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Algal toxin removal in seawater desalination processes

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ABSTRACT

Most marine algal species are beneficial, not harmful, as algae are the foundation of the food chain and provide the bulk of Earth's oxygen through photosynthesis. Mankind also commercially harvests algae for a myriad of uses in the food, pharmaceutical and medical industries to name but a few. However, the sudden prolific growth in algal cell numbers, referred to as harmful algal blooms (HAB), can constitute an operational and/or health risk to desalination plants, threatening water supply security and safety, respectively. The excessive biomass and organics associated with HAB can lead to the closure of desalination plants, particularly sea-water reverse osmosis (SWRO) plants due to overloading of the pretreatment facilities or potential irreversible RO membrane fouling. While these impacts are well documented, the removal of potent marine algal toxins, which represent a potential public health risk if not removed by desalination plant processes, is not well researched. The incidence of HAB has escalated throughout the world with algal specialists reporting that "compared to 30 years ago, we have more algal toxins, more toxic algal species and more areas affected". Therefore, this paper examines the major marine algal toxins that may be present at the intake of a desalination plant, their fate in thermal and SWRO desalination plant processes and the potential residual risk to public health in desalinated drinking water. Toxin removal in the various process steps is predicted based on the physico-chemical properties of these marine toxins. Results from bench and pilot studies investigating the efficacy of barriers in the desalination technology processes to remove cell-bound toxins and extracellular toxins from ruptured algal cells are also reviewed.

Keywords: Harmful algal blooms; Algal toxin removal; Thermal desalination; Reverse osmosis; Water safety plans

1. Introduction

Algae collectively refer to a diverse group of aquatic plants, generally containing chlorophyll, which can vary in size from microscopic single cells in the micrometre range to multi-cellular forms, such as giant kelp with fronds up to 65 m in length. Most algal species are beneficial to mankind, producing about 90% of Earth's oxygen while absorbing carbon dioxide from the Earth's atmosphere, acting as a carbon sink. Red marine algae have been a nutritional

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food source and an alternative medicine in Asia for centuries as algae are rich in minerals, proteins, fibre and sugars such as polysaccharides. Commercially, the total algae biomass market is estimated to be worth between €3.5 and 5 billion, of which health food remains the key sector, accounting for €1.5 billion [1]. Concentrating algae biomass in the harvesting process is an emerging market in membrane filtration systems. Algae are also being researched as biofuels and for carbon sequestration.

However, sudden prolific blooms of algae, commonly referred to as "red tide", are an increasing global issue with potentially dire economic and environmental consequences. In China's Yellow Sea, a bloom of the macro-algal seaweed *Enteromorpha prolifera* wreaked havoc, threatening the 2008 Qingdao Summer Olympic event, resulting in $30 million in clean-up costs and $100 million in damages to coastal fisheries. Nonetheless, this did not deter tourists from swimming the algae due to the health benefits associated with algae in the region (see Fig. 1(A)). In contrast, a bloom of the red-pigmented *Noctiluca scintillans*, closed 10 of Sydney's beaches, including the iconic Bondi beach, turning it a spectacular blood-red (shown in Fig. 1(B)) and imparting a fishy smell to the water due to ammonia being excreted from algal cells. *Noctiluca scintillans* also occurs annually in the Gulf of Oman, resulting in massive occasional fish kills due to toxic levels of ammonia where the ammonia may also be a skin irritant at sufficiently high concentrations [2].

"Red tides" is a misnomer as algal blooms are not associated with tides, nor only coloured red as shown by the "green tide" in Qingdao. Therefore, the term harmful algal blooms (HAB) is more accurate. HAB can be classed as toxic or non-toxic. Toxic HAB release potent toxins, causing illness or mortality in humans, fish, marine mammals and other marine life through either the direct exposure to the toxin or ingestion of bioaccumulated toxin in higher tropic levels, for example shellfish consumption. In contrast, non-toxic HAB may detrimentally impact tourism, aquaculture and marine ecosystems through depletion of dissolved oxygen and production of hydrogen sulphide during the oxidation of the high algal biomass by bacteria or reduction in light penetration to the seabed preventing photosynthesis leading to the death of marine organisms.

Algal blooms also have major detrimental impacts on desalination plant operation. Seaweed and other macro-algae can cause the blinding of intake screens of both thermal and seawater reverse osmosis (SWRO) desalination plants, while smaller microscopic unicellular algae (phytoplankton) in HAB may pass through screens causing massive problems downstream in the pretreatment and/or desalination processes. The increase in suspended solids can exceed the design limits of dual–media filters (DMF) in SWRO pretreatment systems. While the associated algal organics so important in the health industry, such as polysaccharides and proteins, are now known to be major constituents of sticky transparent exopolymer particles (TEP) which form microgels with a high hydraulic resistance and which are increasingly recognised to promote biofouling of reverse osmosis membranes [4,5].

The notorious HAB event in the Arabian Gulf and Gulf of Oman in 2008/2009 persisted for 8 months and affected 1,200 km of coastline. Cell counts of 11–21 million cells/L were recorded from surface waters during the bloom period near Fujairah and

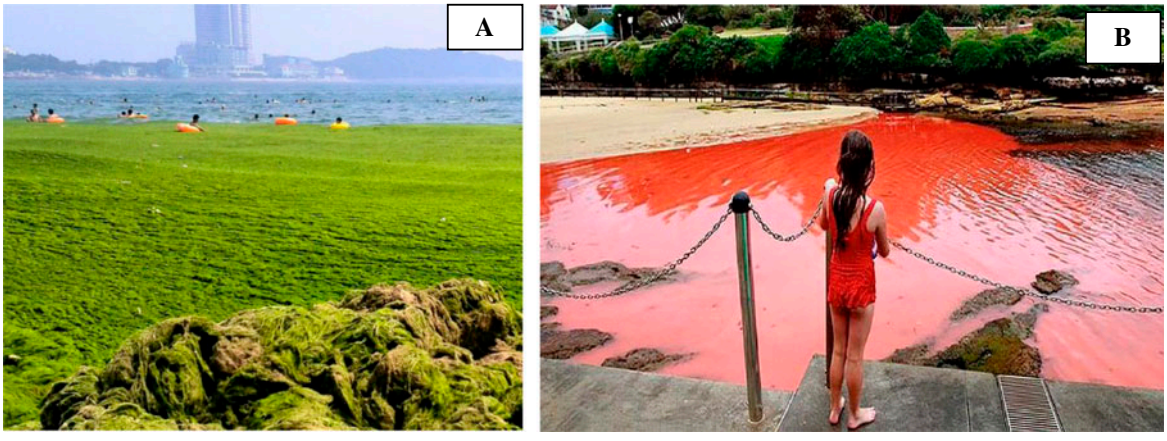

Fig. 1. Bloom of the nontoxic seaweed *Enteromorpha prolifera* in Qingdao in 2008 and *Noctiluca scintillans* in Sydney in November 2012 [3].

lead to the closure of several SWRO desalination plants and a reduction in capacity from some thermal plants [6,7]. Plant shutdowns were up to 32–55 d for some SWRO plants in the UAE as pretreatment processes struggled to remove the increased biomass and produce feedwater of the correct quality to meet RO membrane manufacturer's guarantees. The reduction in plant availability and reliability due to these unplanned plant outages threatened water supply security. While this algal bloom (*Cochlodinium polykrikoides*) did not release toxins, it raised awareness that there was a paucity of systematic studies demonstrating the removal of marine toxins by desalination plant processes. In the absence of such information, some plants may assume the algal species is toxic and adopt the precautionary and costly measure of shutting down a desalination plant to address community perceptions related to marine algal toxins, especially if the sea-water becomes malodorous, the algae is an irritant or fish deaths are evident. As algal blooms are increasing in severity and frequency throughout the world, they are more likely to occur at desalination plant intakes and it becomes more pressing to address the concerns of algal toxins as a water supply risk.

The World Health Organisation (WHO) [8] advocates a risk management approach to water quality where biological (e.g. toxins), physical and chemical hazards to water quality are identified, multiple barriers to hazards are developed and critical control points (CCP) determined to ensure the hazards are controlled to reduce the residual risk to a negligible level. The purpose of this paper is to examine the fate of marine algal toxins in thermal and SWRO desalination plant processes and the potential (residual) risk in desalinated drinking water. This paper reviews the four major classes of marine toxins that may be present at sea-water desalination intakes, their physical and chemical properties and how these properties may affect their removal. The global status of research into the efficacy of barriers in the desalination technology processes to remove intracellular toxins in intact algal cells and extracellular toxins from ruptured cells is examined. Finally, plant monitoring procedures to ensure the integrity of these processes used in Water Safety Plans for desalination plants are discussed.

2. Major marine HAB toxins

2.1. Symptoms, chemical and physical properties of marine HAB toxins

Marine algal toxins have a number of different routes of exposure and toxic effects on human health. These include the direct contact of toxins in water or aerosol on skin, throat and intestinal walls causing respiratory irritation and severe contact dermatitis. Other more potent toxins can have an impact upon specific organs if swallowed. The major route for human illness is through consumption of seafood where algal toxins may bioaccumulate. Even low densities of toxic algae may be sufficient to cause such illnesses or death in humans, while some species can selectively kill fish by inhibiting their respiration (ichtyotoxic toxins) [9].

This paper focuses on four of the most potent and well-characterised groups of marine toxins; saxitoxin, domoic acid, okadaic acid and brevetoxin which could appear at desalination plant intakes. The toxins have been classified based on the poisoning syndromes; the toxins illicit from studies of shellfish poisoning: paralytic (PSP), amnesic (ASP), diarrhoetic (DSP) and neurotoxic (NSP) shellfish poisoning [10]. Ciguatera fish poisoning, the most commonly reported marine toxin disease worldwide, is not discussed here as a biotransformation of the initial precursor toxin present in the dinoflagellate species *Gambierdiscus toxicus*, needs to take place to produce the more toxic ciguatera toxins. Hence, these toxins are not expected to be present in sea-water or algal cells.

Chemical structures for these four classes of HAB marine toxins are shown in Fig. 2, and the physical and chemical properties of these toxins are summarised in Table 1. Algal toxins are structurally and functionally diverse of varying charge, polarity and size with many being derived from unique synthetic pathways [10]. Most of the marine toxins that have high molecular weights are acid stable and non-volatile, for example brevetoxins are reported to survive heat up to 300˚C.

The toxins responsible for PSP are a suite of heterocyclic guanidines collectively called saxitoxins (STX), of which there are currently over 21 known congeners with varying molecular weights based on the parent STX molecule of which STX is the most toxic. STX that have relatively low molecular weights are nitrogen rich, polar with a positive charge at pH 7.7 and are very stable in biological and physiological solutions [11]. Due to their polarity, STX are largely excluded from traversing the blood–brain barrier. STX toxins are the most powerful marine toxins currently known and among the most dangerous poisons on Earth, except for some bacterial toxins such as botulinum. PSP symptoms include tingling and numbness of the extremities manifesting within 5–30 min from exposure [12]. In severe cases, more severe neurological symptoms such as ataxia, weakness, dizziness and complete paralysis may occur. Death may result from respiratory paralysis within 2–12 h without medical intervention [12]. Unlike oral intoxication with

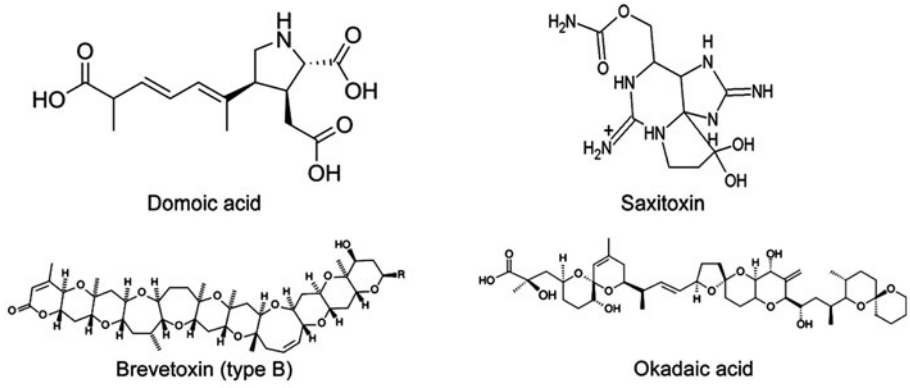

Fig. 2. Chemical structure of major classes of HAB toxins (adapted from [11]).

Table 1
Physico-chemical properties and acute toxicity doses of major marine toxins [13,16–19]

Toxin	Shellfish poisoning syndrome	Properties	Molecular weight (Da)	Boiling point (°C)	Vapour pressure mmHg at 25°C	LD_{50} (μg/kg)	Acute reference dose ARfD (60 kg adult)
Saxitoxin (STXs)	Paralytic (PSP)	Water soluble at pH < 7; stable	299	693	0	10	0.7 μg/kg (42 μg)
Brevetoxin	Neurotoxic	Liposoluble			NA	180	Insufficient data none established
Brevetoxin 2	(NSP)		895	Melting Point 265–270°C			
Brevetoxin 3			897	NA			
Brevetoxin 9			899				
Domoic acid	Amnesic (ASP)	Water soluble at pH < 7	311.3	321	0	3,600	100 μg/kg (6 mg)
Okadaic acid	Diarrhetic (DSP)	Slightly water soluble	805	921.6	0	200	0.33 μg/kg (19.8 μg)

saxitoxin, inhalational intoxication with saxitoxin can be lethal in a few minutes. Not surprisingly with a reported LD_{50} (median acute lethal dose of a toxic agent to kill 50% of a sample population after a specified test duration) of just 10 μg/kg [13], STX are listed as a chemical weapon in Schedule 1 of the Chemical Weapons Convention [14].

Domoic acid is an amino acid derivative belonging to the kainoid class of compounds containing three carboxyl groups and one secondary amino group with a reported negative charge at sea-water pH [15]. Like saxitoxin, domoic acid is polar and water soluble with a molecular weight of 311.3 Da. ASP symptoms include nausea, vomiting, abdominal cramps, diarrhoea, seizures, disorientation and permanent loss of short-term memory. Although, the specific toxicity of domoic acid is reported to be relatively low compared to saxitoxin, (LD_{50} of domoic acid is 360 times higher), domoic acid is reported to have been responsible for several deaths. Unlike saxitoxin, domoic acid can also cross the blood–brain barrier.

In contrast, okadaic acid responsible for DSP, has a molecular weight more than double saxitoxin and domoic acid. Okadaic acid is a monocarboxylic acid linear polyether molecule, the carboxyl group results in it being slightly water soluble with a slight negative charge [11]. Okadaic acid has been found in natural water in polar and non-polar esteric forms [11]. Typical DSP symptoms include vomiting and diarrhoea, varying in severity but are never fatal.

The toxin group responsible for NSP, brevetoxins, are a suite of ladder-like lipid soluble polycyclic ether, non-polar compounds with no charged groups and a molecular weight of approximately 900 Da, the highest molecular weight of the marine toxins considered here. Typical NSP symptoms include tingling,

dizziness, nausea, diarrhoea, respiratory irritation, vomiting, headache, reduced heart rate and pupil dilation, but are never fatal.

While there are no specific health guidelines in the WHO Guidelines or in the European Union Drinking Water Directive governing marine toxins in drinking water, the European Food Safety Authority has adopted acute reference dose (ARfD) of various toxins based on epidemiological data [16]. The ARfD is defined as an "estimate of the amount of a substance in food or drinking water normally expressed on a body weight basis that can be ingested in a period of 24 h or less without appreciable health risks to the consumer on the basis of all known facts at the time of the evaluation" [16]. The ARfD are included in Table 1 on a μg/kg basis and the mass of toxin to be consumed for a 60-kg person which corresponds to the body weight assumed by WHO in deriving guidelines for an adult [8]. The lower ARfD for okadaic acid than saxitoxin may be due to the fact that okadaic acid has been shown to be carcinogenic and a strong tumour promoter [20].

2.2. Causative organisms and geographical distribution

Most marine algal species are harmless, of the more than 4,000 marine phytoplankton species, only 90 or <3% are believed to be toxic to aquatic organisms and humans. Toxic algae can release toxins into the surrounding seawater, referred to as extracellular toxins, or retain them intercellularly within the algal cell. Generally, toxins remain within a cell unless damage, stress or cell death and lysis cause their release.

With the exception of domoic acid, produced by diatoms, almost all of the marine toxins are synthesised by a class of algae called dinoflagellates. Dinoflagellates are typically unicellular photosynthetic flagellate species, armoured with cellulosic thecal plates which can move through the water column or drift with currents. Interestingly, a large fraction of dinoflagellates are mixotrophic combining photosynthesis with ingestion of prey, and this feature may lead to the persistence of HAB in oceanic water where nutrients are low [21]. This coupled to their motility means dinoflagellates can act opportunistically to successfully exploit resources and conditions, allowing them to bloom or out compete other species potentially leading to their global expansion and the increasing severity of HAB.

Although diatoms are non-motile, drifting with currents and tides, they can adjust their buoyancy through adjustment of the ion composition in their vacuoles so that in favourable conditions, they are found mainly on or near the surface. To overcome limitations in nutrients, they adopt a "sink strategy" under the weight of their siliceous cell walls and remain dormant until conditions improve.

2.2.1. Saxitoxins STX

PSP is the most widespread shellfish poisoning syndrome with toxin events being recorded on the west coast of the United States (from California to Alaska), in the Mediterranean, Chile, South Africa, Europe, Asia and along the southern coastline of Australia. PSP producers have also been found in Kuwait Bay [22]. STX are biosynthesised by dinoflagellates such as the *Alexandrium* spp, *Gymnodinium* spp, *Pyrodinium* spp in marine ecosystems and are found in subarctic, temperate, and tropical locations. The size range of *Alexandrium* spp, is in the range of 15–48 μm, as shown in Fig. 3(A) for *Alexandrium Catenella*, an armoured dinoflagellate with two flagella, which typically clumps together in chains of 2–8 cells.

Toxic levels of saxitoxins can be attained at dinoflagellate abundances that do not significantly discolour the water because of the exceptional high potency of saxitoxin; for example, a maximum concentration of approximately 10^3 cells/mL was found in a toxic event in Chile of *Alexandrium Catenella* [23].

2.2.2. Okadaic acid

Diarrhoetic shellfish poisoning events are the second most reported after PSP with events recorded in Australia, New Zealand, Canada, Chile, Europe and the Mediterranean. Causative species are *Dinophysis* spp and *Prorocentrum*. *Dinophysis* spp range in size from 54 to 94 μm in length and 43 to 60 μm in diameter as shown in Fig. 3(B). They are found as solitary cells not connected to others like *Alexandrium Catenella*.

2.2.3. Brevetoxins

Brevetoxins are produced by dinoflagellate and raphidophyte algae, for example. *Chatonella* spp. The most commonly studied dinoflagellate that produces brevetoxins is *Karenia brevis* others are *K. mikimotoi*, *K. brevisulcata*, and *K. papilionacea* [24]. *K. brevis*, known as the "Florida Red Tide", has occurred almost annually in Florida since the 1940s and is considered endemic to the Gulf of Mexico. *K. brevis* are approximately 10 to 15 μm in size at the smallest dimension (refer Fig. 3(C)). The largest recorded NSP outbreak occurred in New Zealand in 1992–1993 with *K. mikimotoi* identified as the likely causative agent.

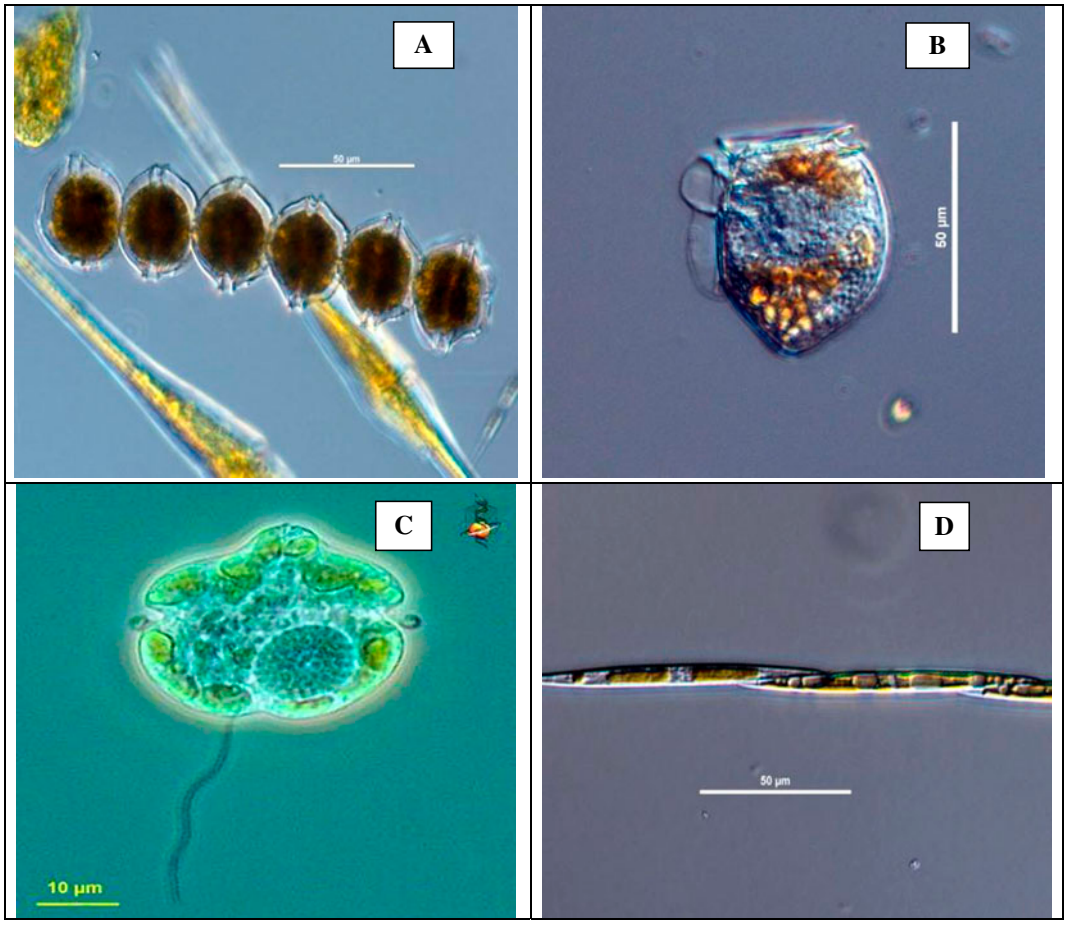

Fig. 3. Toxin producers *Alexandrium catenella* (A), *Dinophysis acuta* (B), *Karenia brevis* (C) and *Pseudo-nitzschia pungens/australis* (D) [26,27].

Unlike other dinoflagellate producing toxins, the *Karenia* spp is an unarmoured dinoflagellate and is therefore relatively fragile and easily lysed by wave and wind action, releasing brevetoxin extracellularly, directly into the water column causing significant fish kills, bird deaths and marine mammal mortalities. Alternatively, the hydrophobic toxin can accumulate inside bubbles in the ocean and as these bubble rise, they are injected into the wind in the surf zone and become aerosolised, [25] providing an additional route of exposure for these toxins. These aerosolised extracellular toxins can cause respiratory distress when inhaled and constitute a significant health risk to marine animals and humans as a result.

2.2.4. Domoic acid

ASP events have been recorded on the East Coast of USA, Chile, Australia's Coral Sea and South Pacific seaboards. Causative species synthesising domoic acid, and its isomers are confined to a dozen chain forming pennate diatom species within the genus *Pseudo-nitzschia* which are ubiquitous in sea-water. An example from this genus, *Pseudo-nitzschia pungens/australis*, shown in Fig. 3(D), has long-needle like algal cells (25–160 µm in length and 0.5–8 µm in width), which forms chains by overlapping the tips of their cells. This species is also of concern in California.

3. Assessment of marine algal toxins as a water quality hazard

The goal of desalination plants is to provide a sustainable water supply which provides safe drinking water, continuity of supply and is environmentally acceptable. The central tenant of drinking water treatment is to incorporate multiple barriers from the source water catchment to the tap to reduce the risks of pathogenic agents such as bacteria, viruses, protozoa, and other water quality hazards should any enter

a drinking water plant. Due to the toxicity of the aforementioned marine algal toxins, they are clearly identifiable as a biological hazard with a potential detrimental impact on human health. Water Safety Plans often incorporate the risk-based approach of the Hazard Analysis and Critical Control Point (HACCP) methodology, derived from the food industry, to assure safe drinking water. Hence, instead of addressing risk solely through end-product inspection, HACCP takes a systematic preventative approach that addresses (water quality) hazards through anticipation and prevention. Some water treatment plant operators elect to have their HACCP plans, independently audited and/or certified to ISO 22000 "Food Safety Management", which provides further confidence to consumers in the safety of the drinking water.

A typical assessment of the risk of marine algal toxins in desalinated water would consider their risk with and without treatment. The assessment would semi-quantitatively rate the likelihood of their occurrence based on categories, ranging from rare to almost certain, and their consequences, ranging from insignificant to almost certain. It remains difficult to predict the likelihood of marine toxins occurring at a desalination plant intake and their potential health impact for a HAB. Toxic algal species may be present at low background levels around a plant intake on the order of 100s or 1,000s cells/L or as resting cysts which can remain dormant for several years in ocean sediments as "seed beds". Alternatively, they may be brought to an intake via prevailing wind and currents or through ship ballast exchange in the area. During favourable conditions such as seasonally warmer water, low winds or as a result of nutrient enrichment due to ocean upwelling events, wind-driven iron-containing dust storms [28] or anthropogenic discharges, these algae suddenly "explode" to 10^3–10^9 cells/L depending on the species and seem to appear out of nowhere.

The risk of toxins in a HAB to be abstracted at a desalination plant intake often goes unrecognised as some toxic HAB never reach the densities to colour the water. In addition, toxic blooms are normally only short lived intermittent phenomena in a particular location, dispersing within days. Similarly, shellfish contaminated with toxins in the area will not normally show any visible signs and many marine algal toxins are tasteless and odourless to humans. When a bloom is detected by on line monitoring of various water quality parameters at the intake such as; chlorophyll-a specifically designed to detect algae, UV_{254} and dissolved organic carbon (DOC) for measuring organics or turbidity, Silt Density Index and Modified Fouling Index to assess particulate fouling [29], or through remote satellite sensing, these methods do not discriminate between toxic and non-toxic HAB. Therefore, illness or mortality of marine life may be the first indicator of a potentially toxic algal bloom in that area of an intake.

The potential risk to human health prior to desalination treatment could be assessed using the Acute Reference Dose if information is known on the concentration of marine toxins in sea-water (intracellular and extracellular) and the concentration of algal cells. Both are difficult to ascertain. Direct ingestion of contaminated sea-water is not normally harmful to humans as the concentrations of extracellular toxins are not high enough. However, only a few studies have examined the concentrations of extracellular toxins in sea-water [11]. Moreover, toxic HAB are complex as many different algal species (and associated bacteria) may be present in a bloom assemblage which produce different toxins and other compounds which can change over time in different hydrographic environments [30]. Furthermore, the specific conditions that induce toxin production and concentration in HAB are poorly understood. Factors which play a role in toxin production include the following: salinity, temperature, light, nutrient availability, physiological stress etc. If toxins are indeed produced, their concentrations can vary widely depending on the age of the cell and nutrient conditions. Some organisms produce maximum toxins during the log phase of growth, while others produce maximum concentrations after the cells have stopped growing [21]. While some literature suggest that resting cysts can contain up to ten times more toxins than motile stages [31].

Nevertheless, an example estimate can be made for the volume of (sea)water that would need to be consumed by a 60-kg adult in order to exceed the ARfD of 42 μg for saxitoxin using the following assumptions:

- only one toxic species is present in a bloom assemblage, for example *Alexandrium Catenella*;
- concentration of *Alexandrium Catenella* cells in a bloom is 10^6 cells/L (as noted in Section 2.2.1 for the Chile bloom);
- all the toxin is contained within the algal cells, that is no extracellular toxin and the intracellular toxin is subsequently completely released into the seawater during processing; and
- an intracellular toxin concentration range of 2.1–62.6 pg of saxitoxin per cell as reported in the study of Jester cited in Caron et al. [11].

Based on the above assumptions, between 670 mL to 20 L of water would need to be consumed in order

for a 60-kg adult to exceed the ARfD of 42 μg. Considering the daily drinking water volume assumed by WHO is 2 L for a 60-kg adult, the acute toxic threshold may be reached for the higher intracellular concentration of 62.6 pg prior to desalination treatment. At the lower intracellular concentration of 2.1 pg, a 60 kg adult would have to consume ten times the daily water intake volume assumed by WHO to exceed the ARfD. Obviously, the potential risk of toxins in drinking water for a child or bottle-fed infant would be much higher, for example, the volume of water to be consumed to exceed the ARfD for a 10-kg child based on the above assumptions would reduce to 112 mL to 3.33 L noting that WHO assumes a daily intake for a 10-g child is 1 L [8].

The above example illustrates the potential health risk of marine algal toxins in seawater in the case of a dense algal bloom of the most toxic species with a high toxin concentration and clearly shows the amplified risk of toxin poisoning through the ingestion of contaminated seafood where bioaccumulation of toxins occurs.

Consequences considered in addition to human health in the risk assessment, would typically include public perception, commercial, reputation, financial loss and legal. The net result in a water supply risk assessment, could classify such toxins as "moderate-to-high" risk for plant operation.

4. Removal of marine algal toxins in desalination plant processes

Following HACCP principles, the source water around the seawater intake is characterised, and each treatment step in the thermal and SWRO desalination processes are systematically examined to determine barriers to the water quality hazard, in this case, marine toxins (intracellular and extracellular).

Various control points are defined in HACCP and Water Safety Plans. Critical control points (CCP) are process steps at which control can be applied and are essential in preventing or eliminating the water quality health hazard or reducing it to an acceptable level [8]. Critical operational points (COP) are process steps which control hazards not related to human health but affect continuity of supply/quality when non-conformance could lead to a plant malfunction and possibly plant shut-down. Quality control points can also be defined and refer to a process step that while important is not critical to ensure water quality or quantity. Systems and procedures would then be implemented to minimise the risk of failure of these control points. CCP for marine toxins are identified for the two desalination technologies in the following sections.

4.1. Thermal and SWRO plant intakes

4.1.1. Sea-water abstraction, catchment protection and screening

There are a variety of sea-water intake arrangements for thermal and SWRO desalination plants; intakes can be shared with power generating stations (dual purpose plants) or be dedicated to the desalination plant process. The majority of intakes employed by large desalination plants are classed as open intakes abstracting water at the surface or at depth. Traditionally, thermal desalination plants and co-located plants are based on open surface water intakes, due to local bathymetry, while larger RO desalination plants employ intakes at depth with submarine pipelines which can extend a few hundred meters offshore to more than a kilometre.

In conventional water treatment plants, source water protection and catchment management is commonly the first step in assuring water safety. Moreover, ideally a risk is controlled as close as possible to the source of a hazard in this case marine algal toxin. However, this is more difficult for seawater desalination plants as abstraction is typically from large ocean areas, seawater flow rates can be considered especially for co-located thermal and power plants. In addition, the coastal areas are often multi-use, for example industrial cooling, recreation, marine etc. where different regulations may apply.

As previously discussed, the presence of toxins in HAB at plant intakes can be difficult to predict. Common methods to detect algal blooms at plants include chlorophyll-a measurement at the intake. Where particular HAB occur seasonally or under specific marine conditions, it may be possible to forecast them based on satellite tracking combined with water quality measurements at the intake (see Section 3) and meteorological analysers deployed at sea to provide advance warning that a bloom may develop or move to a plant intake area.

Limiting nutrients in coastal effluent discharges along with ballast water exchange regulations are important in preventing HAB, but marine algal blooms can travel large distances with currents. Moreover, algae are opportunistic, not always responding to limiting anthropogenic nutrient input. Dinoflagellates have evolved ecostrategies to bloom in nutrient-rich and nutrient-poor conditions. This extends another level of complexity and uncertainty into the monitoring and management of marine algal blooms at source. Hence, algal bloom management measures are often reactive with incident planning in place to address the potential presence of marine algal toxins. Incident planning should involve determining laboratories with the capability of analysing marine algal

toxins which would be on stand-by to facilitate timely results should a HAB occur.

Abstracting seawater at depth, for example (−8 to −20 m) below sea surface, is a strategy often put forward in the industry to prevent the intake of algal cells into desalination plants as algae are thought to typically float within 1 m of the surface. However, while most algae are non-motile, changing their position in the water mass passively through turbulence, tides and currents, dinoflagellates, the causative species for most toxic HAB, have the ability to move using their flagella. These algae often display diel vertical movement in the water column, whereby they migrate up to the surface during the day to access photosynthetically active radiation and swim towards more-nutrient-rich waters at the deep during night [32]. In addition, as cells age and die, they lose their buoyancy and contribute to the oceanic "snow" which falls slowly to the seabed. Therefore, algal cells and toxins may still be entrained into intake screens (commonly located 1.5–4 m off the seabed), albeit at very reduced numbers so as to prevent plant shutdown due to the impact of excessive biomass. The intake of marine algae and toxins was demonstrated at the El Segundo pilot plant where the intake was at −10 m depth [33]. Intra -and extracellular domoic acid was sporadically detected over 5 years of monitoring, and saxitoxin (extracellular) was also detected in the intake seawater in almost all samples collected over a two year period.

Open intake screening commonly comprises coarse bar screening (75–150 mm) to remove large debris and flotsam followed by mechanical fine screening (3–5 mm), for example travelling band screens, drum screens, to remove finer material and protect downstream processes. Alternatively, only wedge wire screen may be employed with apertures ranging between 0.5 and 10 mm. Dinoflagellate and diatom cells can easily pass through these screens such as the *Alexandrium* spp (the potent saxitoxin producers), which are 15–48 μm in size. Hence, screening will not serve as a barrier for algal cells and cell -bound intracellular toxins. Instead, shear forces during intake pumping and screening may break down algal cell walls, particularly the unarmoured *Karenia brevis* whose cell walls are fragile, releasing toxins and fouling TEP extracellularly into the sea-water. Brevetoxins produced by *Karenia brevis* may then become aerosolised around onshore screens and could pose a respiratory risk to plant personnel if not enclosed.

4.1.2. Prechlorination

Most thermal desalination plants practice continuous chlorination at the sea-water intake to provide a residual chlorine concentration of approximately 0.25 mg/L to prevent marine growth in piping and biofilm formation on heat exchange surfaces. In contrast, SWRO plants typically practice intermittent shock chlorination at the intake at higher doses. Intermittent chlorination regimes are site-specific and can be up to 5 mg/L for 60 min daily or weekly to give a chlorine residual <2 mg/L at the intake in some Australian plants. In contrast, SWRO plants in Saudi Arabia practice intermittent chlorination to give a much lower residual chlorine of 0.25 mg/L for 3 h every week.

Chlorination is known to almost completely oxidise some freshwater algal toxins, for example hepatoxins, at pH <8 with a chlorine residual of 0.5 mg/L and a minimum contact time of 30 min. Whereas for the more potent saxitoxins, the effect was minimal at a pH of 7.5 and oxidation only improved to >90% when raising the pH to >9 [34]. As alkaline chlorination will significantly reduce the disinfection efficiency of chlorination, it is not a standard practice in drinking water treatment.

Recent research conducted by Laycock et al. [35] examined the effect of chlorination on the four classes of marine algal toxins in high -salinity synthetic seawater (45 g/L) at 37˚C and for between 10 and 60 min duration. The pH of the sea-water was not provided by Laycock et al. In these experiments, brevetoxin (3 and 300 μg/L concentration) was unaffected by exposure to hypochlorite up to 30 ppm for one hour, whereas exposure to ≥4 ppm hypochlorite for 10 min at 37˚C completely destroyed saxitoxin, domoic acid and okadaic acid (concentration of each toxin was 1,250 μg/L). Domoic acid was the most sensitive, with degradation requiring only 1 ppm hypochlorite. No decomposition products were detected for the hypochlorite–saxitoxin reaction, so Laycock et al. suggested that saxitoxin was extensively degraded to low molecular weight compounds which are not likely to be toxic. Breakdown products were found for domoic and okadaic acids which were unlike the original toxins.

While these results are interesting, it is unlikely that continuous chlorination of intake sea-water can be applied at 4 ppm hypochlorite in either thermal or SWRO plants. In addition to increasing chemical consumption costs, the higher concentration of chlorine will have a deleterious effect on the venting system and plant corrosion in thermal desalination plants and the guarantee values of various equipments may be exceeded. Changing to continuous chlorination during a HAB is not recommended for SWRO plants as it increases the amount of assimilable organic carbon in water which leads to increased RO membrane

biofouling. Moreover, during chlorination algal cell walls may be broken down to release toxins extracellularly. Algal cell rupture will also lead to an increase in TEP which can then promote membrane fouling in downstream membrane filtration processes namely ultrafiltration and reverse osmosis systems.

Finally, the experiments from Laycock et al. [35] were conducted on extracellular toxins in synthetic sea-water; the background concentration of total and DOC in the commercial seawater product was not provided. During an algal bloom, the organic content of sea-water will rise significantly, TOC concentrations up to 700 ppm have been recorded in the Red Sea at plants in Saudi Arabia, which will consume chlorine, thereby reducing the efficiency of toxin degradation by chlorination, rendering it impractical. Associating with high chlorine and high organics in the feedwater is an increased risk of disinfection by-product formation, and the reaction of ammonia produced by algae such as *Noctiluca scintillans* with chlorine to form the suspected carcinogen, N-nitrosodimethlyamine (NDMA), which is poorly removed by RO membranes.

Therefore, screening and pre-chlorination are not barriers to remove algal cells/toxins or to detoxify toxins, respectively, at the intake. However, it is recommended that on-line intake monitoring is conducted for chlorophyll-a as Ladner et al. [36] suggests that an increase in fluorescence is a useful method to detect cell rupture, thereby potentially monitoring the potential increase in extracellular toxins. Similarly, the MFI-UF using 10 kda membranes has also shown promise for measuring algal TEP and could be measured at the intake for detecting the presence of algal blooms, associated organics and the effect of shear on algae [5,29].

4.2. MSF and MED thermal desalination plants

Thermal desalination methods account for 30% of the total desalinated capacity worldwide (80.9 Mm^3/d) and are the most commonly employed methods in the Middle East to desalinate sea-water for municipal use and for drinking water supply [37]. Salt is removed by causing the source water to go through a phase change where the water is evaporated, under normal atmospheric or reduced pressure conditions, leaving the salts behind in a brine stream.

The two key thermal processes for large-scale municipal water supply are multi-stage flash (MSF) and multi-effect distillation (MED). For the purposes of this paper, the key distinguishing feature between the two technologies is that MSF operates at higher temperatures than MED with top brine temperatures (TBT) around 90 to 112˚C, while the TBT in the first MED effect is between 60 and 64˚C. Flow schematics for the MSF configuration with brine recirculation and for the MED with thermocompression are shown in Figs. 4 and 5, respectively. Pressure in the first MSF stage corresponds to saturation temperature (1.351 bar), and the pressure in the last stage corresponds to almost full vacuum at 0.079 bar. For MED, the first effect pressure is around 0.261 bar, and the last effect pressure is 0.094 bar.

The total dissolved salts (TDS) concentration in the distillate produced by MSF and MED are similar, normally in the range of 20–30 mg/L. For Arabian Gulf sea-water this represents a salt removal from sea-water of greater than 99.8% for thermal desalination processes.

4.2.1. Pretreatment for thermal desalination plants

Thermal desalination systems are very forgiving of source water quality. Physical pretreatment of the source water is often limited to only intake screening to remove coarse debris in order to prevent equipment erosion by suspended solids and prevent equipment from blocking. MSF is very robust with the allowable particle size for sea-water entering the tubes varying between 5 and 15 mm [38]. On the other hand, MED needs finer filtration, with the allowable particle size for sea-water going through the spray nozzles <0.5 mm. As mentioned previously, intake screens used for thermal plants will not remove algal cells unless severely blocked by other material where some removal may be achieved.

Chemical conditioning is utilised in thermal desalination in two treatment streams: the sea-water cooling water component and the seawater make-up water (used within the desalination process). An oxidising agent (usually chlorine) or biocide is continuously added to the cooling water to prevent marine fouling, while antiscalants are continuously dosed to prevent scaling on the heat exchanger surfaces. In addition, antifoaming agents are continuously added to thermal process to prevent foaming in the deaerator and flash chambers. Neither the antifoaming chemicals (polypropylene/polyethylene oxide, isopropanol) nor the antiscalants (commonly polyacrylactes, polycarboxylic acids) are expected to assist in removal of algal cells or detoxification of extracellular toxins. Antiscalants are designed to modify crystal formation and disperse scaling ions and not oxidise organic matter. Antifoam agents may have an effect on organic compounds suppressing foams associated with algal blooms but are not expected to degrade the organic toxin itself.

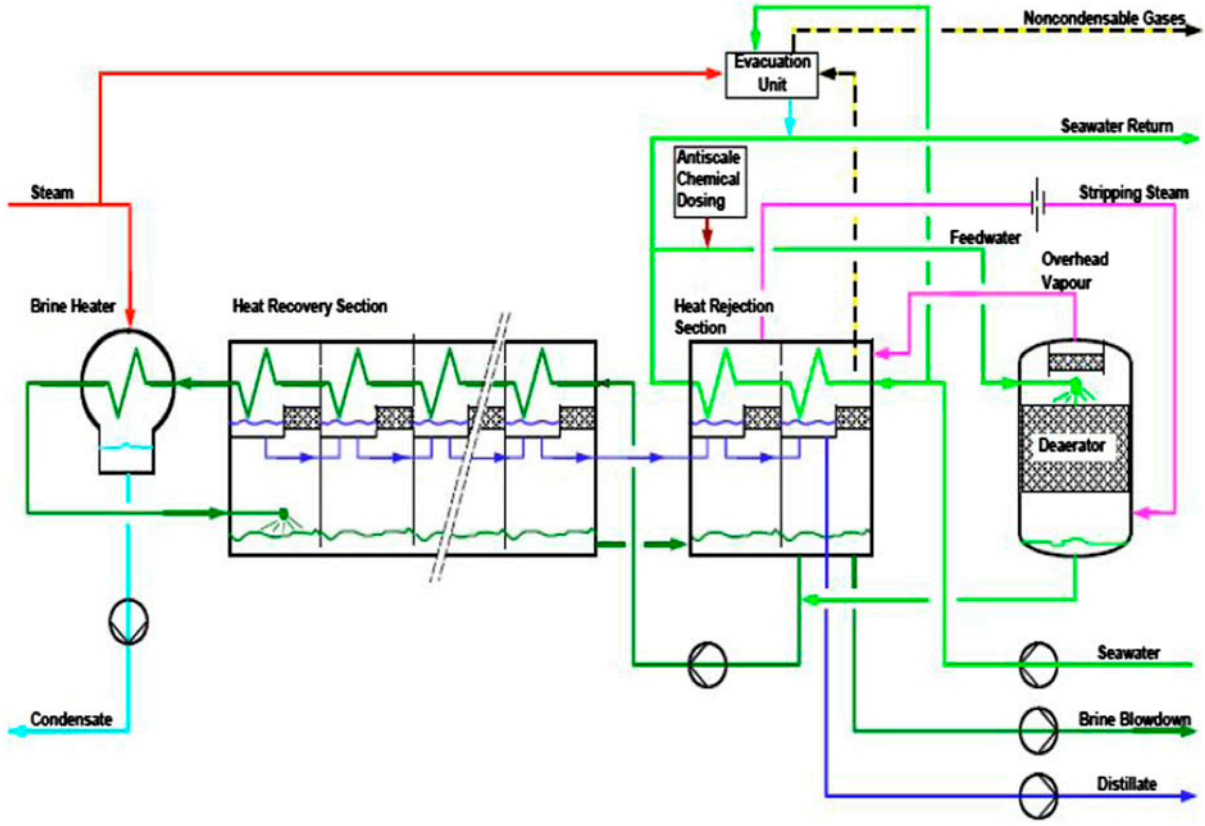

Fig. 4. Schematic of the MSF desalination process with brine recirculation.

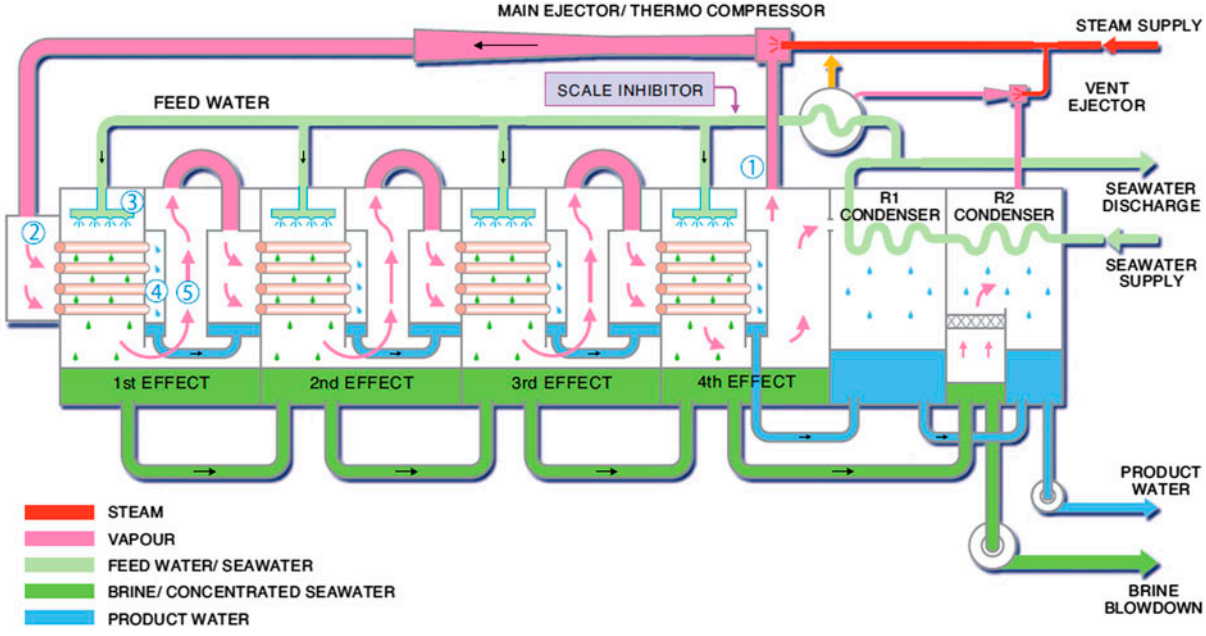

Fig. 5. Schematic of the MED–TC desalination process.

4.2.2. Thermal desalination step—critical control point 1

In thermal desalination systems, volatile organics with boiling points lower than water's may carry over in the steam and therefore are vented out in the process. It is often assumed that high molecular weight organics with high boiling points will remain in the brine which can sometimes be erroneous [39]. This is because the evaporation of organics from sea-water and their condensation into distillates are governed by a multitude of factors such as the temperature and pressure of the MSF stage or MED effect and the concentration, vapour pressure, latent heat of condensation of the individual compounds.

The four major toxins presented in Table 1 are all reported to be heat stable, have low vapour pressures and are non-volatile. The boiling points of saxitoxins, domoic acid and okadaic acid are significantly higher than water (at atmospheric pressure). Similarly, the melting point of brevetoxin is higher than water's. These factors would suggest that the toxins will not carry over in thermal desalination systems or co-distil but remain in the flashing brine. This may explain why cooking shellfish contaminated with toxins does not significantly reduce the toxicity of the shellfish, and in some cases, a part of the toxin may transfer from the shellfish flesh to the water during boiling without detoxifying or degrading it.

The removal of algal toxins by thermal desalination processes has not been well researched. The study by Laycock et al. [35], examined the removal of the four classes of marine toxins in the dissolved form i.e. extracellular, using a bench-scale micro distillation system. No other studies were found in the literature. Laycock et al. identified that of these four classes of toxins, the aerosolisation nature of brevetoxin may result in carry-over in a MSF plant. However, this is expected to be very unlikely in MSF (and MED) plants as the toxins are non-volatile and if present in droplets will be captured by the demisters. The maximum temperature in this study was 104˚C which is approaching the TBT of MSF but above MED. Three of the toxins, at unusually high test concentrations for the marine environment, saxitoxins (10,340 μg/L), domoic acid (17,150 μg/L) and okadaic acid (400 μg/L), produced from laboratory cultures of toxin-producing species with optimal nutrient conditions, were combined in one test solution for a synthetic sea-water solution salinity of 37 g/L. Algal cell walls may be broken down under the varying temperature and pressure conditions of MSF and MED (if not already broken down by shear forces of pumps at screen). Therefore, the majority of toxins are expected to be extracellular, justifying the approach of using dissolved toxins in these laboratory desalination studies.

Distillation results from Laycock et al. showed 99.5–99.9% removal of the three extracellular toxins to below the detection limit, demonstrating that thermal desalination, assuming no leaks in the system, is an effective treatment method for the removal of these toxins. The fate of these non-volatile toxins is then to be discharged with the brine which is combined with power plant cooling water for co-located plants or recirculated into thermal systems with brine recycling.

Removal of the fourth toxin, brevetoxin, was conducted in a separate series of tests with the removal of toxin in synthetic sea-water somewhat less than for the other toxins but was still high at 98.3% removal. Similar to the other toxins, the test concentration of brevetoxin (900 μg/L) is considered unusually high for the marine environment.

The research conducted by Laycock et al. [35] is promising. However, more research on toxin removal is recommended, whereby temperature and pressure conditions in MSF and MED plants are simulated in a laboratory study to provide a higher level of confidence in the results.

Based on the above, Water Safety Plans for MSF and MED desalination plants would define the thermal desalination step as the first critical control point to prevent algal toxins from contaminating drinking water.

4.2.3. Monitoring of thermal desalination CCP 1 during HAB

The main barrier for removal of algal toxins in thermal desalination plants is the thermal desalination step. The integrity of the thermal desalination process is therefore paramount with direct carry-over from the sea-water to the distillate limited to the greatest extent possible. Seawater and potential algal toxin carry-over in MSF and MED systems may occur due to possible joint leakage or tube failure, allowing bypassing of the separation process or the displacement of demister pads (used to separate the entrained brine liquid droplets entrained with the vapour and to allow the vapour to pass through the mesh). The integrity of the tubes and joints can be checked and confirmed by hydro-testing; however, failures are readily identified by rapid increases in distillate conductivity as the rejection of salts was demonstrated to be similar to marine toxins in the work of Laycock et al. [35].

Tube leaks in MSF plants generally lead to greater contamination of the distillate as the brine recycle is at higher pressure with brine ejected through the tube

leak at 2–3 bar into the distillate. Hence, the distillate conductivity increases.

In the case of MED, distillate conductivity (and potential algal toxin) from sea-water carry-over arises mainly from spray carry-over through demister displacement rather than joint leakage or tube failure within the main or vacuum system condensers. In MED systems, the integrity of tubes and joints is not considered an issue as the distilled water side of the process is at a higher pressure than the feed side. Hence, any loss of integrity at the heat transfer surface will lead to a generally smaller sea-water carry-over but should it occur it will be detectable by an increase in distillate conductivity.

From the above, monitoring of the MSF or MED critical control point will be through monitoring of distillate conductivity as a surrogate for salinity to monitor the integrity of a desalination unit. Should the conductivity increase above a threshold alert for a desalination unit, corrective action could be taken to regain process control, or if an alarm value is exceeded, the distillate could be rejected and isolated and the individual unit could be shut down while the cause for the loss of integrity is investigated. In the case of a HAB event, the alert and alarm levels could be reduced further to ensure an higher salt removal efficiency and corresponding removal of toxins. These alert and alarm can be input into the SCADA, so they are monitored in the control room.

4.3. Toxin removal in SWRO plants

4.3.1. Pretreatment for SWRO plants

Unlike thermal desalination plants, SWRO plants may require extensive pretreatment, depending on feedwater quality to prevent RO membrane fouling or scaling. As with conventional water treatment of blue-green cyanobacteria blooms, SWRO plants often adopt the strategy to remove intact algal cells, avoiding their rupture and release of intracellular toxins and algogenic organics, including intracellular TEP, which may foul downstream membranes. However, cells naturally lyse on death and may be damaged and rupture during the treatment process through hydrodynamic shear in valves, piping, screens and due to pressurisation of feedwater or through chlorination.

Pertinent sea-water pretreatment technologies for the removal of algal cells and toxins include dissolved air flotation (DAF), conventional granular media filtration and/or microfiltration (MF) or ultrafiltration (UF) or a combination thereof (refer Fig. 6). With the exception of DAF which is based on flotation, algal cells and toxins are principally removed by size exclusion. The size of particles removed is indicated in Fig. 6.

Historically, SWRO pretreatment comprised of ferric chloride/ferric sulphate coagulation followed by single-stage dual-media filtration (pressure or gravity). Two-stage filtration was employed for feedwater with a high concentration of organics, suspended solids and algae. Particles as small as 0.2–0.5 μm are removed in well-operated filters with optimised coagulation [40]. Consequently, algal cells from the causative species of the toxins considered here, for example *Karenia brevis* (10–15 μm at its smallest dimension) and *Alexandrium* spp (20–30 μm), are some 20 times larger and will be removed. Indeed, DMF are often the primary barrier in conventional water treatment for removal of smaller pathogenic protozoa such as *Giardia lamblia* Cysts (7–10 μm diameter) and *Cryptosporidium* oocysts (4–6 μm). To prevent the rupture of algal cell walls, gravity filters are used in preference to pressure filters as they operate at a lower pressure drop across the filter beds than the pressure required to rupture some algal cells [40]. Cells (and intracellular toxins) are removed during filter backwashing and typically returned back to sea with the brine from desalination plants in many countries. Alternatively, the cells may be separated with ferric hydroxide flocs during residual treatment and sent to landfill for disposal. During a toxic HAB event, it is recommended that both the solids and supernatant produced during residual treatment are analysed for marine toxins prior to disposal.

Intracellular toxins released during the process are not expected to be efficiently removed as DMF remove only 20–60% of soluble organics from feedwater depending on coagulation regimes, filter depth etc. [40]. Marine toxin removal was investigated for various pretreatment options in the Santa Cruz SWRO pilot study, whereby kainic acid, a marine acid derived from seaweed and commonly used as surrogate for domoic acid, was spiked into the feedwater as no toxins were discovered during feedwater monitoring [41]. Granular media filtration with coagulation and clarification resulted in only 24% removal of kainic acid which falls into the aforementioned range for removal of soluble organics.

The removal of soluble organics is expected to be higher in slow sand filtration where filtration rates are slow enough to allow the formation of a biofilm with bacteria in the biofilm biodegrading the toxins. Indeed, a higher removal of kainic acid (89–94%) was found in slow sand filtration in the Santa Cruz pilot study [41]. Although these results are positive, it should be noted that slow sand filtration is not typically applied in SWRO due to the high land area requirements.

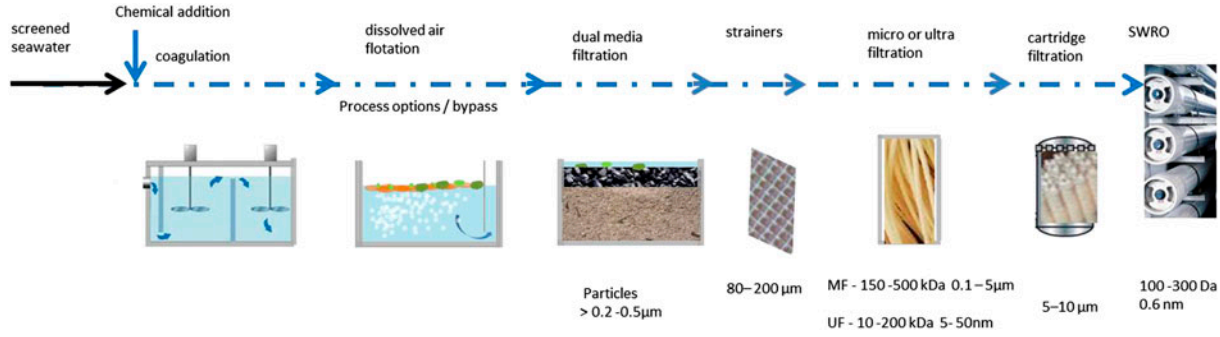

Fig. 6. Typical treatment process options for SWRO pretreatment.

In areas subject to frequent and severe algal blooms, the associated increase in biomass and organics has led to overloading of DMF, early filter break through, increased backwashing and failure to produce the required feedwater quality for RO membranes. In addition, biofouling of RO membranes was observed with bacterial species succession following an algal bloom feeding off algogenic matter. In the worst case, SWRO plants were shut down.

To ensure continuity of supply, other processes have been required upstream of DMF to reduce the algal load to filters. Sedimentation is not efficient in removing algae due to their buoyancy and the ability of dinoflagellates to swim. Hence, in areas prone to algal blooms, plants are increasingly incorporating DAF, specifically designed to remove floating matter such as oil and algal cells, downstream of/or combined with coagulation and DMF, such as the Tuas plant in Singapore (2005), Llobregat plant in Barcelona (2008) and Shuwaikeh plant in Kuwait (2011) amongst others.

In DAF, algal flocs attach to the fine bubbles generated in DAF, float to the surface where they accumulate and are skimmed off for disposal. Removal of algal cells by DAF can be very efficient, yielding up to 95–99% removal of algal cells as measured by cell counts [42]. The DAF may be bypassed in the absence of algal blooms. DAF conditions are gentle enough to reduce cell rupture and release of any potential marine toxins and therefore remove cell-bound intracellular toxins. As brevetoxin is hydrophobic and accumulates in bubbles, this toxin may be removed in this step.

In conventional SWRO pretreatment, cartridge filtration is normally employed upfront of RO membranes as a final protection measure. Cartridge filters have a pore size of 5 or 10 μm which is smaller than algal cells, and will therefore remove any algal cells, (and intracellular toxins for intact cells) not removed in the preceding filtration or flotation steps.

More recently, microfiltration or ultrafiltration membranes are being used in SWRO pretreatment as these processes can remove fine particles, suspended organics and colloids without coagulation. They do require additional microscreening of the feedwater through strainers with apertures ranging in size from 80 to 200 μm to prevent damage to downstream membrane fibres through which algal cells will generally pass unless blocked by other debris.

MF membranes pore sizes are on the order of 0.1 μm. While UF membranes have pore sizes that are a factor of 10 times lower than MF and are normally defined by their molecular weight cut-off which typically varies between 10,000 and 150,000 Da, depending on the manufacturer. Blocking of MF and UF pores or the formation of a dense cake layer of low porosity on the membrane surface will increase rejection of the membranes further. MF and UF yield 4-log removal of *Giardia* and *Cryptosporidium*. UF also removes waterborne viruses such as the poliovirus which has a large 2.6×10^6 da molecular weight but small particle size of 20–30 nm. Hence, MF and UF can act as barriers to intracellular toxins but would not significantly remove extracellular toxins, especially in the absence of coagulation. This was demonstrated in the Santa Cruz Study where only 9% removal of kainic acid was achieved using submerged UF membranes with a rated pore size of 0.04 μm [41].

As the pressures employed during MF and UF pretreatment may damage cells causing them to release toxins extracellularly, lower operational pressures may be applied during a HAB event to reduce this effect where feasible as a preventative measure. This is already advocated in membrane pretreatment plants to prevent the release of fouling TEP reaching the RO membranes.

Based on the above, DAF, DMF, UF and MF would not be considered as CCP as a reliable barrier to remove algal toxins; instead, they would be classified as quality control points where intracellular toxins in

intact algal cells could be removed. One or more of these steps may also be classified as COP for water supply security.

Monitoring of DAF, DMF, UF and MF typically comprises turbidity, SDI_{15}, pressure drop across the DMF/MF/UF. Of these parameters, continuous on—line turbidity of individual filters/membrane banks would most commonly be used as a surrogate to monitor algal cell removal as a critical operational point/quality control point. Should turbidity increase above a threshold alert or alarm value for a unit, the filtrate may be rejected and the individual unit could be cleaned or shut down. In addition, as noted earlier, chlorophyll-a and MFI-UF measurement may provide some indication of whether cells are rupturing, a higher concentration of TEP is present in feedwater and that toxins are more likely to be extracellular during a HAB event and is worthy of future research.

4.3.2. RO membranes

Feedwater to the SWRO system should be essentially free of algal cells but may contain any intracellular algal organic compounds (toxic or otherwise) which have been released upstream of the SWRO system when algal cell walls have been ruptured. SWRO membranes are effective in removing almost all contaminants in feedwater, rejecting 99.5% or more of the salts and providing effective removal of pathogens (bacteria, viruses, *Giardia* and *Cryptosporidium*).

Removal of organics such as marine toxins by SWRO membranes is classically believed to be due to differences in solubility and diffusivity between the membrane and molecules which is a function of molecular polarity, size and charge. Recent research suggests the pore size of SWRO membranes range from 0.6 to 0.7 nm, while the molecular weight cut-off of RO membranes is between 100 and 300 Da [43]. Generally, organics of molecular size of approximately 200 Da or larger are well removed, while low-molecular-weight polar compounds may not be fully rejected in some cases. Similarly, as RO membranes are often negatively charged, negatively charged compounds are well rejected through electrostatic repulsion.

Therefore, rejection of brevetoxin and okadaic acid is predicted to be high as their molecular weights (>800 Da) are four times the molecular weight cut-off of RO membranes despite brevetoxins being uncharged and okadaic acid bearing only a weak negative charge and slightly water soluble. This was confirmed by Laycock et al. with rejection >99.7% for these two toxins in RO laboratory bench-scale testing [35].

The more challenging marine toxins to be removed are the polar low molecular weight domoic acid (311 Da) and saxitoxin (299 Da). The latter has the highest toxicity being classified as a chemical weapon, bears a positive charge and has the lowest molecular weight. For these marine toxins, there are several other competing factors which may play a role in their rejection. For instance, the condition of the membrane surface may lead to an increase in rejection whereby some types of fouling such as chemisorption of organics on RO membranes will increase rejection. In addition, calcium is known to form bridges with organic compounds such as alginate by complexing the carboxyl groups on adjacent alginate molecules leading to higher observed fouling [44]. As domoic acid has a carboxyl group (as does the higher molecular weight toxin, okadaic acid), this may lead to a higher rejection of these toxins by RO membranes in organic-rich feedwater during an algal bloom. Other factors such as ionic strength and pH of a feedwater might lead to a reduction in rejection, whereby the increasing ionic and decreasing pH are both reported to cause linear organic molecules to coil into more compact sphero colloidal molecules [45,46]. Therefore, predicting rejection of the smaller toxins is more complex.

However, early research conducted by the U.S. Army Biochemical R&D Lab in 1993, demonstrated a removal greater than 98.9% by RO membranes for saxitoxin. Most likely, this research was conducted with lower rejection brackish water RO membranes than what are currently used in the SWRO desalination industry. Indeed, the bench-scale study of Laycock et al. [35] which used DOW FilmTec seawater membranes (SW30) gave a higher rejection of >99.4%, while the lowest rejection obtained in these set of experiments was for domoic acid at 99.0%. As noted previously, this study was conducted with purified toxins in synthetic sea-water with no other algal organics present.

Therefore, these results were compared to those obtained in pilot and bench-scale studies in Southern California where there are more than 20 SWRO desalination projects in the planning stage and where blooms of the genus *Alexandrium* spp and *Pseudo-nitzschia* producing saxitoxin and domoic acid (most prevalent), respectively, are known to occur. In the SWRO Santa Cruz pilot study [41], RO rejections of >99.8% were observed for kainic acid (231 Da) spiked at 40 μg/L, which has a lower molecular weight than domoic acid (311 Da). The higher rejection observed in the Santa Cruz study for kainic acid than that found by Laycock et al. for domoic acid may be attributable in part to the effect of organics in the natural seawater being used in the Santa Cruz experiments as

compared to synthetic sea-water in the experiments of Laycock et al. and/or differences in the test RO membranes. This would need to be confirmed in further experiments.

At the El Segundo SWRO pilot plant, the intake feedwater and desalinated water were monitored for the two molecule weight toxins, saxitoxin and domoic acid plus okadaic acid (intracellular only over two years) and brevetoxin (intra- and extracellular over 2 months) [33]. The latter two toxins were not detected in the pilot plant feedwater, while domoic acid and saxitoxin were observed as mentioned previously. Maximum intake intracellular concentrations of 4 μg/L and extracellular of 10.1 μg/L were recorded for domoic acid over the five years of monitoring (128 samples) particularly in spring and early summer. Monitoring of the more potent saxitoxin extracellular concentration was conducted for two years (25 samples) with a maximum concentration of 0.3 μg/L found. Complete removal of these two toxins was achieved by the pilot SWRO system to below the intracellular (0.007 μg/L) and extracellular (0.2 μg/L) upper test detection limits for domoic acid and extracellular saxitoxin detection limit of 0.02 μg/L. Pilot plant monitoring was coupled to bench testing using a Hydranautics SWC4 + RO membrane in a series of experiments testing toxin removal in high-salinity sea-water (mixture of seawater and brine) spiked with domoic acid (50 μg/L), saxitoxin (2 μg/L) and brevetoxin (20 μg/L) at extracellular (dissolved) concentrations significantly higher than expected in natural blooms events. None of the three toxins were found above detections limits in the RO permeate.

The above studies demonstrate that should any cell-bound algal toxins remain in the source water to a SWRO plant or be released extracellularly during pretreatment, they will be almost completely removed by the RO membranes. Hence, the RO step is the first critical control point in SWRO plants for removal of extracellular algal toxins. If a SWRO desalination plant operates a second-pass brackish water desalination to further desalinate the water, then this would be classed as the second critical control point.c

4.3.3. Monitoring the SWRO desalination process during HAB

Based on the above, various pretreatment steps can act as a barrier to remove algal cells and intercellular toxins for intact algal cells as summarised in Fig. 7. These processes would then be defined as COP and/or quality control points which would typically be monitored continuously by on-line turbidity meters which would most likely form part of the Water Safety Plan.

However, as with thermal desalination systems the critical control point which acts as a barrier to the dissolved or extracellular algal toxins is the SWRO desalination step. The integrity of the SWRO membranes is therefore integral to the entire desalination process. Consequently, membrane integrity would be continuously monitored in SWRO plants by conductivity as part of the desalination plant Water Safety Plan to detect any leakage due to membrane failure, defective interconnections, O-rings, etc. The RO trains will be defined as a critical control point in the water safety plan and should the permeate conductivity increase above a threshold alert for an RO train corrective action could be taken to regain process control, or if an alarm value is exceeded, the permeate could be rejected and isolated and the RO train could be shut down while the cause for the loss of integrity is investigated. In the case of a HAB event, the alert and alarm levels could be reduced further to ensure a high salt removal efficiency and corresponding removal of toxins.

Finally, for plants without DAF pretreatment, the plant may shut down for process reasons in the event of an algal bloom with an extremely high algal abundance resulting in a high suspended solids load and organics above the capacity of the pre-treatment system or with toxic species present. Such blooms can take days to manifest, whereas plant shut down can occur within hours and the sea-water intake within minutes. It is important to note that as excessive algal blooms and associated organics may result in biofouling or organic fouling of the high rejection SWRO membranes, it may be more desirable to shut down the RO system to avoid fouling.

4.4. Final chlorination for disinfection in thermal and SWRO plants

Following remineralisation of the distillate/permeate, the water may be chlorinated for distribution to the consumer so that there is a chlorine residual at the customer tap. As noted in Section 4.1.2, the study of Laycock et al. [35] showed chlorination (in sea-water) was ineffective in detoxifying brevetoxin. Above 1 ppm chlorination was effective in detoxifying domoic acid, while saxitoxin and okadaic acid required 4 ppm or more. However, chlorine is not normally dosed in drinking water at 4 ppm due to the objectionable taste. If required, this process might provide a final barrier (critical control point 2) for some of the marine toxins not removed during the desalination process and reduce the residual risk of these toxins even further.

It is therefore recommended to carry out chlorination experiments on remineralised distillate/permeate to see whether chlorination is effective in fresh water

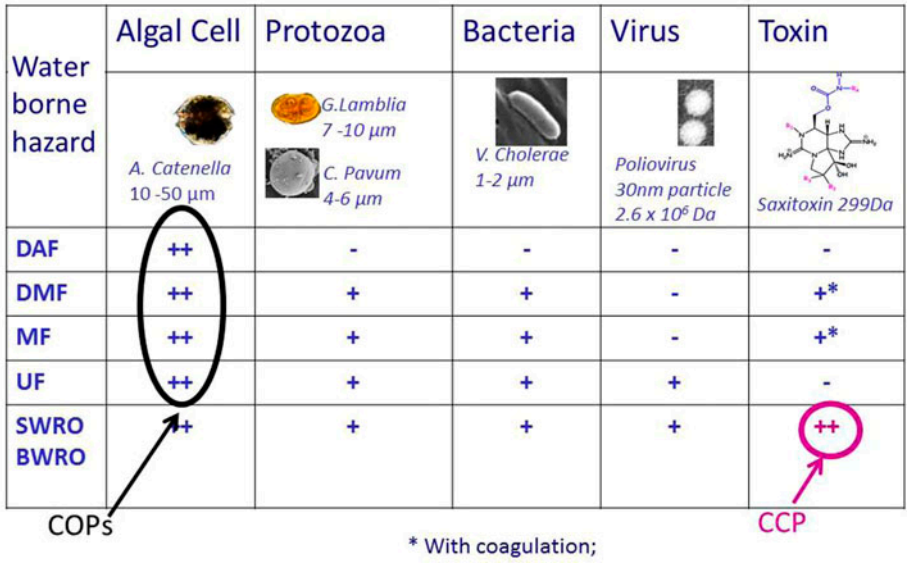

Fig. 7. Removal of water borne hazards for typical SWRO pretreatment processes and RO membranes. COP for removal of algal cells and CCP for extracellular toxins identified for SWRO plants. (++) refers to successful removal, (−) no removal and (+*) limited removal with coagulation optimisation.

and a lower dose might be effective to degrade saxitoxin and okadaic acid. As degradation of toxins is pH dependent, this would need to be investigated in these experiments.

Given the current status of research of the effect of chlorination in detoxifying these four marine toxins, final chlorination cannot be considered as a barrier or critical control point for removing them.

5. Residual risk to public health in desalinated drinking water

Given that greater than 99% of dissolved marine toxins were removed in distillation and SWRO bench -scale studies, the residual risk of the marine toxins studied here to human health in drinking desalinated water is expected to be low. Using the same assumptions presented in Section 3 to calculate the volume of drinking water that would need to be consumed to exceed the ARfD for the potent saxitoxin, following desalination treatment assuming 99% removal results in the volume increasing to between 67 and 2,000 L for the range in intracellular concentration given in Section 3. This is many times the assumed average daily drinking water intake of 2 L assumed by WHO.

Rejection of these toxins may be even higher than 99% in SWRO desalination plants as pretreatment processes are effective barriers for intact algal cells and will therefore remove intracellular toxins. In addition, the presence of high organics in RO feedwater during an algal bloom may lead to increased rejection of toxins in practice due to membrane fouling. However, there are no studies of marine toxin removal in full-scale SWRO plants in the literature.

6. Conclusions

Marine algal blooms are increasing in frequency and severity worldwide. HAB can challenge desalination plants to provide continuity of supply and impact on the public's perception of the safety of drinking desalinated water during a bloom. Indeed, marine algal toxins may be a risk to human health if present at high ambient concentrations at the plant intake and if not successfully removed during treatment.

Fortunately, most algal blooms do not produce algal toxins. Based on the physico-chemical properties of the four major classes of marine toxins considered here, these toxins should be efficiently removed by thermal and RO desalination processes. This has been confirmed in the literature for bench-scale tests using sea-water RO membranes and a micro distillation system with dissolved toxins (representing extracellular toxins). Further evidence was found in pilot studies conducted at SWRO pilot plants for the most potent toxin, saxitoxin and for the low molecular weight domoic acid. No toxins were detected in the RO pilot plant permeate.

For thermal desalination plants, there is only one barrier for the removal of intracellular and/or

extracellular toxins, the thermal desalination processes itself as there is limited pretreatment of the feedwater.

A significant portion of marine toxins are intracellular or cell bound. Therefore, SWRO desalination plants provide a multi-barrier approach for the removal of cell-bound toxins through size exclusion in commonly used pretreatment processes such as DMF with coagulation, MF or UF filtration and cartridge filtration. DAF is increasingly used in areas prone to algal blooms, specifically to remove algal cells by flotation. All these pretreatment processes will almost completely remove algal cells and toxins from intact cells. Should the cells lyse or be ruptured by hydrodynamic shear or pressurisation to release their toxins extracellularly, the toxins will then be removed downstream by the SWRO membranes, the final barrier in the process.

Water Safety Plans would define the thermal and RO desalination steps as a critical control point for algal toxin removal and continuously monitor the integrity of these processes using conductivity (as a surrogate for salt rejection) to ensure toxin removal.

Based on the above, the residual risk of these algal toxins to be present in the drinking water produced in MSF, MED or SWRO processes (assuming integrity of the desalination step) at a concentration high enough to cause an acute impact on human health is expected to be small. However, only one research study for the removal of marine algal toxin by distillation was identified, and this was based on bench-top experiments using synthetic sea-water. Therefore, more research on algal toxin removal is required, especially in full-scale plants and in laboratory studies where temperature and pressure conditions of MSF and MED plants are simulated.

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