017). These factors combined could facilitate establishment of NIS present within internal pipework.

#### 2.2.3 Susceptibility of various pipework systems to biofouling

Pipework systems that have a continuous flow of seawater or open exchange of seawater with the ocean pose the highest risk for biofouling accumulation. Commercial vessel inspections have shown that biofouling is typically concentrated in seawater systems with high volume water demands, such as air-conditioning systems (Biofouling Solutions, unpublished data). Many of the industry experts and vessel owners interviewed stated that pipework immediately adjacent to inlet or outlet skin fittings (i.e., the skin fitting and the first 10-20 cm of pipework) is the most common location for biofouling to accumulate on board recreational vessels, likely due to the high degree of water exchange. Intake grates, where they are present, are also a common location for biofouling. Biofouling can accumulate further into pipework systems if exchange of seawater with the ocean is sufficient but well maintained vessels do not typically have noticeable biofouling past the first 10–20 cm of pipework. When biofouling is found further into pipework systems, it is most commonly encountered at discontinuities, such as joins, bends, valves, or restrictions. This trend is particularly true in the early stages of colonisation, presumably because discontinuities provide 'refuges' for larvae to attach and grow. It follows that once biofouling has gained a foothold at a discontinuity the flow characteristics inside the pipe will alter, favouring further accumulation of biofouling organisms.

Pipework systems that are not open to the ocean or are operated sporadically are unlikely to contain biofouling greater than a slime layer (i.e., no macrofouling). Due to the inherent

<sup>&</sup>lt;sup>4</sup> Hull partially or completely covered in slime fouling. Absence of any macrofouling.

 <sup>&</sup>lt;sup>5</sup> Light fouling. 1–5 % of visible hull surface covered by macrofouling or filamentous algae. Usually remaining area covered in slime.
 <sup>6</sup> Considerable fouling. Macrofouling clearly visible but still patchy. 6–15 % of visible hull surface covered by macrofouling or filamentous algae. Usually remaining area covered in slime.

nature and operation of such pipework systems, larvae of biofouling organisms will only occasionally be drawn into the systems. Once inside the system, biofouling organisms will be vulnerable to starvation or suffocation when the system is not in operation. Patterns of operation for a given pipework system vary between vessel types. For example, sail boats often rely on wind power and, as a result, will limit the use of auxiliary power (i.e., to enter port or to charge house batteries). In contrast, motor launches continuously operate their engines while at sea. It follows that the engine cooling systems on sail boats ought to pose a lower biosecurity risk than engine cooling systems on motor launches. The itinerary of the vessel also influences patterns of operation of pipework systems. For example, vessels on prolonged voyages are less likely to have recently spent extended periods in port (i.e., opportunities for biofouling to establish) but are more likely to have continuously operated pipework systems for extended periods (i.e., potential for biofouling to survive further into pipework systems) and had lay-up periods in a variety of ports en route. Likewise, refrigeration and air-conditioning systems are often in continual operation when vessels transit the tropics but these systems are usually not operated when vessels are in more temperate climes.

There are pipework features where biofouling is highly unlikely to accumulate, the most notable example being desalination plants. Desalination plants are only operated sporadically and while at sea, are regular flushed with freshwater, and are 'pickled' when not in use (Section 2.1.2). Not only is biofouling unlikely to establish, the patterns of operation of desalination plants would prevent survival or growth of biofouling organisms.

# **3** Operational considerations for treatment agent selection

In addition to understanding pipework configurations and associated biofouling (Section 2), a range of operational criteria exist for selecting a suitable treatment agent(s). The treatment agent(s) must kill all relevant taxa within allotted exposure times, whilst being safe for operators, the environment, and the pipework itself. The treatment must not exacerbate biosecurity risk, must be able to be consented for use, and be cost-effective and relatively simple to apply. The following criteria were used to evaluate each of the treatment agents:

- effectiveness;
- safety;
- biosecurity;
- consenting;
- compatibility;
- feasibility; and
- quality control.

### 3.1 EFFECTIVENESS

#### 3.1.1 Treatment efficacy

The chemical and non-chemical treatment agents listed in Section 1.3 were mainly identified by Growcott *et al.* (2016) because they have previously been evaluated against biofouling organisms, either inside vessel pipework or in related land-based scenarios. Comparing relative effectiveness will help to narrow down the treatment options but direct comparisons are difficult because different studies have relied on different methodological approaches. Some treatment agents have been evaluated against single target taxa, whilst others have been evaluated against multiple taxa or intact biofouling communities. Although it is difficult to directly compare treatment agent effectiveness between published studies, three factors can be considered:

- spectrum of activity;
- lethal concentration or intensity; and
- required exposure time.

Treatment agents should ideally be effective against juvenile and adult life stages of all commonly encountered biofouling organisms but, based on the outcomes of our review, at least mussels, oysters, hydroids, barnacles, and tubeworms (Section 2.2.1). Because studies often employ a single target taxon or a subset of model taxa, it is not possible to accurately gauge spectrum of activity in many instances. Nevertheless, inferences can be made towards spectrum of activity based on mode of action (where such information is available). As discussed in Section 1.3.1, treatment agents that act on ubiquitous physiological processes or pathways, have multiple physiological targets, or are generally cytotoxic are likely to have broad spectrums of activity. Treatment agents that target specific physiological pathways or processes are likely to have narrow spectrums of activity.

The potency of a treatment agent is either reported as: (1) a modelled value corresponding to the treatment concentration or intensity lethal to 50% (LC<sub>50</sub>) or 99% (LC<sub>99</sub>) of individuals of the target organisms; or (2) the lowest concentration or intensity tested that resulted in 100% mortality of the targeted organisms. The later scenario is most common in the literature relating to vessel pipework treatment. Barring potential methodological inconsistencies, treatment agents that are lethal at lower concentrations or intensities can generally be considered to be more effective and have several potential benefits, including less treatment agent required and reduced volume of treatment waste. At the same time, highly effective

treatment agents are often also toxic to non-target organisms, with treatment solutions and wastes posing risks to operators and the environment.

Efficacy also depends on exposure time, with reported potency values typically related to set exposure durations (e.g., OECD guidelines<sup>7</sup> or ASTM testing methods<sup>8</sup>). In the case of vessel pipework treatment, MPI has specified a maximum allowable exposure time of 48 h. Although 48 h is considered acceptable, shorter effective exposure times will be given precedent. Decommissioning vessels for several days will interfere with the schedules of some vessel owners, and increasing treatment time will increase the overall cost of applying a treatment (Inglis *et al.*, 2012).

#### 3.1.2 Resilient taxa

For each treatment agent considered, there is interplay between spectrum of activity, lethal concentration or intensity, and exposure time. Identifying resilient taxa–able to withstand or recover quickly–is an important consideration for both the selection of the treatment agent and subsequent protocol development. The precautionary approach is to develop a protocol that is effective against the most resilient taxa, as the treatment will be at least as effective against less resilient taxa. Bivalves are highly resilient to a number of treatment types because they can close their valves and seal out the external environment (Forrest *et al.*, 2007; Piola and Hopkins, 2012; Atalah *et al.*, 2016; Hopkins *et al.*, 2016). Although bivalves appear to be generally applicable for inclusion as resilient taxa that require exposure testing, resilience is often species-specific and can vary between life stage and environmental conditions (i.e., thermal or toxicity tolerance). Any insight into resilience of particular biofouling organisms to given treatment protocols. It is likewise important to consider the relevance of particular taxa to vessel pipework to avoid focussing on those that are rarely found in these systems (Section 2.2.1).

## 3.2 SAFETY

A treatment agent must be safe for both operators and the environment without prohibitive handling or containment requirements. In most instances, the safety of a treatment is dependent on concentration or intensity. For example, concentrated stock solutions of chemical agents can be orders of magnitude more hazardous to handle than the corresponding working solutions to be applied to pipework. Safety requirements should be considered in light of concentrations to which operators or the environment are likely to be exposed.

#### 3.2.1 Operator safety

Operator safety hazards potentially posed by treatment agents include:

- contact with skin or eyes;
- inhalation of fumes;
- accidental ingestion;
- combustion or reaction with other substances; and
- mechanical injury.

Although handling highly hazardous substances is not deemed practical in the context of pipework treatment, many operator safety hazards can be managed using straight forward handling procedures and personal protective equipment (PPE). Material Safety Data Sheets (MSDS) provide overviews of handling and personal protection requirements for chemical treatment agents. The Chemical Classification and Information Database (CCID),

<sup>&</sup>lt;sup>7</sup> <u>http://www.oecd-ilibrary.org/environment/oecd-guidelines-for-the-testing-of-chemicals-section-2-effects-on-biotic-systems\_20745761</u> 8 <u>http://www.astm.org/BOOKSTORE/BOS/1106.htm</u>

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administered by the Environmental Protection Authority (EPA), classifies the hazards posed by chemicals in accordance with the Hazardous Substances and New Organisms regulations. An overview of the CCID classifications is outside of the scope of this report but detailed information is available on the EPA website<sup>9</sup>. Although MSDS and CCID information is not typically available for non-chemical treatment agents, managing risks associated with this class of treatment will be covered under workplace safety protocols.

Using readily available PPE (e.g., safety glasses, gloves, and covered shoes) and common handling procedures (e.g., preventing contact with skin or eyes, secondary containment of stock solutions) is considered feasible for pipework treatment. Specialised PPE (e.g., hermetically sealed suits) or complex handling procedures (e.g., onerous transport requirements) are not deemed viable in this context. The likelihood that divers will be required to administer treatments also needs to be considered. In particular, any safety requirements for treatment agents should not interfere with safe diving practices.

#### 3.2.2 Ecotoxicological safety (non-target effects)

Chemical and non-chemical treatment agents have potential to harm the environment. It may be possible to completely isolate treatments from the environment and subsequently collect treatment wastes. However, this approach is not feasible for some treatment agents and the potential for accidental spillage or failure of containment systems cannot be ignored.

Chemical treatment agents used to reactively treat biofouling are typically non-specific (Section 1.3.1) and, as such, have potential to harm a wide range of organisms if released into the environment in sufficient quantities. The relative volumes of treatment agent released, persistence in the environment (Jones and De Voogt, 1999), potential to bioaccumulate (Katagi, 2010), and bioavailability to relevant organisms (Semple *et al.*, 2004) all influence the relative ecological risk of a chemical (Newman, 2014). When some chemicals breakdown in the environment they form toxic by-products, either as primary by-products or via side-reactions, and some of these by-products can pose equal or greater ecological risks than the parent compound(s). A commonly cited example is the halogenated by-products formed when halogen-based disinfectants (e.g., chlorine) react with organic compounds to form persistent organic pollutants (Khalanski and Jenner, 2012). It is worth noting that certain chemical treatment agents can be neutralised post treatment to reduce ecotoxicological risk (e.g., treating chlorine with sodium thiosulphate; Morrisey, 2015).

In general, non-chemical treatment agents pose fewer ecotoxicological risks compared to chemical treatment agents. Because non-chemical treatment agents rely on exceeding tolerance of biofouling organisms to environmental parameters, dilution of any associated discharges in the sea is typically sufficient to negate ecotoxicological risk. For example, discharging tens of litres of freshwater into a marina is unlikely to have detectable effects on the environment. If discharge volumes are sufficient to alter the receiving environment, pre-treatment options are often available. For example, heated water can be cooled prior to discharge.

## 3.3 **BIOSECURITY**

The aim of treating biofouling in pipework is to minimise or, ideally, eliminate the likelihood of introduction and establishment of marine NIS; but, in some instances, treatments may inadvertently exacerbate biosecurity risks. For example, applying treatments to pipework inlets could result in the escape or dislodgement of viable biofouling organisms. This kind of universal treatment risk is largely manageable via standardised containment protocols, careful

<sup>&</sup>lt;sup>9</sup> http://www.epa.govt.nz/hazardous-substances/approvals/group-standards/Pages/HSNO\_classification\_information.aspx

implementation of treatments by approved or licenced treatment providers, and compliance monitoring. Treatment areas (i.e., inside of pipework) should be isolated from the environment until biofouling organisms have been rendered nonviable (i.e., after the allotted exposure period).

Other risks are specific to given treatment agents and can be difficult to mitigate. Some treatment agents may stimulate biofouling organisms to spawn or treatment specific procedures may preclude adequate isolation of the treatment areas from the environment (isolation from the environment is a key requirement for any treatment). Specific biosecurity risks posed by that treatment agent are considered when assessing candidate treatment agents, including their relative magnitude, and the potential for mitigation.

## 3.4 CONSENTING

Activities that involve discharges into the marine environment require resource consent from the relevant local authority (usually a regional council). Discharge can include chemical treatment waste, viable or nonviable biofouling organisms, and water. In the context of pipework treatment, the key parameter determining whether consent is required is the *likelihood and characteristics* of any associated discharge. An overview of consenting requirements for treatment agents to be discharged into New Zealand's marine environment has recently been prepared by Morrisey (2015). The discharge of treatment agents must satisfy a number of legislative obligations:

- the Resource Management Act (RMA);
- approval for use by the EPA;
- the New Zealand Coastal Policy Statement; and
- local body Resource Management Plans.

#### 3.4.1 Resource Management Act

The Resource Management Act 1991 promotes sustainable management of natural and physical resources. The following sections of the Act are relevant to vessel pipework treatment:

- Section 12(1)(d) stipulates that no person may deposit in, on, or under any foreshore or seabed any substance in a manner that has or is likely to have an adverse effect on the foreshore or seabed unless the discharge is allowed by a national standard or other regulations, a rule in a regional plan, or a resource consent;
- Section 15(1)(a) prohibits the discharge of contaminants or water into water unless the discharge is allowed by a national standard or other regulations, a rule in a regional plan, or a resource consent. It prohibits the dumping of any waste from or other matter from any ship or other offshore installation unless allowed by a resource consent;
- Section 15B(1) prohibits the discharge of water or contaminants from a ship or offshore installation into water unless permitted or controlled by regulations in the Act, a rule in a regional coastal plan, a resource consent or if, after reasonable mixing, the water or contaminant discharged is not likely to give rise to significant adverse effects on the receiving environment, including aquatic life. Discharge as part of normal operation of a ship or offshore installations is allowed under the Resource Management (Marine Pollution) Regulations 1998; and
- Section 330 allows for emergency works and power to take preventive or remedial action where an adverse effect on the environment is otherwise likely to occur (e.g., biosecurity incursion).

#### 3.4.2 Environmental Protection Authority

Although Section 330 of the RMA contains provisions for the off-licence use of treatment agents during incursion scenarios, wide-scale use of any chemical treatment agent should be certified for that use by the EPA. The EPA weighs up any environmental and safety considerations against potential benefits of a treatment agent, and provides a set of controls to govern the application of treatments and disposal of treatment wastes. These controls can include allowable discharge rates, reporting requirements, operator safety considerations, containment practices, and monitoring procedures. Note that EPA approval is only relevant to chemical treatment agents.

#### 3.4.3 New Zealand Coastal Policy Statement

The New Zealand Coastal Policy Statement aims to safeguard the integrity, form, function, and resilience of the coastal environment. Policy 23(1) requires that discharge of water be managed in relation to:

- the sensitivity of the receiving environment;
- the nature and concentrations of the contaminants to be discharged;
- the capacity of the receiving environment to assimilate the contaminants and the capacity for mixing; and
- minimising mixing zones and associated adverse effects on life-supporting capacities of water.

#### 3.4.4 Local body Resource Management Plans

Local bodies (i.e., regional councils) around New Zealand have a range of provisions in place to protect the coastal environment. Provisions vary between local bodies, and a detailed synopsis is outside of the scope of this report. It can be generally considered that local bodies will weigh up the potential for discharges to harm the environment against any associated benefits. Councils can accordingly grant consent for one-off activities or blanket consent for on-going activities.

#### 3.4.5 'Precedent' for consent

Given the legislative complexities inherent to consenting a treatment agent, it is proposed that the most robust approach is to select a treatment agent with some existing precedent for discharge or use in the marine environment. For example, a treatment agent may have been:

- granted EPA approval for use a biocide in the marine environment;
- used in biofouling incursion scenarios under Section 330 of the RMA; or
- issued prior consents by regional bodies for discharge to the marine environment.

Limiting treatment agents to those with existing precedent for use in the marine environment should safeguard (as far as is feasible) any consent process because the treatment has previously been assessed as suitable for use in the marine environment. Supporting information required for any consent application (e.g., ecotoxicological data; Section 3.2.2) should be at least partly available. It should be noted that even if treatment waste is to be collected and disposed of on land the likelihood for accidental spillage needs to be accounted for. Best practice is to consult relevant regional councils and seek precautionary consent or a certificate of compliance, as appropriate.

## 3.5 COMPATIBILITY WITH PIPEWORK MATERIALS

Treatment agents must be compatible with a range of material types to avoid damaging pipework systems or other components of a vessel. Damaging a vessel would, at best, incur monetary penalties and alienate vessel owners, and, at worst, present a dangerous scenario if vital vessel components were affected. Materials commonly used to construct vessel pipework include plastics (HDPE, Perspex®, and PVC), metal alloys (mainly brass, bronze, and marine grade stainless steel), glass, and rubber and synthetic seals (Section 2.1.4). Ensuring that treatment agents will not react directly with any of these material types is a key consideration. The potential for spilt or discharged material to react with other components of a vessel, such as antifouling paints, should also be taken into consideration.

Damage could be caused if dislodged biofouling organisms block pipework systems. This scenario may occur immediately post treatment or be delayed, from days to weeks, for well attached biofouling organisms, such as mussels. Complex pipework systems, especially heat exchangers, are most likely to become blocked in this way. Strainer baskets are typically located upstream of heat exchangers and should intercept dead biofouling material. Nevertheless, flushing or cleaning procedures may be needed in conjunction with treatments to avoid unforeseen blockages. Alternatively, treatment agents that remove or dissolve biofouling could be used.

## 3.6 FEASIBILITY

If a treatment is to be used by a range of operators around New Zealand, procedures to deliver the treatment agent must not be overly complex or expensive.

#### 3.6.1 Delivering the treatment agent

Chemical treatment agents must maintain sufficient concentrations throughout the pipework system for the required exposure period, with the potential for chemical binding, breakdown, or dilution accounted for. Non-chemical treatment agents rely on exceeding tolerance of biofouling organisms to a given environmental parameter. In this way, both chemical and non-chemical treatment agents present engineering challenges—systems to deliver chemical treatments or alter the environment inside pipework would need to be developed, respectively.

Both chemical and non-chemical treatment agents could be actively or passively delivered to a pipework system. Active delivery would involve pumping or recirculating the treatment agent through a pipework system for a required exposure period. Passive delivery would involve adding a treatment agent to one or several inlet(s), drain(s), or inspection port(s) and decommissioning the vessel for the required exposure period. Passive delivery presents the simplest scenario but will only be applicable to some treatment agents or pipework systems (e.g., introduction of chlorine tablets to a pipe inlet or outlet or insertion of flexible heating elements).

There are commercially available systems for treating biofouling in internal pipework of recreational vessels. These systems are aimed to remedy restricted water flow in fouled pipework, using descalers to dissolve calcareous organic matter. Portable units capable of actively or passively delivering treatment agents to pipework include the Port-O-Flush® (Trac Ecological, 2016) and SeaFlush® (SeaFlush Inc., 2016) systems, respectively. These systems have not been designed for biosecurity purposes and recommended operating procedures leave portions of pipework systems untreated. Nevertheless, these systems, or similar systems built from scratch, could provide a basis for developing a biosecure treatment application protocols that treat all portions of pipework likely to contain biofouling.

#### 3.6.2 Infrastructure requirements and other costs

Provisioning specialised equipment to apply treatments at multiple ports of entry could incur significant monetary costs. These costs should be weighed up against the benefits of undertaking the treatment. Treatment agents that do not require specialised equipment or could utilise existing equipment (e.g., pumping systems) are preferable but such treatment agents may not exists. Commercial diving companies typically have access to a range of

pumping systems, pipework, and blanking devices that could be utilised for pipework treatment.

Other treatment costs that will vary between treatment agents include:

- purchasing the treatment agent;
- labour to mobilise, apply, monitor, and demobilise the treatment;
- neutralising or disposing of treatment waste; and
- other consumables, including electricity.

### 3.7 QUALITY CONTROL

Quality control procedures are an essential component of any field operation using a treatment system to render all biofouling nonviable. The quality control must ensure that the target treatment concentration or intensity threshold is maintained for the required period. There needs to be suitable field measurement systems available for measuring the biocide concentration or condition at sites representative to the target organisms. For substantive pipework systems, an externally circulated treatment system could simplify monitoring to ensure that the required treatment conditions are adequately maintained (i.e., monitoring at the outlet).

Measuring biocide concentration or condition is also a key consideration for decommissioning of any pipework treatment. In many cases it will be necessary to completely flush all treatment wastes from pipework systems. Treatment waste could then be collected and disposed of on land, neutralised and discharged to the sea, or discharged directly to the sea. Each of these scenarios require the ability to monitor biocide concentration or condition to ensure treatments are handled appropriately, neutralisation is effective, or maximum allowable discharges are not exceeded, respectively.

# 4 Evaluating candidate treatment agents

The criteria discussed in Section 3 form the basis of a decision framework (Figure 4) that is applied to assess the operational feasibility of each of the chemical and non-chemical treatment agents identified by Growcott *et al.* (2016).

- **Effectiveness**: lethal to adults and juveniles of relevant biofouling taxa at realistic working concentrations or intensities and within 48 h.
- **Safety**: does not pose undue ecotoxicological or operator safety risks at relevant concentrations or intensities—CCID classifications and links to MSDS are provided for chemical treatment agents.
- **Biosecurity**: will not exacerbate likelihood of release of marine NIS.
- Consenting: some existing precedent for use in the New Zealand marine environment.
- **Compatibility**: will not damage pipework or other vessel components.
- Feasibility: manageable resource, cost, and infrastructure requirements.
- **Quality control**: able to monitor that the treatment concentration or intensity has been met for the required duration.



Figure 4. Decision framework to evaluate the operational feasibility of prospective treatment agents for rendering biofouling in the pipework of recreational vessels nonviable.

There are conflicting reports and incomplete information on treatment agent characteristics in many instances, and it has been necessary to make some partially subjective decisions. Where information is severely limited, the decision 'uncertain' has been assigned. 'Pass' or 'fail'

decisions were assigned where sufficient information was deemed to be available to be confident of informed outcomes.

## 4.1 CHEMICAL TREATMENT AGENTS

Because of the range of biofouling taxa that have been observed in the internal pipework of vessels, chemical treatment agents suitable for application at the border need to have broad spectra of activity. Such non-specific modes of action heighten the likelihood of operator and environmental harm, necessitating careful selection of treatment agents and the design of treatment protocols. Growcott *et al.* (2016) identified a range of oxidising (i.e., chlorine, chlorine dioxide, bromine, hydrogen peroxide, ferrate, peracetic acid, acetic acid, and commercial descaler formulations) and one non-oxidising chemical treatment agent (i.e., QACs) potentially suitable for treating internal pipework.

#### 4.1.1 Chlorine

Chlorine is the most commonly used biocide in aquatic systems. Chlorine is a non-specific toxin that disrupts cellular integrity and compromises attachment strength of biofouling organisms (Mackie and Claudi, 2009a). Chlorine is available in a number of forms, but dichloroisocyanurate dihydride (dichlor) and trichloroisocyanuric acid (trichlor) have been suggested as the most appropriate forms for marine biosecurity applications (Morrisey, 2015).

Criteria	Evidence	References	Decision
Effectiveness	200 mg L <sup>-1</sup> for 16 h killed 93% of Mediterranean fanworm <i>Sabella spallanzanii</i> on an encapsulated yacht.	Morrisey <i>et al.,</i> (2016)	
	10 mg $L^{-1}$ is 100% effective against the mussels <i>Perna viridis, Perna perna</i> , and <i>Mytilopsis leucophaeata</i> in 48, 120, and 168 h, respectively.	Rajagopal <i>et al.</i> , (1994); Rajagopal <i>et al.</i> , (1995); Rajagopal <i>et al.</i> , (2003c)	-
	5 mg L <sup>-1</sup> is 100% effective against the bivalves <i>Brachidontes variabilis</i> and <i>Brachidontes striatulus</i> in 27 and 156 h, respectively.	Rajagopal <i>et al.</i> , (1997); Rajagopal <i>et al.</i> , (2005b)	<b>Uncertain</b> – not
	15 mg L <sup>-1</sup> is 100% effective against the barnacle <i>Megabalanus tintinnabulum</i> in 4 h.	Sasikumar <i>et al.,</i> (1992)	clear if effective against resilient
	5 mg L <sup>-1</sup> is 100% effective against the oyster <i>Magallana bilineata</i> (formerly <i>Crassostrea</i> <i>madrasensis</i> ) <sup>10</sup> with chronic exposure (weeks).	Rajagopal <i>et al.,</i> (2003b)	taxa within 48 h and not tested on general biofouling
	Susceptibility varies with size: medium <i>M</i> . <i>leucophaeata</i> are most tolerant while tolerance increase with size for <i>M. edulis</i> ,	Rajagopal <i>et al.</i> , (2002); Rajagopal <i>et al.</i> , (2005a);	
	<i>M. tintinnabulum</i> , and <i>M. bilineata</i> .	Rajagopal <i>et al.</i> , (2003b); Sasikumar <i>et al.</i> , (1992)	_
	1 mg $L^{-1}$ took 816 h to kill <i>P. viridis</i> at 29°C.	Rajagopal, (2012)	-
	Even low doses of chlorine (1 mg L <sup>-1</sup> )	Rajagopal <i>et al.</i> ,	
	stimulate bivalves to seal their valves, with mussels attached via byssal threads more	(2003a); Rajagopal <i>et al.,</i>	

Table 1. Overview for using chlorine to treat marine biofouling inside the pipework systems of recreational vessels.

 $<sup>^{10} \ \</sup>underline{http://www.marinespecies.org/aphia.php?p=taxdetails&id=819168}$ 

Criteria	Evidence	References	Decision
	resistant to chlorine (presumably because they are better able to stay sealed).	(2005a)	
	Reproductively active mussels ( <i>M. leucophaeata</i> ) are less resilient to chlorine, probably due to increased filtration rates.	Jenner <i>et al.,</i> (1998); Rajagopal, (2012)	-
Safety	Dichlor: 5.1.1B – Medium oxidising substance 6.1D (oral) – Acutely toxic 6.4A – Eye irritant 9.1A – Very ecotoxic (aquatic) Trichlor: 5.1.1B – Medium oxidising substance 6.1D (oral) – Acutely toxic 6.3A – Skin irritant 8.3A – Corrosive to eyes 9.1A – Very ecotoxic (aquatic) 9.3B – Ecotoxic to vertebrates	HSNO CCID	<b>Pass</b> – operator and environmental risks can be
	Dichlor and trichlor are available in granular or pellet form for use in swimming pools and can be handled safely with appropriate precautions. Chlorine breaks down in seawater; some by- products are persistent in the environment but chlorine is generally considered to pose low environmental risk.	MSDS <sup>1</sup> Allonier <i>et al.</i> (1999)	managed
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species actively avoid chlorine.	Cherry <i>et al.</i> (1977); Inglis <i>et al.</i> (2012)	Pass – risks mitigated by isolation from environment during treatment
Consenting	Approved by the EPA for use as a biocide to eradicate pests from boats and marine structures for biosecurity purposes, including provisions for discharge to the environment.	Chief Executive of the Environmental Protection Authority (2016)	Pass – approved for - use by EPA and
	Nelson City Council has granted blanket consent for Diving Services New Zealand to treat marine biofouling. Has been used to treat biofouling in	Bishop and Evans (pers. comm.)	some regional bodies
	emergency scenarios (Section 330 of RMA).		
Compatibility	Accelerates corrosion of some metals, such as stainless steel, but this process takes weeks to months.	Ma (2012); Wallen and Henrikson (1989)	Pass – will not harm pipework within stipulated treatment timeframe

Criteria	Evidence	References	Decision
Feasibility	Efficacy is affected by temperature and pH, plus chlorine is consumed by organic and inorganic substance in seawater.	Chou <i>et al.</i> , (1999); Mackie and Claudi, (2009a); Rajagopal, (2012)	
	Dichlor costs approximately \$10 kg <sup>-1</sup> .	Various online stores	<b>Pass</b> – available
	Dichlor or trichlor tablets could be useful provided rates of consumption of the active ingredient do not exceed rates of release from the tablet and adequate dispersion throughout the pipework could be achieved.		<ul> <li>in cheap, user- friendly formats</li> </ul>
	Free available chlorine can be neutralised with sodium thiosulphate.	Morrisey (2015)	_
Quality control	Easy measurement with indicator strips or field-usable portable colourimeter.	Morrisey <i>et al.</i> (2016)	<b>Pass</b> – readily monitored for field application

<sup>1</sup> <u>http://www.essef.be/images/documenten/004800\_vf1\_E.pdf</u> http://www.ronasgroup.com/msds/water%20treatment/MSDS%20of%20TCCA.pdf

Chlorine could be suitable for developing a treatment protocol for internal pipework but there is uncertainty around its efficacy and spectrum of activity that requires validation. While chlorine has been demonstrated to be effective against a range of biofouling taxa, it is unclear whether it will kill all relevant species of bivalves within the stipulated 48 h timeframe. Available exposure studies assessing bivalve susceptibility to chlorination have used relatively low concentrations, and higher chlorine concentrations (e.g., 200 mg L<sup>-1</sup>) may act more quickly. The efficacy of chlorine against resilient bivalves could also potentially be increased via the addition of a small quantity of chlorine-resistant surfactant (e.g., Dowfax 2A1). The presence of the surfactant should increase the bioavailability of any chlorine taken in by bivalves (e.g., for intermittently opening or gulping bivalves), resulting in a more rapid biocidal effect. The formulation of this proposed optimised biocidal product is unknown and would need to be validated by laboratory testing. The capacity of bivalves to detect chlorine and seal out the external environment may prove sufficient to counteract the effect of either elevated chlorine doses or the addition of a surfactant.

Notwithstanding the uncertainty around efficacy, chlorine poses generally a low risk to operators or the environment and has existing precedent for discharge to the marine environment. If neutralised via addition of sulphite or dithionite (see Morrisey *et al.* (2016) for look-up tables), this biocide can readily be discharged to the marine environment with minimal likelihood of adverse effects on local biota. Quality control procedures for monitoring of chlorine in seawater are also established, with concentrations easily monitored using indicator strips or a portable hand-held colourimeter with addition of sachets of chemical indicators. Chlorine concentrations would need to be actively monitored in pipework systems because the efficacy of chlorine is dependent on temperature, pH, and the presence of organic matter.

#### 4.1.2 Chlorine dioxide

Chlorine dioxide is considered a 'strong' oxidising agent, and is widely used in water treatment (Aieta and Berg, 1986) and bleaching of wood pulp (Kolar *et al.*, 1983). A highly water-soluble gas, chlorine dioxide can be formulated into tablets (Sanderson, 2010) but is usually generated on-site for immediate use.

Criteria	Evidence	References	Decision
Effectiveness	Effective against early life stages of some macrofoulers at 25 to 250 mg L <sup>-1</sup> .	Hose et al., (1989)	
	40 mg L <sup>-1</sup> is effective against zebra mussels,	Matisoff <i>et al.</i> ,	Uncertain –
	Dreissena polymorpha, in under 10 min;	(1996);	insufficient
	5 mg L <sup>-1</sup> effective in 70 h.	Holt and Ryan, (1997)	information available and not
	Effective as a preventative treatment in industrial water cooling systems.	Petrucci and Rosellini, (2005)	tested on general biofouling
	Effective as a disinfectant of drinking water.	Aieta and Berg, (1986)	
Safety	Sodium chlorite:	HSNO CCID	
	5.1.1B – Medium oxidising substance		
	6.1B (dermal) – Acutely toxic		
	6.1B (inhalation) – Acutely toxic		
	6.1C (oral) – Acutely toxic		
	6.3A – Skin irritant		
	6.4A – Eye irritant		
	6.8A – Known or presumed human		
	reproductive or developmental toxicants		Uncertain –
	6.9B – Harmful to human target organs or		poses some risks
	systems		to environment
	9.1A – Very ecotoxic (aquatic)		
	9.3B – Ecotoxic to vertebrates		_
	Gaseous chlorine dioxide can spontaneously	MSDS <sup>1</sup>	
	combust but tablets are relatively benign.	Jin et al., (2009)	_
	Chlorine dioxide rapidly breaks down in the	Hoigné and Bader,	
	environment but can reduce metals, nitrites,	(1994)	
	and sulphides to yield persistent organic		
	pollutants.		
Biosecurity	No specific biosecurity risks have been	Inglis et al., (2012)	<b>Pass</b> – risks
	described but many marine organisms		mitigated by
	broadcast spawn when exposed to stressful		isolation from
	conditions and mobile species may avoid		environment
	chemical treatments.		during treatment
Consenting	No precedent for use in New Zealand's		Fail – no
_	marine environment.		precedent
Compatibility	Corrosive at high concentrations but is	Srinivasan et al.,	Pass –
	widely used in industrial cooling systems	(2003)	compatible with
	with no major ill effect.		pipework
	Can degrade some plastic pipes over	Yu et al., (2011)	within stipulated
	continual exposure (months to years).		treatment
Feasibility	Reacts strongly with organic matter and		timeframe
-	would require continual monitoring.		_
	Cost is several times higher than similar	Venkatesan and	-
	chemical treatment agents, such as chlorine.	Murphy, (2009); Grandison <i>et al.</i> , (2011)	<b>Fail</b> – cost prohibitive
	Can be generated on-site using a chlorine	Aieta and Berg	-
	dioxide generator or applied in tablet form;	(1986)	
	dissolved gas degrades over time.		
Quality	Practical field monitoring method unknown.		<b>Fail</b> – monitoring

Table 2. Overview for using chlorine dioxide to treat marine biofouling inside the pipework systems of recreational vessels.

Chlorine dioxide is relatively unexplored as a reactive treatment agent for marine biofouling, but it is used successfully as a preventative treatment in industrial cooling systems. Although chlorine dioxide is available in a tablet form, no preliminary data is available as to the efficacy of chlorine dioxide tablets against marine biofouling. Within the context of this review, chlorine dioxide is considered unsuitable for reactively treating pipework of recreational vessels.

#### 4.1.3 Bromine

Bromine containing salts, primarily sodium bromide and bromine chloride, presents a more stable alternative to chlorine for disinfecting swimming water (Koski *et al.*, 1966) and treating industrial cooling systems (Bartholomew, 1998). Bromine has comparable biological activity to that of chlorine but is less volatile and more temperature and pH stable (Koski *et al.*, 1966).

Table 3. Overview for using bromine to treat marine biofouling inside the pipework systems of recreational vessels.

recreational vess Criteria	Evidence	References	Decision
Effectiveness	No information available on effectiveness against adult or juvenile marine biofouling organisms.		Uncertain – insufficient information
	Effective as a preventative treatment for biofouling of industrial cooling systems.	Burton and Margrey (1979); Yang <i>et al.</i> (2002)	available and not tested on general biofouling
Safety	Sodium bromide: 6.1E (oral) – Acutely toxic	HSNO CCID	-
	Bromine is a strong oxidiser but commercial formulations (i.e., for spa pool use) are relatively benign when handled according to manufacturer specifications.	MSDS <sup>1</sup> Sagi <i>et al.</i> (1985)	Pass – safe for operators and only low environmental
	Side-reactions in seawater yield organobromines, some of which may be persistent organic pollutants.	Rae (2014)	risk
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> (2012)	Pass – risks mitigated by isolation from environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Bromine can increase rates of corrosion of metals but this process is slow (weeks to months).	Daniel and Rapp (1976); Franklin <i>et al.</i> (1991)	Pass – compatible with pipework within stipulated treatment timeframe
Feasibility	Bromine is generally considered a 'stable' oxidising agent (i.e., longer half-life than chlorine) but does break down in seawater.		- Dors cost
	Commercial formulations containing bromine salts are readily available. Although cost (~\$30 kg <sup>-1</sup> ) is higher than chlorine-based formulations, lower effective doses should be anticipated.	Various online stores	Pass – cost- effective and user-friendly

Criteria	Evidence	References	Decision
Quality	Readily monitored with field suitable		Pass – readily
control	equipment.		monitored for
			field application

<sup>1</sup> <u>http://www.sciencelab.com/msds.php?msdsId=9927262</u>

Although little information pertaining to the effectiveness of acute exposure of marine biofouling organisms to bromine containing compounds is available, information from other scenarios is available. Fisher *et al.* (1999) found that the toxicity of bromine oxidants was two to five times greater than chlorine oxidants for six freshwater species; namely the daphnid *Daphnia magna*, the amphipod *Hyalella azteca*, the golden shiner *Notemigonus crysoleucas*, and the rainbow trout *Oncorhynchus mykiss*. Additionally, the toxicity of bromine was enhanced in the presence of ammonia. Bromine biocides have also been used successfully for disinfection of ballast water prior to discharge (Chattopadhyay *et al.*, 2004). Extrapolating from the known utility of chlorine (Section 4.1.1), it is likely that acute exposure to bromine will be effective against at least some biofouling taxa. The exception may be shelled organisms like bivalves, which, based on documented reports for chlorine exposure (Rajagopal *et al.*, 2005a), may detect bromine and seal themselves from the external environment. Bromine containing compounds have not been consented for use in the New Zealand marine environment.

#### 4.1.4 Hydrogen peroxide

Hydrogen peroxide is an oxidising agent that is widely used as a bleach and disinfectant. The activity of hydrogen peroxide stems from its unstable oxygen-oxygen bond which, when reduced, yields water and oxygen. Although highly reactive in pure form, aqueous solutions of hydrogen peroxide are widely available and have been evaluated for efficacy against some macrofouling organisms, primarily mussels.

Criteria	Evidence	References	Decision
Effectiveness	Adult zebra mussels <i>D. polymorpha</i> exposed to 5.4 mg L <sup>-1</sup> for 21 days experienced 90% mortality; at 40 mg L <sup>-1</sup> 100% mortality of zebra mussels took 3 days, while Asian clams died after 14 days.	Petrille and Miller, (2000)	Uncertain– insufficient information available and not tested on general biofouling
Safety	<ul> <li>5.1.1B – High hazard oxidising substance</li> <li>6.1D (inhalation) - Acutely toxic</li> <li>8.2A – Corrosive to skin</li> <li>8.3A – Corrosive to eyes</li> <li>6.9B (inhalation) – Harmful to human target organs or systems</li> <li>9.1D – Ecotoxic (aquatic)</li> <li>9.3B – Ecotoxic to vertebrates</li> </ul>	HSNO CCID	biofouling <b>Pass</b> – safe for operators and
	Concentrated hydrogen peroxide is corrosive but dilutions applicable to treating biofouling are generally considered safe if handled appropriately.	MSDS <sup>1</sup> Watt <i>et al.</i> , (2004)	the environment
	Breaks down rapidly in seawater to yield water and oxygen.	Petasne and Zika, (1997)	
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful	Inglis <i>et al.</i> , (2012)	<b>Pass</b> – risks mitigated by isolation from

# Table 4. Overview for using hydrogen peroxide to treat marine biofouling inside the pipework systems of recreational vessels.

Treating biofouling in internal pipework of recreational vessels • 27

Criteria	Evidence	References	Decision
	conditions and mobile species may avoid chemical treatments.		environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Accelerates corrosion of most metals but this process takes days to weeks at realistic working concentrations (< 10%). Has a bleaching effect on some materials.	Uchida <i>et al.,</i> (1998); Miyazawa <i>et al.,</i> (2006)	Pass – compatible with pipework within stipulated treatment timeframe
Feasibility	Because hydrogen peroxide breaks down rapidly in seawater, maintaining effective concentrations will be difficult. The cost of hydrogen peroxide is relatively low (approx. \$10 L <sup>-1</sup> at 35%).	Jenner <i>et al.</i> , (1998) Various online stores	Pass – readily available and cost-effective
Quality control	Practicable measurement methods are available for field use.		<b>Pass</b> – measurement practicable in field

<sup>1</sup> <u>https://www.sciencelab.com/msds.php?msdsId=9924299</u>

Hydrogen peroxide can be considered safe for operators, the environment, and vessels but the stipulated treatment times would preclude using this compound as a reactive treatment for internal pipework (i.e., > 48 h exposure period required for lethal effect). Likewise, maintaining effective treatment concentrations would present a logistical challenge due to the rapid degradation of hydrogen peroxide in seawater.

#### 4.1.5 Ferrate

Ferrate is an oxidising ion that has recently been considered as a reactive treatment for marine biofouling (Mackie and Claudi, 2009b). The parent compound potassium ferrate has been employed for wastewater treatment, and a patented system for onsite production of liquid ferrate is available (Ferrate Treatment Technologies LLC, 2014). Ferrate is considered a stronger oxidiser than chlorine, while having fewer environmental concerns (Sharma, 2002).

vessels. Criteria	Evidence	References	Decision
Effectiveness	No relevant information is available.		Uncertain – insufficient information available and not tested on general biofouling
Safety	No data on CCID for potassium ferrate Although potassium ferrate in solid form is combustible and an irritant, it can be handled safely with common safety procedures.	MSDS <sup>1</sup>	<b>Pass</b> – safe for operators and
	Degrades relatively rapidly (hours to days) in seawater to yield environmentally benign iron oxides.	Sharma (2002) Li <i>et al</i> . (2005)	the environment
Biosecurity	No specific biosecurity risks have been	Inglis <i>et al</i> .	Pass – risks

Table 5. Overview for using ferrate to treat marine biofouling inside the pipework systems of recreational	
vessels.	

Criteria	Evidence	References	Decision
	described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	(2012)	mitigated by isolation from environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Ferrate solutions are used to protect metals against corrosion.	John (1955)	Pass – compatible with pipework
Feasibility	Decays rapidly in seawater, likely necessitating repeated dosing. Onsite production of ferrate requires specialised equipment, procedures, and precursor chemicals (sodium hydroxide, sodium hypochlorite, ferric chloride).	Ferrate Treatment Technologies LLC (2014)	- <b>Fail</b> – requires specialised infrastructure and cost-
	Potassium ferrate costs upwards of \$100 kg <sup>-1</sup> .	Various online stores	- prohibitive
Quality control	Special procedures would be required for field measurement of biocidal concentrations.		Fail – requires special analytical procedures

<sup>1</sup> <u>http://www.lookchem.com/msds/2011-06%2F3%2F480010(39469-86-8).pdf</u>

Although the efficacy of ferrate against adult biofouling organisms has not been examined, the general oxidative properties of this agent imply that it is likely to be effective in some capacity. Of the two application methods available, potassium ferrate is the most viable option because onsite production requires highly specialised equipment. The paucity of preliminary efficacy data, lack of precedent for consented use, and potentially high expense excludes ferrate as a viable treatment option.

#### 4.1.6 Peracetic acid

Peracetic acid reacts in water to form acetic acid (Section 4.1.7) and hydrogen peroxide (Section 4.1.4), both of which are biocidal compounds. Peracetic acid is used as a general disinfectant in food-processing facilities (Rossoni and Gaylarde, 2000) and for wastewater treatment (Kitis, 2004), and is increasingly being used to control biofouling in industrial cooling systems (Cristiani, 2005).

Criteria	Evidence	References	Decision
Effectiveness	Has not been evaluated against adult biofouling organisms but is generally considered a non-specific and fast-acting biocide.		Uncertain – insufficient information available and not tested on general biofouling
	Effective against embryos of the mussels <i>Mytilopsis leucophaeata</i> and <i>D. polymorpha</i> at around 5 mg L <sup>-1</sup> for 15 min exposure.	Verween <i>et al.,</i> (2009)	
Safety	<ul> <li>6.1D (dermal) – Acutely toxic</li> <li>6.1D (inhalation) – Acutely toxic</li> <li>6.1D (oral) - Acutely toxic</li> <li>8.1A – Corrosive to metal</li> <li>8.2A – Corrosive to skin</li> <li>8.3A – Corrosive to eyes</li> </ul>	HSNO CCID	<b>Pass</b> – safe for operators and the environment

Table 6. Overview for using peracetic acid to treat marine biofouling inside the pipework systems of recreational vessels.

Criteria	Evidence	References	Decision
	6.7B – Limited evidence of carcinogenicity 9.1A – Very ecotoxic (aquatic)		
	Concentrated peracetic acid is a strong oxidiser and primary irritant but is relatively benign when diluted to realistic working concentrations.	MSDS <sup>1</sup> Pechacek <i>et al.,</i> (2015)	_
	Breaks-down in seawater, with no persistent by-products.	Steiner, (1995); Kitis, (2004)	_
	Commercial peracetic formulations, such as Tsunami 100 <sup>2</sup> , contain other ingredients (surfactants, salts, etc.) that have unknown effects on the environment.		_
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> , (2012)	Pass – risks mitigated by isolation from environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Corrodes many metals but this process is not relevant at realistic working concentrations and exposure times.	Qu et al., (2008)	Pass – compatible with pipework within stipulated treatment timeframe
Feasibility	Relatively rapid decay should be expected in seawater so recirculation and monitoring for the treatment period would be essential.		Pass –
	Peracetic acid is available in commercial formulations, such as Tsunami $100^2$ . Cost is in the order of \$5 L <sup>-1</sup> .	Various online stores	commercially available and cost-effective
	Biocidal activity is maintained in the presence of organic matter.	Kramer, (1997)	
Quality control	Practical field monitoring systems are available for peracetic acid using a portable colourimeter.		<b>Pass</b> – suitable field monitoring available

<sup>1</sup> <u>https://www.sciencelab.com/msds.php?msdsId=9926439</u>

<sup>2</sup> <u>http://salustarim.com/uploads/Tsunami\_orjinal\_etiket.pdf</u>

Despite the lack of quantitative data in the literature, peracetic acid should be similarly or more effective than either of its' two active products. Acetic acid (see Section 4.1.7) in particular has been demonstrated to kill a range of biofouling organisms. Peracetic acid also fulfils the criteria of compatibility and feasibility but has no previous precedent for consented use in New Zealand. Peracetic acid is manufactured in New Zealand and sold commercially under the trade names Degaclean 150 (Degussa) and Tsunami 100 (EcoLab) so would be readily available for biosecurity applications. Multispecies toxicity testing for freshwater and marine species has been undertaken by NIWA for Degaclean 150, however, that report remains confidential to the client (Chris Hickey, pers. obs).
## 4.1.7 Acetic acid

Acetic acid, the primary constituent of household vinegar, is a weak acid that partially dissociates in seawater to yield free hydrogen and acetate ions. Unlike most acids, the biocidal activities of acetic acid is due not only to reduced pH but also un-dissociated molecules and acetate ions (Reid, 1932). Recent work has evaluated the effectiveness of acetic acid as a reactive treatment for marine biofouling on encapsulated vessels (Atalah *et al.*, 2016) and in specialist aquaculture scenarios (Forrest *et al.*, 2007). When the vessel *Columbus* arrived in Nelson fouled with *Sabella spallanzanii*, encapsulation with acetic acid was used to kill biofouling on the vessel's hull. Although the initial encapsulation system failed and may have influenced the rates of mortality subsequently observed, once the system was repaired further addition of acetic acid rendered the biofouling nonviable within 3 days (Javier Atalah pers. comm., Cawthron Institute).

Criteria	Evidence	References	Decision
Effectiveness	4% acetic acid is effective against a range of soft foulers in aquaculture, including ascidians, bryozoans, tubeworms, and seaweeds.	Forrest <i>et al.</i> (2007); Locke <i>et al.</i> (2009)	Uncertain –
	Encapsulating 'old' and 'young' biofouling communities with 5% acetic acid was 100% effective inside 48 h; included oysters and mussels.	Atalah <i>et al.</i> (2016)	- limited information available suggests
	Effective against flatworms and biofouling assemblages (including ascidians, bryozoans, and tubeworms) in oyster aquaculture at $\geq$ 1% for 30 seconds; does not harm cultured oysters at these exposures.	Cahill and Forrest (unpublished)	<ul> <li>effective against resilient taxa within 48 h</li> </ul>
Safety	<ul> <li>6.1E – Acutely toxic</li> <li>6.9B – Harmful to human target organs or systems</li> <li>8.1A – Corrosive to metal</li> <li>8.2C – Corrosive to skin</li> <li>8.3A – Corrosive to eyes</li> </ul>	HSNO CCID	<b>Pass</b> – safe for
	Corrosive and flammable at > 80% concentration but typical working concentrations (< 10%) are analogous to household vinegar.	MSDS <sup>1</sup>	- operators and the environment
	Acetic acid is biodegradable and has no persistent by-products.	Raj et al., (1997)	
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> , (2012)	<b>Pass</b> – risks mitigated by isolation from environment during treatment
Consenting	Has been used to treat biofouling in emergency scenarios (Section 330 of RMA).		<b>Pass</b> – used for biosecurity incursions
Compatibility	Accelerates corrosion of some metals but this process is not relevant at realistic working concentrations and within 48 h.	Singh and Singh, (1995); George <i>et al.</i> , (2004); Amri <i>et al.</i> ,	<b>Pass</b> – compatible with pipework

Table 7. Overview for using acetic acid to treat marine biofouling inside the pipework systems of
recreational vessels.

Criteria	Evidence	References	Decision
		(2008)	
Feasibility	May be some loss of the undissociated acetic acid during the treatment period – this is expected to be lower than for other oxidants.		_
	Comparatively cost-effective at approx. \$2 L <sup>-1</sup> for 80% concentration.	Various online stores	<b>Pass</b> – readily
	Sodium diacetate is an alternative to concentrated acetic acid; this solid compound yields acetic acid in water and is safer to handle and transport.	Morrisey, (2015)	available and cost-effective
	Biocidal activity is maintained in the presence of organic matter.	Kramer, (1997)	-
Quality control	Practical measurement in the field using colorimetric titration method.	Cahill and Forrest (unpublished)	<b>Pass</b> – monitoring practicable

<sup>1</sup> <u>http://www.sciencelab.com/msds.php?msdsId=9922769</u>

Acetic acid is a promising treatment approach that may be effective against a range of adult biofouling organisms, including bivalves, within the maximum allowable treatment time for vessel pipework of 48 h and at relatively low concentrations. However, only a single study has tested the efficacy of acetic acid against intact biofouling communities (Atalah *et al.*, 2016)—further work is needed to fully gauge the utility of acetic acid for reactive biofouling treatment. At relevant working concentrations (e.g., 5%), this treatment agent is safe for operators, the environment, and vessels. Although concentrated acetic acid is hazardous, alternative starting materials such as sodium diacetate are available. Treatment solutions of acetic acid could be neutralised via the addition of a strong base (e.g., sodium hydroxide) following treatment and prior to discharge to the marine environment. Taking the above considerations into account, further investigation of acetic acid as a treatment agent for internal pipework is warranted.

## 4.1.8 Descaler formulation – Triple7 Enviroscale Plus®

Triple7 Enviroscale Plus<sup>®</sup> is a formulation of non-ionic surfactants and fruit based acids (including citric acid: 30–60% and lactic acid: 30–60%) with 'botanical additives' produced by Envirofluid (<u>https://envirofluid.com/</u>). This product is designed and commonly used to remove scale from heat exchangers, condensers, and chillers without corroding the surface material.

Criteria	Evidence	References	Decision
Effectiveness	Adult mussels ( <i>Mytilus planulatus</i> ) exposed to a range of descaler concentrations at ~16°C experienced a 10–25% reduction in weight due to acidic digestion of shells over 24 h.	Lewis and Dimas, (2007)	Uncertain – capable of achieving 100% mortality of mussels under certain conditions but not tested on general biofouling
	Adult mussels ( <i>M. planulatus</i> ) exposed to 25% descaler experienced 100% mortality after 24 h at 26°C, or at 11°C where water was circulated. Some mussels ( $n = 4$ ) survived exposure after 24 h at 11°C where water was not circulated.	Bracken <i>et al.,</i> (2016)	
Safety	No information for active ingredients on CCID.		Uncertain – safe for

# Table 8. Overview for using Triple7 Enviroscale Plus<sup>®</sup> to treat marine biofouling inside the pipework systems of recreational vessels.

Criteria	Evidence	References	Decision
	Not considered a hazardous substance. Not considered to cause adverse effects to animal or plant life if released to the environment in small quantities. Claimed to be non-toxic but contains other	MSDS <sup>1</sup>	operators but environmental effect unknown
	proprietary ingredients ('botanical additives') for which environmental effects cannot be evaluated.		
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> , (2012)	<b>Pass</b> – risks mitigated by isolation from environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Compatible with metals, rubber, and plastics.	Based on manufacturer's product data	Pass – compatible if used as directed
Feasibility	Stability of proprietary acid blend in seawater is unknown.		Pass –
	This descaler is reasonably priced, packaged in convenient volumes, and is available in New Zealand.	Company website	<ul> <li>commercially available and user friendly</li> </ul>
Quality control	Field monitoring is difficult for all components although pH could be used as a proxy for concentration.		Uncertain – pH may be used as an indicative measure of concentration

<sup>1</sup> <u>https://envirofluid.com/worksafe-environmental-chemistries/limescale-calcium-removal/triple7-enviroscale-plus?doc=1177</u>

Available studies demonstrate that Triple7 Enviroscale<sup>®</sup> can kill mussels (*M. planulatus*), though it is less effective than some other descaler formulations (Lewis and Dimas, 2007; Bracken *et al.*, 2016). This preparation has not been assessed against general biofouling assemblages in either laboratory or field settings.

## 4.1.9 Descaler formulation – TermoRens® Liquid 104

TermoRens<sup>®</sup> Liquid 104 cleansing fluid (citric acid: 5-15%; phosphoric acid: < 10%) is designed to remove mussels, barnacles, marine growth, humic substances, salt and other contamination from pipework. The product is marketed as 'environmentally friendly' and does not affect materials other than specified.

Table 9. Overview for using TemoRens<sup>®</sup> to treat marine biofouling inside the pipework systems of recreational vessels.

Criteria	Evidence	References	Decision
Effectiveness	Has been used successfully to treat biofouling-contaminated niche areas on commercial ships and can kill (but not remove all calcium carbonate) all biofouling when systems are rinsed cumulatively for ~ 6 h at a concentration of ~ 12.5%.	Unpublished data Biofouling Solutions (2014)	Uncertain – capable of killing calcium carbonate based biofouling but requires further research
Safety	Phosphoric acid < 10%:	HSNO CCID	Fail – not suitable

Criteria	Evidence	References	Decision
	6.1E – Acutely toxic		for use by
	8.1A – Corrosive to metal		inexperienced
	8.2C – Corrosive to skin		operators and
	8.3A – Corrosive to eyes		may impact the
	9.1D – Ecotoxic (aquatic)		environment
	Causes serious eye irritation—use PPE as directed.	MSDS <sup>1</sup>	
	Contains other proprietary ingredients for which environmental effects cannot be evaluated.		
Biosecurity	No specific biosecurity risks have been	Inglis <i>et al.</i> ,	Pass – risks
	described but many marine organisms	(2012)	mitigated by
	broadcast spawn when exposed to stressful		isolation from
	conditions and mobile species may avoid		environment
	chemical treatments.		during treatment
Consenting	No precedent for use in New Zealand's		Fail – no
	marine environment.		precedent
Compatibility	Should avoid contact with bases, inorganic	Based on	Pass – compatible
	alkalis, sodium nitrite, and potassium	manufacturer's	if used in
	nitrite.	data	accordance with
	May produce carbon oxides as		manufacturer's
	decomposition product.		recommendations
Feasibility	Will be neutralised by reaction with		Fail – currently
	calcareous fouling organisms or scale,		not commercially
	necessitating recirculation and monitoring		available in NZ
	of concentrations.		and not user
	This descaler is produced in Norway and is	Company website	friendly
	not readily available in New Zealand.		menury
Quality	Field measurements of pH with indicator		Uncertain – only
control	strips or a portable meter could be		indirect
	practicable for monitoring biocide		measurements
	concentrations.		available
<sup>1</sup> http://www.tros	as/images/termorens/pdfs/MSDSTermorensliquid1	04 pdf	

<sup>1</sup> <u>http://www.tros.as/images/termorens/pdfs/MSDSTermorensliquid104.pdf</u>

Field applications of TermoRens<sup>®</sup> liquid 104 cleansing fluid have shown that, in some circumstances, this descaler can kill entrained biofouling in niche areas. However, the treatment appears to be less effective than other descaler brands (Unpublished data, Biofouling Solutions), and has operator safety and environmental concerns.

#### 4.1.10 Descaler formulation – Barnacle Buster Concentrate®

Barnacle Buster<sup>®</sup> (phosphoric acid: 85%) is promoted as a safe, non-toxic, and biodegradable marine growth remover specifically formulated to meet an industry wide need for cost effective alternatives to mechanical cleaning of seawater cooled equipment. Barnacle Buster<sup>®</sup> is produced by Trac Ecological Marine Products (<u>http://trac-online.com</u>).

# Table 10. Overview for using Barnacle Buster<sup>®</sup> to treat marine biofouling inside the pipework systems of recreational vessels.

recreational vessels.				
Criteria	Evidence	References	Decision	
				4

Criteria	Evidence	References	Decision
Effectiveness	Adult mussels ( <i>M. planulatus</i> ) exposed to 25% descaler at 26°C experienced 100% mortality after 12 h, or after 24 h at 11°C with circulation. Some mussels ( $n = 2$ ) survived exposure after 24 h at 11°C where water was not circulated.	Bracken <i>et al.</i> , (2016)	Uncertain – capable of achieving 100% mortality of mussels in some scenarios but not tested on general biofouling
Safety	Phosphoric acid > 10%: 6.1D (oral) – Acutely toxic 6.1E (dermal) – Acutely toxic 8.1A – Corrosive to metal 8.2C – Corrosive to skin 8.3A – Corrosive to eyes	HSNO CCID	Uncertain – safe
	9.1D – Ecotoxic (aquatic) Claimed to be non-toxic, biodegradable, non-corrosive, and non-hazardous. Use of rubber gloves and protective eyewear are recommended. Claimed to be non-toxic but contains other proprietary ingredients for which environmental effects cannot be evaluated.	MSDS <sup>1</sup>	for operators but environmental effect unknown
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.,</i> (2012)	<b>Pass</b> – risks mitigated by isolation from environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Will dissolve small quantities of zincs or other sacrificial anodes; these products will etch most metals. Incompatible with strong alkaline bases; generates heat and steam. Compatible with gaskets, seals and plastics.	Based on manufacturer's data	Pass – compatible with pipework if used in accordance with manufacturer's recommendations
Feasibility	Will be neutralised by reaction with calcareous fouling organisms or scale, necessitating recirculation and monitoring of concentrations. This descaler is reasonably priced, packaged in convenient volumes, and is available in New Zealand.	Company website	<b>Pass</b> – commercially available and user friendly
Quality control	Field measurements of pH with indicator strips or a portable meter could be practicable for monitoring biocide concentrations.		Uncertain – only indirect measurements available

<sup>1</sup> <u>http://www.kelloggmarine.com/msds/TRAC-trac%20Ecological%20Marine%20Products/TRAC\_1208M\_MSDS.pdf</u>

Barnacle Buster<sup>®</sup> is effective at killing mussels in controlled experiments (Bracken *et al.*, 2016) but no examples were found where this preparation has been used to treat general biofouling in either laboratory or field conditions. As such, further trials are recommended before considering this descaler as a treatment agent for the internal seawater systems of recreational vessels.

## 4.1.11 Descaler formulation – Descalex®

Descalex<sup>®</sup> (sulphamic acid: 60 - 100%) is a dry acid cleaner formulated to remove rust and scale deposits. Descalex is produced by Unitor and distributed by Wilhelmsen (<u>http://wssproducts.wilhelmsen.com</u>).

Table 11. Overview for using Descalex <sup>®</sup> to treat marine	biofouling inside the pipework systems of
recreational vessels.	

Criteria	Evidence	References	Decision
Effectiveness	Kills a range of biofouling taxa when systems are rinsed cumulatively for $> 10$ h at a concentration of ~10% in heated freshwater (40°C).	Unpublished data Biofouling Solutions (2012; 2015a)	Pass – has been used effectively against a range of biofouling organisms in short timeframes
Safety	Sulphamic acid 60 – 100%: 6.1D – Acutely toxic 6.1E – Acutely toxic 8.1A – Corrosive to metal 8.2C – Corrosive to skin 8.3A – Corrosive to eyes 9.1C – Ecotoxic (aquatic) 9.3C – Ecotoxic vertebrates	HSNO CCID	Fail – not suitable for mixing in confined spaces or for use by inexperienced operators, plus stated environmental toxicity claims are contradictory
	Descalex contains strong acids and should be handled with care and in accordance with the MSDS: use PPE (gloves, mask, eye protection, overalls) as directed. Reaction products from acid components in descaling product may include gasses like carbon dioxide and hydrogen. Contains other proprietary ingredients for which environmental effects cannot be evaluated.	MSDS <sup>1</sup>	
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> , (2012)	<b>Pass</b> – risks mitigated by isolation from environment during treatment
Consenting	Fully biodegradable but no precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Descalex <sup>®</sup> should not be used on aluminium, zinc, tin, or galvanised surfaces.	Based on manufacturer's product data sheet	Fail – is not compatible with some pipework materials
Feasibility	Will be neutralised by reaction with calcareous fouling organisms or scale, necessitating recirculation and monitoring of concentrations. This descaler is not available in New Zealand but can be shipped to New Zealand in commercial volumes (25 kg).	Company website	<b>Fail</b> – currently not commercially available in NZ and not user friendly
Quality control	Field measurements of pH with indicator strips or a portable meter could be practicable for monitoring biocide concentrations.		Uncertain – only indirect measurements available

<sup>1</sup> <u>http://www.esisys.com/Documents/Unitor/MSDS/DESCALEX.pdf</u>

Field applications of Descalex<sup>®</sup> have shown that this descaler can kill entrained biofouling in internal pipework and remove all calcareous biofouling. The concentrated nature of the raw product makes this descaler unsuitable for application to recreational vessels due to the need for specialist PPE. The product could also pose risks to the environment if it were to be spilled or discharged.

## 4.1.12 Descaler formulation – NALCO® 79125 Safe Acid

NALCO<sup>®</sup> 79125 Safe Acid (sulphamic acid: 60 - 100%) is a dry acid product formulated for offline removal of water hardness deposits from marine equipment. Its dry format and built-in dye indicator makes this product convenient for use in routine maintenance cleaning. An incorporated inhibitor minimises base metal attack during cleaning application.

 Table 12. Overview for using NALCO<sup>®</sup> 79125 Safe Acid to treat marine biofouling inside the pipework systems of recreational vessels.

 Criteria
 Evidence

 Decision

Criteria	Evidence	References	Decision
Effectiveness	This descaler has been shown to kill all biofouling when systems are rinsed cumulatively for ~74 h at a concentration of ~5%.	Unpublished data Biofouling Solutions (2011)	Uncertain – has been used effectively against a range of biofouling organisms but experimental timeframes exceeded 48 h
Safety	Sulphamic acid 60–100%: 6.1D – Acutely toxic 6.1E – Acutely toxic 8.1A – Corrosive to metal 8.2C – Corrosive to skin 8.3A – Corrosive to eyes 9.1C – Ecotoxic (aquatic) 9.3C – Ecotoxic vertebrates	HSNO CCID	Fail – not suitable for mixing in confined spaces or for use by inexperienced operators, plus may cause long-term impacts to the environment
	NALCO <sup>®</sup> 79125 Safe Acid contains strong acids, requiring specialised handling procedures, controlled ventilation, and full PPE. Contains other proprietary ingredients for which environmental effects cannot be evaluated.	MSDS <sup>1</sup>	
Biosecurity	No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> , (2012)	<b>Pass</b> – risks mitigated by isolation from environment during treatment
Consenting	No precedent for use in New Zealand's marine environment.		<b>Fail</b> – no precedent
Compatibility	Gives off hydrogen by reaction with metal. Compatibility with plastic materials can vary.	Based on manufacturer's MSDS.	Fail – incompatible with some metals and plastics
Feasibility	Will be neutralised by reaction with calcareous fouling organisms or scale, necessitating recirculation and monitoring of		Fail – currently not commercially

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Criteria	Evidence	References	Decision
	concentrations.		available in NZ
	NALCO has a distributer in New Zealand but product is generally available in commercial volumes unsuitable for small	Company website	and not user friendly
Quality	applications. Field measurements of pH with indicator		Uncertain –
control	strips or a portable meter could be		only indirect
	practicable for monitoring biocide concentrations.		measurements available
<sup>1</sup> http://algoma	a.msdsworld.com/msds/English/21826.pdf		

NALCO<sup>®</sup> 79125 Safe Acid can be used to kill entrained biofouling in internal pipework and remove all calcareous biofouling. The hazardous nature of the concentrated raw product makes this descaler formulation unsuitable for applications in recreational vessels due to the need for specialised PPE and care to ensure that no product is released into the marine environment.

### 4.1.13 Descaler formulation – Rydlyme®

Rydlyme<sup>®</sup> (hydrogen chloride: < 10%) is a descaler heavily fortified with wetting and penetrating agents which dissolve water scale, lime, mud, rust, and other water formed deposits. Rydlyme<sup>®</sup> is produced by Apex Engineering Products Corporation (<u>http://www.rydlymemarine.com/</u>) and is available in a number of varieties including Rydlyme<sup>®</sup> and Rydlyme<sup>®</sup> Marine.

Table 13. Overview of using Rydlyme <sup>®</sup>	to treat marine biofouling inside the pipework systems of
recreational vessels.	

Criteria	Evidence	References	Decision
Effectiveness	Exposing adult mussels ( <i>M. planulatus</i> ) to hydrogen chloride based descalers, including Rydlyme <sup>®</sup> , resulted in a 92% reduction in mussel weight after 12 h when used at concentrations $\ge 25\%$ . At 12.5% concentration, a 92% reduction in mussel weight was achieved after 48 h.	Bracken <i>et al.,</i> (2016)	_
	Adult mussels ( <i>M. planulatus</i> ) exposed to a 50% concentration of descaler experienced a 50% reduction in mussel weight over a 24 h period at ~ $16^{\circ}$ C.	Lewis and Dimas, (2007)	<b>Pass</b> – effective against a range of
	Laboratory tests using oysters ( <i>Saccostrea glomerata</i> ) found that Rydlyme <sup>®</sup> at 20% for 12 h resulted in 35% mortality.	Neil and Stafford, (2005)	- biofouling organisms
	Rydlyme <sup>®</sup> has been successfully used to treat biofouling-contaminated seawater systems on commercial ships. Rydlyme <sup>®</sup> has been shown to remove all biofouling if circulated through seawater piping systems at a concentration of $50 - 65\%$ for $24 - 48$ h.	Unpublished data Biofouling Solutions, (2013; 2015b)	-
Safety	Hydrochloric acid < 10%: 6.1E (oral) – Acutely toxic 6.1E (dermal) – Acutely toxic 8.1A – Corrosive to metals 8.2C – Corrosive to skin 8.3A – Corrosive to eyes	HSNO CCID	Uncertain – safe for operators but environmental effects are unclear

Criteria	Evidence	References	Decision
	Eye protection should be used and protective gloves are recommended. Claimed to be non-toxic but contains other proprietary ingredients for which	MSDS <sup>1</sup>	
Biosecurity	environmental effects cannot be evaluated. No specific biosecurity risks have been described but many marine organisms broadcast spawn when exposed to stressful conditions and mobile species may avoid chemical treatments.	Inglis <i>et al.</i> , (2012)	<b>Pass</b> – risks counteracted by isolation from environment during treatment
Consenting	Fully biodegradable but no precedent for use in New Zealand's marine environment. Use in-water on vessels in Western Australia is dependent on it being contained and disposed of on land.		<b>Fail</b> – no precedent
Compatibility	Rydlyme <sup>®</sup> will not corrode or ruin gaskets, seals, plastic, cork, Teflon, packing, or rubber.	Based on manufacturer's data	<b>Pass</b> – compatible with a range of pipework materials
Feasibility	Will be neutralised by reaction with calcareous fouling organisms or scale, necessitating recirculation and monitoring of concentrations Rydlyme <sup>®</sup> is readily available in New Zealand.		Pass – safe for operators and the environment
	Given the likely small scale of seawater systems on recreational vessels, a relatively high concentration applied over a 24 h timeframe should be cost-effective.	Unpublished data, Biofouling Solutions. See Biofouling Solutions, (2013; 2015b)	
Quality control	Field measurements of pH with indicator strips or a portable meter could be practicable for monitoring biocide concentrations.	,	Uncertain – only indirect measurements available

<sup>1</sup> http://www.rydlyme.co.nz/files/5714/0114/5552/RYDLYME\_Marine\_MSDS.pdf

Although required treatment concentrations are high, available studies demonstrate that Rydlyme<sup>®</sup> can kill a range of biofouling taxa, including bivalves, in relatively short timeframes. This product, which is widely available and safe for operators, has been used successfully in a number of field applications to remove all secondary biofouling from contaminated pipework of commercial vessels but it should be noted that the monetary costs associated with such large volumes of concentrated treatment solution have been considered prohibitive in that scenario (Lewis and Dimas, 2007). Rydlyme<sup>®</sup> is marketed as being 'nontoxic' but some reports question the validity of this claim, especially given the range of other proprietary ingredients for which environmental impacts cannot be accurately assessed (Growcott *et al.*, 2016). The uncertainty around environmental effects requires careful consideration, and likely further testing, if Rydlyme<sup>®</sup> were to be progressed as a pipework treatment agent.

## 4.1.14 Quaternary ammonium compounds

The active ingredient in some disinfectants (e.g., Conquest<sup>®</sup> and Quatsan<sup>®</sup> contain benzalkonium chloride), QACs are used to treat biofouling in the pipework of yachts arriving in the Northern Territory (Murray Barton, pers. comm.) and Australian naval vessels (Richard

Piola, pers. comm.). The exact mode of action of QACs is not well understood but it is thought that they target lipid bilayer membranes (Gilbert and Moore, 2005). As such, QACs are relatively non-specific in their activity.

Table 14. Overview for using quaternary ammonium compounds to treat marine biofouling inside the pipework systems of recreational vessels.

Criteria	Evidence	References	Decision
Effectiveness	1% Quatsan <sup>®</sup> for 7 h kills 100% of black-	Bax et al., (2002)	
	stripped mussels, Mytilopsis sallei.		_
	5% and 10% Quatsan <sup>®</sup> for 12 h kills 10 and	Neil and Stafford,	Uncertain —
	20% of the oyster Saccostrea glomerata,	(2005)	conflicting
	respectively.		reports suggests
	1, 5, or 10% Conquest <sup>®</sup> for 14 h kills 100%	Lewis and Dimas,	may not kill all
	of the blue mussel Mytilus galloprovincialis.	(2007)	bivalves inside
	5% Quatsan <sup>®</sup> for 24 h recommended for	Piola and	48 h
	Australian Navy based on test using M.	Grandison, (2013)	
	galloprovincialis but is not 100% effective.		
Safety	Benzalkonium chloride:	HSNO CCID	
·	6.1C (oral) – Acutely toxic		
	6.1D (dermal) – Acutely toxic		
	6.5A – Respiratory sensitiser		
	6.5B – Contact sensitiser		
	6.9B (dermal) – Harmful to human target		
	organs or systems		
	8.2C – Corrosive to skin		
	8.3A – Corrosive to eyes		
	9.1A – Very ecotoxic aquatic (fish,		
	crustacean, algal)		
	9.3B – Ecotoxic vertebrates		Fail – could
	Benzalkonium chloride is classified as	MSDS <sup>1</sup>	harm the
	'moderately toxic' but Quatsan <sup>®</sup> and	Jenner et al.,	environment
	Conquest <sup>®</sup> are safe for operators if handled	(1998)	
	appropriately.		
	Persists in the environment and may	Knezovich et al.,	-
	bioaccumulate.	(1989); Garcia <i>et</i>	
		<i>al.</i> , (2001)	
	Binds to organic matter and can be removed	Jenner <i>et al.</i> ,	-
	from water using clay.	(1998)	
	Commercial formulations such as Conquest <sup>®</sup>	(1))0)	-
	and Quatsan <sup>®</sup> contain other ingredients		
	(surfactants, salts, etc.) that have unknown		
	effects on the environment.		
Biosecurity	No specific biosecurity risks have been	Inglis <i>et al.</i> ,	<b>Pass</b> – risks
<u>-</u>	described but many marine organisms	(2012)	counteracted by
	broadcast spawn when exposed to stressful		isolation from
	conditions and mobile species may avoid		environment
	chemical treatments.		during
			treatment
Consenting	No precedent for use in New Zealand's		<b>Fail</b> – no
- mound	marine environment.		precedent
Compatibility	Not known to react with metals or plastics.		Pass –
~ oneputionity	mont to react that metals of plastics.		compatible with
			-
			pipework

ences Decision	References	iteria Evidence	Criteria
); a <i>et al.</i> ,	Knezovich <i>et e</i> (1989); Garcia <i>et al.</i> , (2001)	asibility Stable in seawater.	Feasibility
lison <i>et al.</i> , cost is high	Grandison <i>et a</i> (2011)	Price of the base material is high compared to other treatment options and high doses are required.	
•	Murray Barton pers. comm.	Costs approx. \$800 to treat the internal pipework of a recreational vessel using Conquest <sup>®</sup> .	
Uncertain – only indirect measures are available		ality A practical method for direct field	Quality control
		6	<sup>1</sup> <u>http://www.sf</u>

https://www.gfs.com/sites/gfs.com/files/739660.pdf?vanity=www.gfs.com/files/msds/739660.pdf

Although QACs are currently used in the Australian Northern Territory to treat the pipework of arriving international recreational vessels, recent evidence raises questions regarding the efficacy of the treatment being applied. It is uncertain whether 3%, or even 5%, Conquest<sup>®</sup> is sufficient to kill resilient taxa such as bivalves. It has been suggested that QACs are particularly well suited for treating bivalves because they are not readily detected by the organisms (i.e., treatment does not trigger the immediate valve closure observed with chlorine treatment). Quatsan<sup>®</sup> tends to be more successful in this regard, presumably because Conquest<sup>®</sup> contains another ingredient that irritates bivalves (Richard Piola pers. comm.). Regardless, there are environmental concerns that would likely preclude the use of QACs in New Zealand. If relatively large quantities of QAC are required for effective treatment of pipework systems, disposal options may be a significant issue as the concentration in the effluent may be above environmentally acceptable levels for discharge (Neil and Stafford, 2005).

## 4.1.15 Summary

The chemical treatment agents evaluated for use with internal pipework share some common features: they are all non-specific toxins that pose few specific biosecurity risks and most are compatible with pipework materials at working concentrations. While spectrum of activity has not been fully determined for most of the candidate chemical treatment agents, acetic acid and some of the descalers appear most likely to be effective against a range of common biofouling taxa within 48 h. Chlorine is also effective against some biofouling taxa within 48 h but there is insufficient information available with respect to its efficacy, particularly regarding bivalves. Although information pertaining to the efficacy of bromine against biofouling organisms is limited, it is widely noted that bromine is a more potent alternative to chlorine. Both chlorine and bromine can be effectively neutralised after treatment to allow for easier onsite disposal. Of the descaler formulations examined, Rydlyme<sup>®</sup> should be considered the most generally suitable for application to the pipework of recreational vessels because it is safe to handle and has been shown to be effective against a range of biofouling organisms. However, there is uncertainty around the environmental impacts of Rydlyme<sup>®</sup>. A key advantage of descalers over other chemical treatment approaches is that calcium carbonate deposits are removed though acidic digestion, making verification of treatment success relatively straightforward and reducing the likelihood of unforeseen pipework blockages.

Consenting is a major consideration for chemical treatments due to the associated potential to contaminate the environment, with only chlorine and acetic acid having precedent for discharge to the New Zealand marine environment. Although acetic acid appears to be more generally effective against biofouling, chlorine is the most developed chemical from a consenting perspective and has recently been granted EPA approval for marine biosecurity purposes. The descaler Rydlyme<sup>®</sup> has no precedent for consented discharge in the New Zealand marine environment and the uncertainty around the environmental effects of this formulation would likely hamper any consenting process.

## 4.2 NON-CHEMICAL TREATMENT AGENTS

Non-chemical treatments include: physical removal using brushes, cutting heads, water jets or remote operated vehicles (Morrisey and Woods, 2015); thermal stress; osmotic shock; and deoxygenation. Physical removal systems have primarily been designed to remove biofouling from planar external hull areas and some niche areas (Inglis *et al.*, 2012) but their suitability for pipework systems is questionable. By contrast, manipulating physico-chemical parameters (temperature, salinity, and oxygenation) has potential for pipework application(s) as pipework systems are confined environments with small total volumes.

### 4.2.1 Physical removal

Physical removal involves scraping, pulling, brushing, sucking, or blasting away adhered biofouling (Morrisey and Woods, 2015). These techniques have yet to be adapted for treating internal pipework systems but it is conceivable that such systems could be developed in the future (i.e., conceivably articulated brush or water-jet systems could clean pipework).

Criteria	Evidence	References	Decision
Effectiveness	Effectively removes biofouling from flat or slightly curved surfaces but currently available technologies are unlikely to be applicable for complex pipework systems.	Inglis <i>et al.</i> (2012)	<b>Fail</b> – not applicable to intricate systems
Safety	Some equipment, such as rotary brushes or water blasting equipment, may pose operator or diver safety risks but these risks can be managed via operator protocols.		<b>Pass</b> – safe for operators and the environment
Biosecurity	Biofouling is often viable after removal and there is a risk of release into the surrounding environment. Removing biofouling in-water can preclude effective isolation from environment.	Hopkins <i>et al.</i> (2010)	<b>Uncertain</b> – elevated risk of releasing viable organisms
Consenting	In-water mechanical cleaning is implemented in New Zealand with controls to prevent or minimise discharge of viable biofouling.	Grant Hopkins, pers. comm.	Pass – already implemented in New Zealand
Compatibility	Can harm some coatings, such as antifouling paints, but unlikely to harm pipework providing the removal methods are appropriate (i.e., cutting blades and extreme water pressure could harm pipework).		Pass – compatible with pipework
Feasibility	Currently available methods could be applied at inlets or outlets but it is not feasible to physically remove biofouling further into pipework systems.		Fail – not able to be applied inside of pipework

## Table 15. Overview for using physical removal to treat marine biofouling inside the pipework systems of recreational vessels.

Criteria	Evidence	References	Decision
Quality	Difficult to monitor efficacy of treatment,		Fail - low
control	especially for microscopic life stages.		ability to ensure
			efficacy of
			treatment

There are no physical removal systems currently available capable of gaining sufficient access to internal pipework of recreational vessels. At best, implementing physical removal methods would require an isolating device, such as the 'magic box' system described by Lewis (2013) to isolate and treat sea chests. The efficacy of such treatments may require further evaluation if new technologies are developed (Morrisey *et al.*, 2015) but physical removal is not currently a viable treatment option for internal pipework of recreational vessels.

### 4.2.2 Thermal stress

Heating seawater to above the thermal tolerance of biofouling organisms is a commonly used strategy in industrial cooling plants (Jenner *et al.*, 1998). This approach is beginning to be explored as a reactive treatment for fouled vessels and seems particularly well-suited to the confined spaces typical of niche areas. Although some literature reports relate to chronic exposure to elevated temperatures, consideration has been given to acute exposure scenarios given the stipulated treatment time.

Criteria	Evidence	References	Decision
Effectiveness	With the exception of two hardy taxa (the Pacific oyster <i>Magallana</i> (formerly <i>Crassostrea</i> ) <sup>11</sup> gigas and the barnacle <i>Austrominius</i> (formerly <i>Elminius</i> ) <i>modestus</i> ) <sup>12</sup> , intact biofouling assemblages in a model sea chest were killed in 60, 30, and 20 min at 37.5, 40, and 42.5°C, respectively.	Piola and Hopkins, (2012)	
	The oyster <i>M. gigas</i> is considered highly tolerant to thermal stress because it is capable of isolating itself from the external environment by closing its valves; 100% mortality was achieved at $57.5^{\circ}$ C for 60 min or 60°C for 30 min.	Piola and Hopkins, (2012)	<b>Pass</b> – effective against a range of biofouling organisms
	In a model sea chest, exposure to 60°C for 109 min was effective against the mussels <i>Mytilus edulis</i> and <i>Trichomya hirsuta</i> .	Leach, (2011)	in short timeframes
	Raising temperature to 42°C for 2 h is considered effective against most bivalves in industrial cooling water systems.	Rajagopal and Van der Velde, (2012)	-
	Response to heat can be variable: tolerance is typically lower in winter than in summer; larger individuals are more tolerant than smaller individuals.	McMahon and Ussary, (1995); Rajagopal <i>et al.</i> , (2012)	-
Safety	Potential for burns should be considered	× /	<b>Pass</b> – safe for

Table 16. Overview for using thermal stress to treat marine biofouling inside the pipework systems of recreational vessels.

<sup>&</sup>lt;sup>11</sup> http://www.marinespecies.org/aphia.php?p=taxdetails&id=836033

<sup>&</sup>lt;sup>12</sup> <u>http://www.marinespecies.org/aphia.php?p=taxdetails&id=106209</u>

Criteria	Evidence	References	Decision
	by operators. Poses negligible risk to the environment provided waters are cooled before discharge, adequately mixed post discharge, or are of suitably low volumes.		operators and the environment
Biosecurity	Can cause a reproductive response (i.e., propagule release) in marine organisms, such as <i>Styela clava</i> , necessitating isolation of treatments from the environment.	Wong <i>et al.</i> , (2011)	Pass – reproductive response mitigated by isolation from environment
Consenting	Many industries discharge heated water into the New Zealand marine environment. Requirements relating to total volume of discharged water and relative temperature of the discharged water vary between local bodies.		<b>Pass</b> – common discharge in New Zealand
Compatibility	Antifouling paints are likely to be the most susceptible component of a vessel to heat; ablative antifouling paints can withstand 60°C and foul-release paints can withstand 80°C for extended periods. Plastic fittings and pipe should be at least as resistant to heat.	David Baker, pers. comm., International Paints	<b>Pass</b> – compatible with pipework and vessel components at < 60°C
Feasibility	It can be difficult to ensure uniform heat distribution within system, potentially leading to variable mortality along the length of the pipework. Would require specialised infrastructure to heat and apply water at safe temperatures – recirculating heated water or inserting flexible heating elements with integrated thermostats are potential approaches.	Grant Hopkins pers. comm., Cawthron Institute	Pass – infrastructure needs to be developed but this consideration is common to all treatment approaches
Quality control	Field measurements of treatment systems are practicable using commercially available thermistors (direct measurement of water inside pipework) or infrared thermometers (indirect measurement of external pipe surfaces).		<b>Pass</b> – field thermal measurements are practical

Thermal stress is effective against a range of marine biofouling organisms within short timeframes (minutes to hours), including those organisms considered to be highly resilient (i.e., oysters and other intertidal shelled organisms). Gaining consent for this treatment agent should be comparatively straightforward, with most, if not all, regional bodies in New Zealand having some existing precedent for discharge of heated water. Heated water potentially poses some risks to operators and the environment but these risks are easily mitigated. Common-sense handling procedures and PPE will minimise the likelihood of burns to operators. Cooling water before discharge or ensuring adequate mixing in the receiving environment will prevent harm to non-target organisms. The potential for propagule release with the onset of thermal treatments can be easily counteracted by isolating pipework systems from the environment during treatment (a requirement for all potential treatment agents).

The engineering requirements for delivering thermal stress to pipework systems warrant further discussion because treatment systems capable of accurately controlling thermal limits within pipework would need to be developed. Two potential approaches are apparent; namely active recirculation of heated water or passive heating using insertable heating elements. Systems capable of heating and recirculating seawater are not readily available but continuous hot-water heaters designed for domestic use (e.g., continuous-flow gas califonts) are available for reasonably modest sums (~\$NZ 1200), and could form the basis for portable dock-side heat treatment systems. It may be preferable to use freshwater in such systems, which would also expose biofouling to osmotic shock (Section 4.2.4). Alternatively, flexible heating elements, such as those used to heat drain pipes in refrigeration units<sup>13</sup>, could be inserted at pipework inlets or outlets. An integrated bung device would be used to seal the system and integrated thermostats used to moderate target temperatures. The effectiveness of this passive approach is reliant on adequate diffusion of heat throughout a pipework system via convection and conduction, a consideration that would require testing in a controlled environment. A passive heat delivery system would be relatively cheap to construct (flexible elements cost < \$NZ 100) and compact in size (compared to a califont system), potentially allowing for several independent systems to be constructed that would allow multiple pipework systems on a vessel to be treated simultaneously. Due to the speed at which water cools (compared to the rate of breakdown of a chemical treatment agent), both treatment approaches would require continual monitoring of water temperature to ensure lethal conditions are maintained throughout the pipework system.

### 4.2.3 Deoxygenation

Reducing dissolved oxygen concentrations to below the tolerance of biofouling organisms forms the basis for a technique called encapsulation. Encapsulation has been applied to vessel hulls and other underwater structures, such as pilings and pontoons, and involves wrapping fouled surfaces with impermeable plastic. Oxygen in the isolated body of seawater is consumed by biofouling and microbial respiration, leading to anoxic conditions. However, the time to reach anoxic conditions can be protracted (Hopkins and Forrest, 2008) and many organisms can tolerate hypoxia (low O<sub>2</sub> concentration) for extended periods of time. Anoxic (zero O<sub>2</sub> concentration) conditions are likely required to ensure that all taxa are exposed to lethal conditions. Chemical deoxygenation using an excess of oxygen scavenging agent ensures that any dissolved oxygen which may enter the treatment system is rapidly consumed (e.g., sodium sulphite, sodium dithionite; Clearwater and Hickey, 2003).

Criteria	Evidence	References	Decision
Effectiveness	A minimum of 9 days encapsulation has been recommended to kill any type of biofouling with a patented vessel encapsulation device, the IMProtector <sup>™</sup> .	Floerl <i>et al.</i> , (2010b)	
	For fouled plates encapsulated with cling film and containing a range of taxa including bivalves, bryozoans, and ascidians, complete mortality was not achieved even after 14 days.	Atalah <i>et al.</i> , (2016)	<b>Fail</b> – required treatment times exceed 48 h
	Adding an oxygen scavenging chemical will speed up the development of anoxic conditions.	Inglis <i>et al</i> ,. (2012)	

Table 17. Overview of using deoxygenation to treat marine biofouling inside the pipework systems of
recreational vessels.

<sup>13</sup> http://www.flexelec.com/products/drain-line-heater-cables-flexdrain.html

Criteria	riteria Evidence		Decision		
Safety	Poses few operator or environmental risks.		<b>Pass</b> – safe for operators and the environment		
Biosecurity	Applying encapsulation systems to external surfaces (e.g., ship hulls) poses risk for dislodging viable biofouling and breaches in the containment system can result in viable organisms being released but this is unlikely to be the case with internal pipework (i.e., simpler and more robust containment options are apparent). Many marine organisms broadcast spawn	Inglis <i>et al.</i> , (2012); Morrisey, (2015); Morrisey and Woods, (2015)	<b>Pass</b> – risks counteracted by isolation from environment during treatment		
Consent	when exposed to stressful conditions. Would not require consent unless biofouling is to be discharged or an oxygen scavenging chemical is used.		Pass – unlikely to require consent		
Compatibility	Unlikely to harm pipework but the effect on antifouling formulations has been questioned.	Inglis <i>et al.</i> , (2012)	Pass – compatible with pipework		
Feasibility	Pipework could be encapsulated by applying bungs or blanking devices to inlets and outlets.		Pass – pipework can be encapsulated		
Quality control	Monitoring of dissolved oxygen (DO) concentrations in treatment system will require cabled DO probes and meters or DO loggers.		Pass – practical to monitor		

Although encapsulating pipework would be simple and poses few safety or consenting concerns, this treatment is unlikely to be effective within 48 h. Encapsulating pipework for periods longer than 48 h would disrupt vessel itineraries, and is thus deemed unsuitable for this purpose (Inglis *et al.*, 2012). It should also be considered that many pipework systems regularly experience low oxygen concentrations when not in use and may accommodate organisms tolerant of hypoxia.

## 4.2.4 Osmotic shock

Reduced salinity upsets the osmotic balance of marine organisms. Although partial reductions in salinity may be effective against organisms with tight osmotic tolerances, treatments typically aim to expose target organisms to 'freshwater' (i.e., < 5 PSU). Reaching freshwater conditions is particularly relevant given the estuarine nature of many ports or marinas and the association between NIS and regions of variable salinity (Dafforn *et al.*, 2012). This selective effect may result in disproportionate transport of euryhaline organisms in biofouling assemblages (i.e., species tolerant of a wide range of salinities).

Table 18. Overview for using osmotic shock to treat marine biofouling inside the	pipework systems of
recreational vessels.	

Criteria	Evidence	References	Decision	
Effectiveness	Exposing fouled panels to freshwater for 12 h reduced species richness and abundance but some taxa remained viable (taxonomy unknown).	Davidson <i>et al.,</i> (2009b)	Fail – required	
	A naval vessel exposed to freshwater in the Columbia River for 9 days still had viable biofouling present, including oysters ( <i>M. gigas</i> ), mussels ( <i>M. galloprovincialis</i> ),	Brock <i>et al.,</i> (1999)	<ul> <li>treatment times exceed 48 h</li> </ul>	

Criteria	Evidence	References	Decision	
	and barnacles (several spp.). Two fouled vessels that transited the Panama Canal had 9 out of 22 taxa viable after the 7 days in freshwater, including bryozoans and barnacles.	Davidson <i>et al.</i> , (2008)	-	
	No mortality of the mussel <i>M. galloprovincialis</i> after 6 or 14 h in freshwater.	Lewis and Dimas, (2007)	-	
	Some <i>Mytilus</i> spp. survived more than 4 days when exposed to freshwater at ambient temperatures.	Fox and Corcoran, (1958)	-	
	The seaweed <i>Undaria pinnatifida</i> is killed within 10 min of exposure to freshwater but gametophytes can survive up to 2 days.	Forrest and Blakemore, (2006)	-	
Safety	Poses no specific risks to operators or the environment.		<b>Pass</b> – safe for operators and the environment	
Biosecurity	Some organisms spawn when exposed to freshwater.	Inglis <i>et al.,</i> (2012)	Pass – risks mitigated by isolation from environment during treatment	
Consenting	Many industries discharge freshwater into the New Zealand marine environment. Requirements relating to total volume of discharged water vary between local bodies.		<b>Pass</b> – a common discharge in New Zealand	
Compatibility	Will not harm vessel pipework.		<b>Pass</b> – compatible with pipework	
Feasibility	Freshwater could be pumped into pipework systems or a floating dock could be used to house whole vessel (if $< 30$ m) – providing these were available at treatment location.	Morrisey <i>et al.,</i> (2016)	Pass –	
	Breaches in a containment system that allow seawater incursion or incomplete flushing of seawater from the pipework system would jeopardise successful treatment (i.e., even slight salinity increases can affect treatment efficacy).	Forrest and Blakemore, (2006)	<ul> <li>pipework could be encapsulated and filled with freshwater</li> </ul>	
Quality control	Salinity can be measured practically in the field using a salinity meter or a refractometer.		<b>Pass</b> – practical field measurement available	

Osmotic shock is only partially effective against biofouling, with bivalves being particularly resilient to this treatment. Some marine bivalves can survive weeks in freshwater, presumably due to their capacity to isolate themselves from the external environment. As with deoxygenation, osmotic shock is an environmentally benign treatment option but it is unlikely to be effective within acceptable timeframes.

## 4.2.5 Summary

Non-chemical treatment of vessel pipework has the potential to remove or render biofouling nonviable. However, some of these treatments are not currently able to be implemented in

pipework systems (physical removal) or are not likely to be effective over the stipulated maximum 48 h treatment timeframe (deoxygenation and osmotic shock). Thermal stress is the only non-chemical treatment that is practically applicable to pipework and capable of rendering resilient biofouling (e.g., bivalves) nonviable over short time frames (often less than 1 h). While available technologies for delivering heat to vessel pipework systems are limited, inline heating systems or flexible heating elements could be modified for these purposes. While there are technological and engineering challenges to be overcome, delivering heated water to pipework systems is a potentially highly effective method with low risk for harm to non-target species and good precedent for consented use.

## 5 Conclusions and recommendations

The operational suitability of a range of candidate chemical and non-chemical treatment agents for biofouling in internal pipework systems of recreational vessels has been evaluated (Table 19). In general, insufficient information was available in the literature to ascertain the efficacy of the candidate treatment agents against all relevant biofouling taxa. The exceptions were some descaler formulations and thermal stress, which have been demonstrated to kill a range of biofouling organisms within 48 h or less. Chlorine and acetic acid are known to be effective in some scenarios but further testing is required to fully establish their spectrum of activity. Rydlyme<sup>®</sup> was deemed the most generally suitable descaler evaluated because it is fast acting against biofouling and poses few risks to operators. However, there is conjecture around the environmental fate of Rydlyme<sup>®</sup>. Most of the other candidate treatment agents were deemed safe for operators and the environment provided appropriate personal protective equipment and controls are followed.

Given the complexities associated with gaining consent for discharge to the marine environment, only those treatment agents already used in the New Zealand marine environment were deemed to have satisfied this requirement. For the chemical treatment agents, only chlorine and acetic acid have previously been legally discharged to the New Zealand marine environment. Chlorine and acetic acid have been used to treat biofouling in incursion response scenarios, plus chlorine has recently been granted approval by the EPA and some regional councils for treating biofouling. Chlorine, bromine, and the acid-based biocides can be readily neutralised prior to any discharge. The non-chemical treatment agents posed fewer consenting considerations, with all having some precedent for consenting of associated discharges.

Granting that the potential for treatments to harm materials is dependent on concentration or intensity, the majority of candidate treatment agents were deemed to pose negligible risk to vessel components within the maximum exposure timeframe of 48 h. Exceptions were some descaler formulations, such as Descalex<sup>®</sup> and NALCO<sup>®</sup> 79125 Safe Acid, which react strongly with some metals used in pipework systems. The operational feasibility of the candidate treatment agents was generally favourable. Treatment agents deemed not feasible due to difficulties inherent to their application to pipework or high expense (compared to other candidate treatment) included chlorine dioxide, ferrate, and physical removal.

Although bromine and the descaler formulation Rydlyme<sup>®</sup> potentially warrant further investigation, the decision framework identified three candidate treatment agents that could be considered further for development for an operational pipework treatment protocol:

- chlorine;
- acetic acid; and
- thermal stress.

Each of these candidate treatment agents has specific advantages and disadvantages. The efficacy of chlorine against bivalves is not known at concentrations and exposure durations relevant to treatment of pipework biofouling. The recent EPA approval for chlorine's use for biosecurity purposes may clarify this data gap if chlorine is used widely in operational biosecurity responses. The efficacy of chlorine may possibly be enhanced at high doses or via the addition of a chlorine-resistant surfactant; however, the utility of this surfactant-biocide combination would need to be established in laboratory trials. Acetic acid has been demonstrated to be effective against a range of biofouling taxa, including bivalves, at relatively low concentrations and within 48 h. However, these assertions are based on a small number of studies and further exposure experiments are required to confirm the efficacy of

this treatment agent under a range of conditions. Acetic acid is less well developed than chlorine from a consenting perspective but has been used to treat biofouling in incursion scenarios in the past, such as the treatment used to kill *S. spallanzanii* detected on the vessel *Columbus* in Nelson Marina. Chlorine or acetic acid may be suitable for scenarios where pipework configurations are not amenable to recirculation of treatment solutions (e.g., passive delivery of a chlorine tablet to a closed pipework system). How a passively delivered chemical treatment would diffuse through a complex pipework system is unknown but the small total volume and relative ease of isolation from the environment apparent to internal pipework systems means that 'overkill' treatments could be applied. Chlorine or acetic acid could be dosed into pipework systems at many times the lethal dose for resilient biofouling organisms, potentially accounting for incomplete diffusion throughout the pipework system, chemical degradation over time, and the capacity of bivalves to seal out the external environment. However, the simplicity of this passive delivery approach is tempered by the potential for treatment 'dead spots' within pipework systems, which may necessitate active recirculation of chlorine or acetic acid.

While the efficacy of chlorine or acetic acid against marine biofouling have not been fully characterised, thermal stress has been demonstrated in several independent studies to be lethal to a diverse range of biofouling taxa. A major benefit of this treatment agent is the short treatment times required—treatment times of 2 h or less at temperatures around 50–60°C are able to kill even resilient taxa such as bivalves. Such short treatments would minimise the amount of time that vessels are decommissioned and would reduce the overall cost of a treatment protocol (i.e., less staff time). There is also significant existing precedent for discharge of heated water to the New Zealand marine environment. Due to the speed at which water cools (compared to the rate of breakdown of a chemical treatment agent) it will be necessary to continually monitor and adjust temperatures inside pipework. A califont system could be used to actively recirculate heated water through pipework, with temperatures monitored and adjusted at inlets and outlets. This approach would maximise heat distribution throughout a pipework system but would only be applicable to some pipework configurations. Discharge-only systems (e.g., blackwater discharge) and systems with barriers to water flow (e.g., positive displacement impeller pumps) will be difficult to treat in this way. An alternative approach is the use of flexible heating elements with integrated thermostats. These elements could be inserted into pipework inlets or outlets, and the inlets or outlets sealed using an integrated bung device. Inserting heating elements as far as possible into pipework systems will aid convective and conductive heating to raise the temperature in the entire pipework system to above lethal thresholds. The speed at which this process occurs is unknown, and testing will be required to define required heating times for different pipework configurations and to avoid the likelihood of treatment 'dead spots'. Not only is passive delivery using flexible heating elements likely to be applicable to a wide range of pipework configurations, it appears to present a simple and user-friendly approach requiring less expensive and more compact infrastructure (e.g., a compact heating cable vs a gas califont and pump system). Preliminary enquiries with manufacturers of flexible heating elements indicate that suitable equipment is readily available.

This review aimed to identify the 'best' treatment agent to rapidly develop an operational pipework treatment protocol. Based on existing evidence, thermal stress appears to be the most favourable candidate for developing an operational protocol. Thermal stress presents fewer unknowns than chlorine or acetic acid, having been demonstrated in several independent studies to be rapidly effective ( $\leq 2$  h) against even the most resilient biofouling taxa. Thermal stress is particularly well suited to internal pipework given the confined spaces and small total volumes that need to be treated. By comparison, chlorine and acetic acid require longer exposure times and, particularly in the case of chlorine, it is not currently clear

whether treatments would be fully effective within 48 h. The low ecological risk of thermal stress also negates many of the consenting hurdles that are common to chemical treatment agents. Equipment to accurately control water temperature within internal pipework will need to be developed using controlled laboratory experiments, ensuring lethal thresholds for relevant biofouling taxa are exceeded throughout pipework systems. The outcomes of these experiments will inform the drafting of an operational treatment protocol to be subsequently validated on actual vessels.

Table 19. Summary of the operational suitability of candidate treatment agents for treating biofouling in internal pipework of recreational vessels. V: Pass – requirement is satisfied; **\***: Fail – requirement is not satisfied; and ?: Uncertain – insufficient information available.

Treatment category	Treatment agent	Effective	Safe*	Biosecure	Consenting	Compatible*	Feasibile	Quality control
Chemical treatment agents	Chlorine	?	✓	✓	✓	✓	✓	✓
	Chlorine dioxide	?	?	$\checkmark$	×	$\checkmark$	×	3C
	Bromine	?	✓	$\checkmark$	×	$\checkmark$	✓	$\checkmark$
	Hydrogen peroxide	?	✓	~	×	$\checkmark$	✓	$\checkmark$
	Ferrate	?	✓	✓	×	$\checkmark$	æ	sc
	Peracetic acid	?	✓	×	×	$\checkmark$	<b>√</b>	$\checkmark$
	Acetic acid	?	$\checkmark$	~	✓	×	<b>√</b>	$\checkmark$
	Descaler formulation – Rydlyme <sup>®</sup>	$\checkmark$	?	$\checkmark$	×	✓	$\checkmark$	?
	Quaternary ammonium compounds	?	×	~	×	$\checkmark$	$\checkmark$	?
Non-chemical treatment agents	Physical removal	x	✓	?	✓	$\checkmark$	x	x
	Thermal stress	✓	✓	$\checkmark$	$\checkmark$	✓	$\checkmark$	✓
	Deoxygenation	×	✓	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	✓
	Osmotic shock	×	✓	$\checkmark$	$\checkmark$	✓	✓	✓

\*: at relevant working concentrations or intensities and exposure times.

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