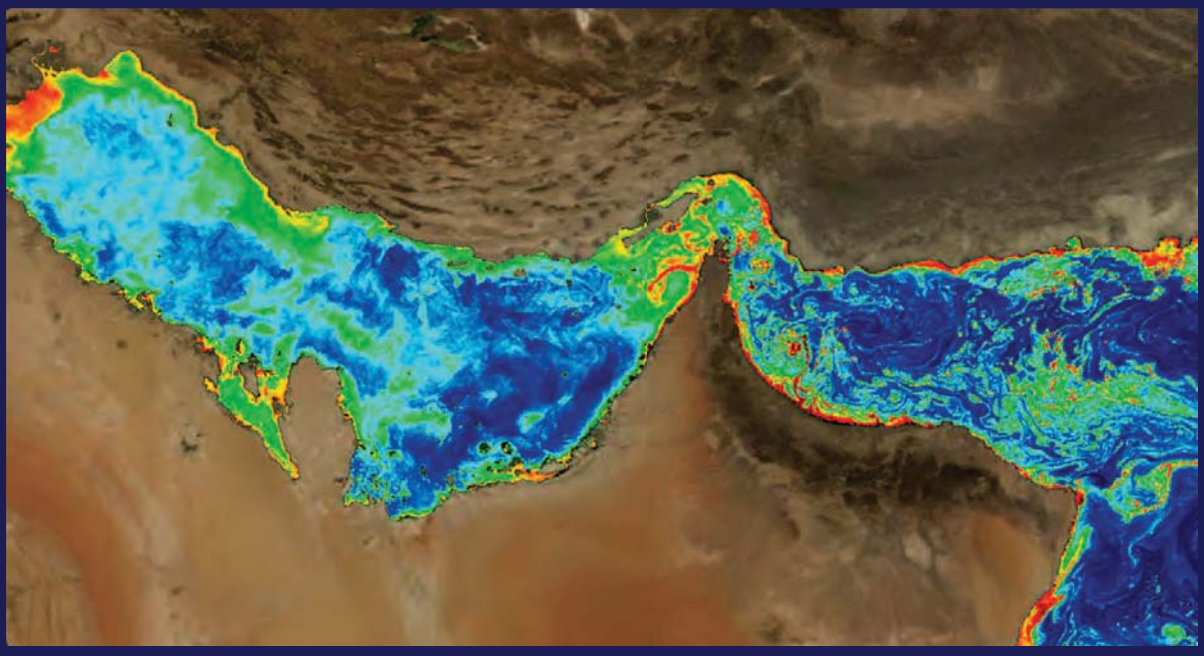
United Nations
Educational, Scientific and
Cultural Organization

Intergovernmental
Oceanographic
Commission

Manuals and Guides 78

# Harmful Algal Blooms (HABs) and Desalination: A Guide to Impacts, Monitoring, and Management



**Edited by:**

**Donald M. Anderson, Siobhan F.E. Boerlage, Mike B. Dixon**

UNESCO

**Manuals and Guides 78**

**Intergovernmental Oceanographic Commission**

# Harmful Algal Blooms (HABs) and Desalination: A Guide to Impacts, Monitoring and Management

Edited by:

**Donald M. Anderson***
Biology Department, Woods Hole Oceanographic Institution
Woods Hole, MA 02543 USA

**Siobhan F. E. Boerlage**
Boerlage Consulting
Gold Coast, Queensland, Australia

**Mike B. Dixon**
MDD Consulting, Kensington
Calgary, Alberta, Canada

*Corresponding Author's email: danderson@whoi.edu

**UNESCO 2017**

# 10 REMOVAL OF ALGAL TOXINS AND TASTE AND ODOR COMPOUNDS DURING DESALINATION

Mike B. Dixon[1], Siobhan F.E. Boerlage[2], Holly Churman[3], Lisa Henthorne[3], and Donald M. Anderson[4]

[1]MDD Consulting, Kensington, Calgary, Alberta, Canada
[2]Boerlage Consulting, Gold Coast, Queensland, Australia
[3]Water Standard, Houston, Texas, USA
[4]Woods Hole Oceanographic Institution,Woods Hole MA USA



## 10.1 INTRODUCTION

A major challenge in desalination is the removal of harmful algal bloom (HAB) toxins and taste and odor compounds (hereafter referred to as algal metabolites) using common treatment techniques. Removal of other compounds such as polysaccharides, proteins or transparent exopolymer particles (TEP) are discussed in Chapter 2. Taste and odor compounds are materials produced during a HAB that are not detrimental to human health, but cause customer dissatisfaction and often a misconception that the drinking water is not suitable for consumption. Toxins are detrimental to human health and are discussed in Chapter 2. Here the objective is to assess each process unit in a common desalination treatment train, both for SWRO and thermal desalination, and address how each is best optimized to act as a barrier to these specific algal metabolites. Where treatment techniques in seawater applications exist, these have been referenced and used as examples. As little documentation exists on removal of algal metabolites from seawater blooms, fresh water algal species are referred to whenever needed. This information is relevant in understanding the removal mechanisms that are possible. For clarity, these are denoted for each example.

Algal metabolites can be either intracellular or extracellular. Many algal species have high percentages of intracellular metabolites, such as *Microcystis* (freshwater) in which the toxin microcystin can be up to 98% intracellular (Chow et al. 1997). Lefebvre et al. (2008) showed an approximate 81% intracellular saxitoxin (STX)-equivalent concentration for an *Alexandrium* (seawater) bloom, although further data are needed to confirm this observation. STX-eq (or STX-equivalents) is a measure of total toxicity due to all saxitoxin analogues in a particular solution. In contrast, Smith et al. (2012) report that 60% of the okadaic acid produced by *Dinophysis* cultures was extracellular, while Kudela (pers. comm.) reported total and extracellular concentrations of 100 and 50 µg/L domoic acid respectively during a massive bloom of *Pseudo-nitzschia* along the US west coast in 2014. Extracellular

metabolites are inefficiently removed by pretreatment processes, and this is discussed below in more detail.

The nutritional status of HAB cells will affect the percentage of extracellular metabolites in a bloom. At the outset of a bloom, HAB cells will be more robust than toward the end of the bloom period when stresses from nutrient limitation, grazing, or other factors can lead to the leakage of metabolites into the seawater. Smith et al. (2012) noted that, in general, the concentration of extracellular toxin in a lab culture of *Dinophysis acuminata* (seawater) significantly increased upon culture aging and decline; cells did not appear to be actively or passively releasing toxin during the stationary phase (see Chapter 1, Figure 1.3), but rather extracellular release was likely a result of cell death.

## 10.2 CHLORINATION

By applying intake chlorination during a HAB event, the cells are lysed (ruptured) and, because of the breakdown of the cell wall, there is a release of cell organelles and dissolved compounds (including metabolites, TEP, polysaccharides, and proteins) which can cause a significant impact on downstream SWRO treatment processes. These dissolved substances are more poorly removed by dissolved air flotation (DAF) and dual media filtration (DMF) and associated flocculation/coagulation processes than the intact cells, and therefore a large amount can pass through pretreatment unit processes to the SWRO process unit, causing biofouling of the elements (Villacorte 2014; see Chapter 2). Daly et al. (2007) showed that for the blue-green algal (or cyanobacterium) species *Microcystis aeruginosa* in fresh water, a chlorine concentration of 7 mg/L completely lysed a cell density of 54,000,000 cells/L in 30 min. Additionally, even a small amount of chlorine (1mg/L) can cause leakage of toxins, as the HAB cell wall is damaged (Daly et al. 2007). Azanza et al. (2001) showed the effect of chlorination (as well as UV) on the marine dinoflagellate *Pyrodynium bahamense*, noting that the cellulose thecal plates of the cell wall turn into mucilage. Figure 10.1 shows the effect of a chlorine dose of 0.5 mg/L on these cells through time. Resosudarmo et al. (2014) also indicated that chlorination (1 - 40 mg/L) of the marine alga *Tetraselmis suecica* caused significant cell lysis and release of cellular contents into the seawater. Thus, the use of chlorine as a pretreatment step should be avoided where possible when a bloom is present in the source water, as chlorine causes intact cells to lyse, releasing intracellular toxin into solution, and removal becomes more difficult. While thermal and SWRO systems should both remove toxins efficiently, as discussed in Chapter 8, maximizing the number of effective barriers against toxins is a prudent removal strategy. Some soluble toxins can be destroyed by chlorine (Laycock et al. 2012), although in untreated raw seawater, the pH and

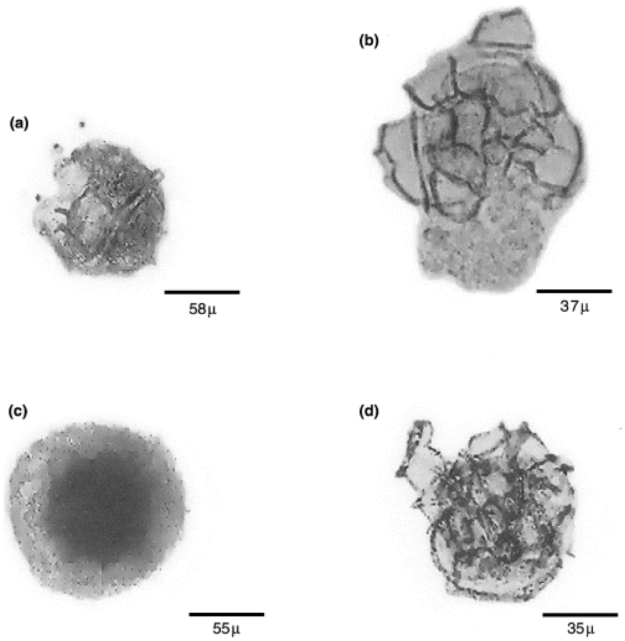



**Figure 10.1**. The effect of chlorination (0.5 mg/L) on the marine dinoflagellate, *Pyrodynium bahamense*, Destruction of UV treated and chlorinated *Pyrodinium* cells in seawater (a and b). Ruptured thecal plates of cells after 2 and 6 min UV exposure. (c) Cell enveloped in mucilaginous-like substance after 2 min of chlorine exposure. (d) Clumping of *Pyrodinium* cells at 8 min chlorine exposure.

chlorine demand may reduce the effectiveness of this reaction and therefore it cannot be relied upon as a viable treatment option (Daly et al. 2007; Boerlage and Nada 2014). Laycock et al. (2012) demonstrated that saxitoxin, domoic acid, and okadaic acid in synthetic seawater were completely destroyed by exposure to 10 ppm hypochlorite at 37 °C for 10 min, whereas brevetoxin was unaffected. While these operating conditions are extreme within desalination plants, it demonstrates possibilities for further investigations. Equipment warranties may need review to ensure that maximum allowable chlorine expose is not exceeded.

By avoiding the use of chlorination at the intake, cell lysis can be avoided and therefore algal metabolites can be kept intracellular and more easily removed by downstream processes. During the majority of the bloom, SWRO pretreatment processes should then remove intracellular metabolites efficiently, but as a bloom dies and the metabolites become extracellular, pretreatment will become less efficient for metabolite removal and downstream processes (such as SWRO and product water chlorination) will become the relevant treatment methods for toxin removal. Taste and odor compounds MIB and geosmin are not denatured by chlorine.

## 10.3 DISSOLVED AIR FLOTATION (DAF)

As mentioned in Chapter 9, DAF will remove cells by floating them to the surface of the DAF tank. Due to the very low shear forces and encapsulation of the HAB cells with coagulant (if used to aid flotation), cells are not lysed and are floated, unharmed, to the surface of the DAF tank (Zhu and Bates 2012; Zhu et al. 2014). As the unharmed cells are skimmed from the surface of the tank, the intracellular metabolites will be removed from the treated water. When the HAB species has a high percentage of intracellular metabolites, the majority will be removed by this step (Teixeira and Rosa 2006, 2007; Teixeira et al. 2010). This metabolite removal technique is practiced at the freshwater Myponga WTP in South Australia, which is regularly challenged with concentrated cyanobacteria that are successfully removed using dissolved air flotation and filtration (DAFF; Qian et al. 2014).

In the DAF process, seawater HAB cell removal is expected to be >75% (Zhu and Bates 2012; Zhu et al. 2014). DAF removal of cells has been studied by many groups previously as detailed in Chapter 9, but cell counts were often either relatively low (less than 1,000,000 cells/L), or counts were not undertaken; however, several studies have incorporated cell counting in their research programs. Wiley et al. (2014) showed that when a bloom consisted of 100,000,000 cells/L of the marine green alga *Tetraselmis*, the removal by DAF was as high as 97%. Zhu et al. (2014) showed that DAF could remove >90% of the marine dinoflagellate *Prorocentrum minimum.*

SWRO desalination plants that incorporate DAF specifically designed for algal removal will also be a barrier for intracellular metabolites, which may be as high as 97% of the total in a HAB. Removal is clearly dependent on the intracellular toxin percentage, and that can vary with the physiological status of the cells, as well as the pretreatment strategies (e.g., chlorination).

Brevetoxin is hydrophobic and accumulates in bubbles, therefore some of this toxin may be removed during DAF (Boerlage and Nada 2014). Pierce et al. (2004) reported that adding a slurry of natural clay at the rate of 0.25 g/L removed 97% of brevetoxins associated with live marine *Karenia brevis* (intracellular toxins) from seawater.

## 10.4 GRANULAR MEDIA FILTERS

GMF, a conventional filtration method, will remove HAB cells by trapping them between the sand granules while the clean water passes out the bottom of the filter. Gravity GMF can achieve around 90% removal of algal cells (Chapter 9), and thus intracellular metabolites will

be removed to the same percentage (Desormeaux et al. 2009). HAB cell removal has been shown to be between 75 and 97% for pressurized GMF, thus metabolite removal percentage is similar when comparing the same cell types (Desormeaux et al. 2011).

Similar to the DAF discussion above, coagulation will aid removal of HAB cells and ensure that those cells remain unharmed by the filtration process as they are encapsulated inside flocs (Dixon et al. 2011b, c). Studies by Velzeboer et al. (1995), Chow et al. (1998, 1999), Dixon et al. (2012) and Drikas et al. (2001) have shown that alum and ferric coagulation/flocculation (with flash mixing at 200rpm) do not compromise the membrane integrity of cyanobacterial cells; if this is borne out with marine HAB species, the process would not cause extracellular metabolite release. As mentioned above, removal of toxin will be maximized if the metabolite remains intracellular, as extracellular metabolites will be poorly removed by both coagulation and GMF. To maximize the effectiveness of the multi-barrier treatment approach, care should be taken to restart the GMF filter properly after a backwash to ensure that a concentrated portion of extracellular metabolite is not sent downstream (see Chapter 9).

In some cases, a biofilm forms in the GMF with bacteria specific for biodegradation of extracellular toxins and taste and odor compounds. Studies at the Morgan Water Treatment Plant (WTP) in South Australia show the biodegradation of geosmin, affording a 70% removal (McDowall 2008) in a GMF.

## 10.5 ULTRAFILTRATION/MICROFILTRATION

Ultrafiltration/microfiltration (hereafter referred to as UF) will remove intracellular metabolites reliably, but not extracellular metabolites. There are many mechanisms for metabolite removal in UF processes such as those illustrated in Figure 10.2 (Schäfer et al. 2011), but the only ongoing reliable method is by size exclusion of the HAB cells and subsequent intracellular toxin removal.

In some cases there may be some incidental absorption of extracellular metabolites onto the UF membrane fibers, but they will become quickly saturated (Dixon et al. 2011a) and therefore this removal method is not operationally reliable. Desormeaux et al. (2009) also observed this phenomenon for extracellular toxin removal, seeing a removal of 9-28% of a 100% extracellular domoic acid surrogate using two different pilot UF systems. Additionally, extracellular metabolites can be removed by foulant-toxin interaction (Figure 10.2); however, a large amount of foulant is required for any efficiency of the process and there is an inherent inefficiency during backwashing, when the foulant is mostly removed from the UF membrane. In one example case in South Australia at the freshwater Cowirra UF Plant on the Murray River, more algal metabolite was removed than expected for a PVDF UF membrane due to absorption by the foulants on the surface of the UF membrane (Newcombe 2011). While regular removal of the extracellular algal metabolites 2-methyl isoborneol (MIB) and geosmin (GSM) is less than 20%, during a serious fouling episode, removal of GSM was 40-60%. This was due to unusually high DOC concentrations in the raw water, a side effect of the conclusion to the Australian drought and referred to as a 'black water' event. DOC was 10mg/L or greater. While this shows that removal mechanisms other than size exclusion of cells are possible, they cannot be relied upon consistently as a treatment barrier for extracellular metabolites.

Many UF operators have concerns that cells can be broken by shear or pressurization during normal UF operation. With UF filtration, shear will only cause minor cell lysis in regular operating conditions. In a study by Ladner (2009), shear was maximized by repeatedly running water through a needle valve with a small aperture (power density was $4x10^{10}$ W/m$^3$).

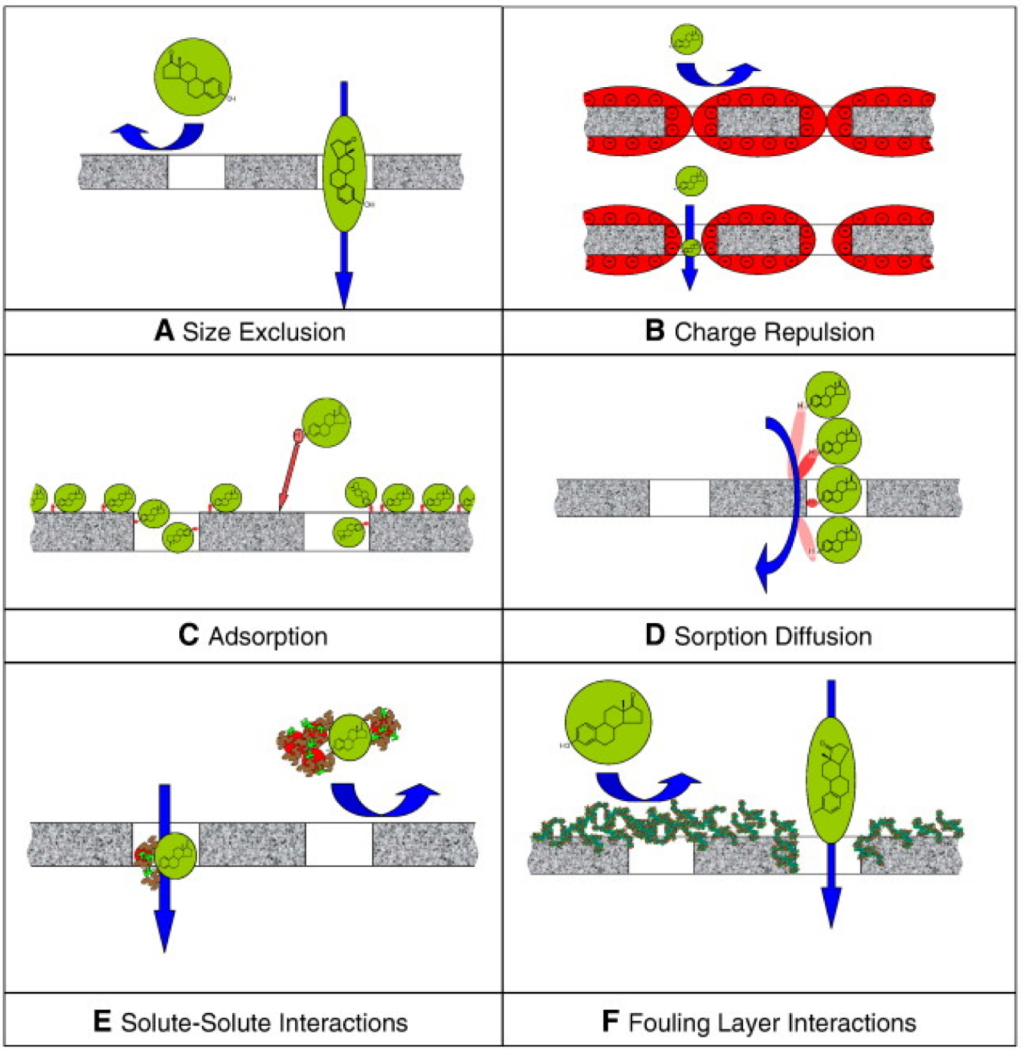



**Figure 10.2.** Mechanisms for algal metabolite removal using membranes (modified from Schäfer et al. 2011).

Ladner (2009) showed that the needle valve lysed cells of the marine dinoflagellate *Heterocapsa pygmaea*, but the pump used to circulate the cells did not cause major amounts of damage. Given that SWRO plants use submerged UF systems, there would be little shear in comparison to Ladner's experiment, in which the shear was maximized to exacerbate the phenomenon.

When considering the conditions experienced in full-scale pressurized UF systems, Resosudarmo et al. (2014) observed minimal lysis by running experiments between 50 to 150 kPa (0.5 to 1.5bar) for marine *Tetraselmis suecica*; however, if transmembrane pressure (TMP) becomes very high, as it might during a HAB event, it can cause a greater amount of cell lysis, so TMP should be controlled to as low as possible by maintaining frequent backwash during bloom periods. Dixon et al. (2011b) and Chow et al. (1997) showed less than 1% cell lysis of freshwater cyanobacterial cells (*Microcystis*) in an outside-in pressurized UF experiment undertaken at 1-3 bar. Campinas and Rosa (2010) found that a small amount of cell lysis occurred throughout the entire algal cell life cycle for the freshwater *Microcystis*; however, it was more pronounced with older cells from a lab culture.

Dixon et al. (2011c) undertook UF experiments using flocculation/coagulation and found that encapsulation within floc protect the cell from damage.

Dixon et al. (2011b, c) showed excellent saxitoxin removal using a pressurized outside-in UF system and by keeping toxin intracellular. In one experiment, Dixon et al. (2011c) found that total saxitoxin concentrations (intracellular and extracellular combined) from the freshwater cyanobacterium *Anabaena circinalis* were 2.2 – 2.7 µg/L STX-eq in the feed water to a UF membrane laboratory system, of which 31–38% was extracellular (0.7–0.8 µg/L STX-eq). Results showed that when using alum coagulant, up to 68% removal of total saxitoxin was achieved in the membrane tank as intact *A. circinalis* cells were removed via coagulation prior to contact with the UF membrane. The majority of saxitoxin that was not removed was extracellular. Extracellular saxitoxin (STX-eq) removal by the UF membrane itself (without the effect of coagulation) was less than 20%.

Thus in UF, if TMP is minimized, intracellular metabolite removal will be maximized. Use of a coagulant can aid cellular removal and help keep toxin intracellular, while keeping TMP lower than if the coagulant was not used.

## 10.6 REVERSE OSMOSIS

If the pretreatment process performs properly, then a very small number of HAB cells should be present entering the RO treatment step. Therefore intracellular metabolite removal is no longer relevant and the RO mechanism is used to remove extracellular metabolites. Additionally, if the pretreatment process is optimized, there should be minimal extracellular metabolite concentration at the entry to the RO.

RO is an excellent barrier for removing extracellular metabolites and the removal mechanism is the same as for removal of 'organic micropollutants' such as personal care products and pharmaceuticals, which has been well studied in Europe and North America (Bellona et al. 2004; Verliefde et al. 2007, 2009; Schoonenberg Kegel et al. 2010).

Metabolite removal is governed by the properties of the RO (or in some cases nanofiltration (NF)) membrane and the properties of the specific metabolite itself. Bellona et al. (2004) reported that in estimating the rejection of a solute by high pressure membranes (RO, NF), properties such as molecular weight cut-off (MWCO), desalting degree, porosity, membrane morphology, and hydrophobicity of the membrane, and the molecular weight, molecular size, charge, and hydrophobicity of the solute as well as the feedwater chemistry must all be considered. A complete understanding of the solute and membrane characteristics that influence rejection could lay the foundation for a modeling approach capable of predicting the fate of specific compounds during high pressure membrane applications.

Given these mechanisms, if a metabolite is larger in molecular weight than approximately 200-300 Da (as a guide), then there will be excellent removal of the metabolite using RO. Molecules 50-200 Da are more difficult to remove by RO. While the MWCO of RO is theoretically approximately 100 Da (Dixon et al. 2012), the charge of the molecule becomes more important for the 50-200 Da molecular weight range. If the molecule is negatively charged, then the molecule will be repelled from the negatively charged RO surface. If the molecule is positively charged, then it will be attracted to the surface of the membrane and might be sorbed into the polyamide and pass into the permeate (Bellona et al. 2004; Verliefde et al. 2007, 2009; Schoonenberg Kegel et al. 2010).

Fortunately, the most common HAB toxins are above 200 Da as discussed in Chapter 2. Common toxins such as domoic acid and brevetoxin are far larger than saxitoxin in MW and molecular size and will be well removed by size exclusion. Desormeaux et al. (2009) undertook a pilot study in Monterey Bay, California, and due to a lack of a natural HAB,

kainic acid was selected as a toxin surrogate to spike into the treatment system as it has a similar chemical structure to domoic acid, but is non-toxic. Kainic acid is a natural marine acid contained in some species of seaweed and is a commonly used surrogate for domoic acid. Dissolved kainic acid was spiked at concentrations 100 - 1,000 times greater than observed during blooms of domoic acid-producing algae. Removal of the toxin surrogate was greater than 99.5% for two different RO pilot systems, with a detection limit of 0.6 µg/L in seawater and 0.017 µg/L in the RO product water. Seubert et al. (2012) undertook bench-scale RO experiments to explore the potential of extracellular algal toxins contaminating RO product waters. Concentrations exceeding maximal values previously reported during natural blooms were used in the laboratory experiments, with treatments comprised of 50 µg/L of domoic acid, 2 µg/L of saxitoxin and 20 µg/L of brevetoxin. None of the algal toxins used in the bench-scale RO experiments were detectable in the desalinated product water. In the same study by Seubert et al. (2012) monitoring for intracellular and extracellular concentrations of domoic acid and saxitoxin within the intake and RO treated water from a pilot RO desalination plant in El Segundo, California was conducted from 2005 to 2009. During the five-year monitoring period, domoic acid and saxitoxin were detected sporadically in the intake waters but never in the RO treated water. Another relevant study is that of Laycock et al. (2012) in which a small laboratory-scale RO device was used to study HAB toxin removal. Starting with 10.3 µg/mL of saxitoxin, 17.2 µg/mL of domoic acid, and 0.4 and 0.9 µg/mL of okadaic acid and brevetoxin respectively, removal was 99.4, 99.0, 99.7 and 99.9 %, respectively. While only a single pass through an RO membrane, the results are consistent with previous studies mentioned above.

Given that the only existing relevant water quality guidelines relating to algal toxins (Brazil and New Zealand) are in the range of 0.2 to 3 µg/L for saxitoxin and a worst case scenario bloom may contain up to 600 ug/L of extracellular toxin (Chapter 8, Table 8.3), 99% membrane removal can be an adequate treatment barrier for HAB toxins, depending on local guideline concentrations. With the relatively low molecular weights of saxitoxin and domoic acid (299 and 311 Da, respectively) and their hydrophilic nature, they are the most likely of the common HAB toxins to pass through RO, as their molecular weights are the closest of any HAB toxin to the theoretical MWCO of a RO membrane (~100Da). Brevetoxin (895 Da) and okadaic acid (805 Da) are approximately eight times the MWCO of a RO membrane and will therefore be easily removed. Despite saxitoxin being a smaller molecule, a study by Dixon (2014) showed that saxitoxin and its congeners were removed to 99% or greater by a tight nanofiltration membrane with a MWCO of ~100 Da (Table 10.1). The saxitoxin analogues STX, GTX 3 and 4, and C1 and 2 were removed to greater than 99% by both NF membranes. In parallel studies by Dixon et al. (2010, 2011a), it was shown that both SWRO and BWRO membranes always removed toxin more efficiently than nanofiltration membranes for toxins similar to saxitoxin in charge and size, such as cylindrospermopsin. One can thus expect RO to remove saxitoxin just as well as this particular NF membrane. This saxitoxin removal information correlates well with the work undertaken by Seubert et al. (2012).

Dixon (2014) also showed that the smaller molecular weight non-toxic taste and odor compounds MIB and geosmin were removed less efficiently than for saxitoxin (71-94%) owing to their smaller molecular weight and size (168 and 182 Da respectively) (Table 10.1). Given a heavily concentrated HAB producing MIB or geosmin, if the pretreatment system completely fails and all the MIB and geosmin is extracellular, then a small amount of material may pass into the product water. Given the non-toxic nature of taste and odor compounds, the worst-case scenario would be customer complaints, but no risk to public health exists.

**Table 10.1.** Removal percentages for algal metabolites using two NF membranes (NF90 and NF270, Dow Filmtec).

| Table Cyanobacterial metabolite | % removal | |
|---|---|---|
| | NF90 | NF270 |
| 2-Methylisoborneol (MIB) | 71 | 83 |
| Geosmin | 94 | 89 |
| Microcystin (mLR equiv.) | 93 | 100 |
| Saxitoxin (STX) | 100 | 100 |
| Gonyautoxin 3 (GTX3) | 100 | 100 |
| Gonyautoxin 4 (GTX4) | 100 | 100 |
| C1 | 99 | 99 |
| C2 | 99 | 99 |

Unlike removal of salts and inorganics by RO, there is a less pronounced effect of feedwater concentration when calculating organic micropollutant removal (such as toxins and taste and odors). When considering salts, while membrane rejection will be ~99.7%, system rejection may be around 98-99% depending in part upon the feed salinity and membrane array design. This may not be so with organic micropollutants, as Fujioka et al. (2014) showed that a larger concentration of N-Nitrosodiethylamine (NDMA) (up to 800 ng/L) did not increase the permeate concentration of NDMA. Therefore, removal of saxitoxin and other toxins should be somewhat independent of the membrane array and feed concentration (at maximum feed concentrations of 600 µg/L) and be maintained through the first pass at approximately 99%. Given many SW plants are two pass, then the total removal of saxitoxin would be 99% of the original first pass 99% removal. Any blending of 1$^{st}$ and 2$^{nd}$ pass permeate should be considered, but the net result may still be very low residual concentrations of the toxin.

Salt passage increases (due to membrane ageing or oxidation) in the RO process unit would occur far sooner than any increase in product water HAB toxin concentration. For this reason a major increase in permeate TDS could be used to detect an integrity breach that could later lead to an increase in permeate toxin concentration. In a hypothetical study by Dixon et al. (2015) a set of theoretical RO projections were undertaken to understand the failure mode of how damage to the RO membrane may affect the permeate saxitoxin concentration during a typical bloom. LG Nano$H_2O$'s Q+ RO projection software was used as it allows the user to model membrane deterioration independently of simple ageing factors. A typical SWRO system from the Gulf was modeled (38,000 mg/L TDS, 110 pressure vessels (PV) per train, 7 membranes (M) per pressure vessel, 35 $^{o}$C feed water temperature, 42% recovery, 5 year old membranes, with supporting full second pass appropriately sized). For this hypothetical modeling study, a feed water saxitoxin concentration of 10 µg/L was used, and it was assumed that the pretreatment experienced full failure for removal of saxitoxin, meaning the RO inlet saxitoxin concentration was also 10 µg/L. To exceed a hypothetical local saxitoxin guideline value after the first pass of 1 µg/L, the plant would need to experience a first pass permeate TDS of 2000 ppm. This corresponds to a gross loss of rejection in the elements, for example from 99.7 to 99.0% NaCl rejection (when measured using a standard wet test, 32,000 mg/L NaCl, 25 $^{o}$C, 800 psi, 8% recovery, pH 8). This also assumes a gross loss of saxitoxin rejection from 99% to 95% in the first pass, to give a very large safety factor,

particularly for the higher water temperature in this case study. Given a full two pass system, the second pass permeate would be approximately 0.3ug/L, despite the damaged first pass elements. Given a partial split system with only 25% of water sent to second pass, this would still produce a combined permeate saxitoxin concentration under the 1 µg/L guideline limit for the above hypothetical scenario. Figure 10.3 summarizes the above theoretical case study by showing plant conditions, saxitoxin concentration, and probable conductivity alarms throughout the plant.

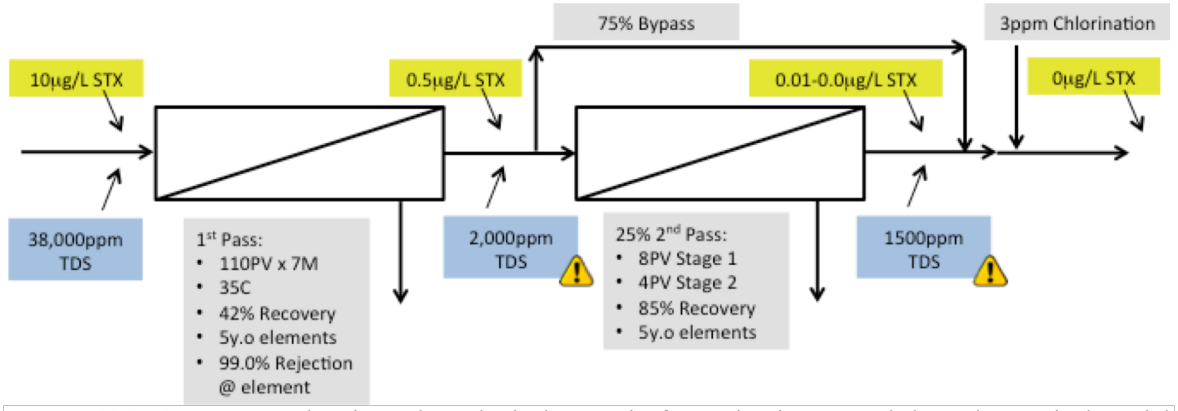



**Figure 10.3.** A summary showing a hypothetical scenario for saxitoxin removal through a typical partial two pass RO system. The figure illustrates that alarms will be generated for 1st pass and 2nd pass TDS before saxitoxin reaches a hypothetical local guideline concentration of 1µg/L. Figure: Dixon et al. 2015.

Such rejection losses could occur in several ways: 1) chlorination and oxidation of the membranes; 2) accidental overdose of acid to below pH 3 for an extended period of time; or 3) an abundance of rolled permeate seals in the pressure vessels. In each case, the allowable permeate TDS would be exceeded, causing plant alarms for high conductivity in the first and second pass permeate. Regular plant TDS monitoring would show any membrane damage in the first pass and a plant with two passes with a permeate TDS of less than the typical 300 mg/L is very unlikely to have detectable saxitoxin in the product water in given this hypothetical case. Plant designers and operators could use this modeling exercise to analyze their plant performance at maximum toxin concentrations predicted for certain plant localities. While this hypothetical study used a saxitoxin concentration of 10 µg/L, some localities may predict higher toxin concentration from data previously collected in that specific seawater. By using this tool they could assess for potential alarm limits for conductivity that indicate a potential presence of toxin in the permeate.

Despite this, toxin analysis during a bloom is prudent, as any unforeseen errors during treatment could have a major impact on local public health. Some details on HAB toxin analysis methodology are given in Chapter 2, and relatively simple methods for toxin screening using ELISA kits and other assays are found in Appendix 2.

It is important to note that during toxic bloom conditions, toxin will most likely remain in the waste brine from the SWRO process. Algal toxins are unlikely to be destroyed by most pre-treatment processes, unless chlorination is undertaken in one or more of the unit processes. Chlorination appears to degrade saxitoxin (Zamyadi et al. 2010; Laycock et al. 2012), domoic acid, and okadaic acid, but not brevetoxins (Laycock et al. 2012). Hypochlorite concentrations of 4 ppm or higher were sufficient to react with all of the saxitoxins, domoic acid and okadaic acid in the samples that contained initial toxin concentrations up to 1250 ng/mL. Brevetoxins appeared to be unaffected in experiments in which the toxins were exposed to up to 30 ppm hypochlorite in seawater at 35 °C for 60 min (Laycock et al. 2012).

Given the complications associated with HABs and chlorination such as biofouling, it is unlikely that chlorination will be performed during pre-treatment. Consequently, the concentration at the outfall will be no more than double that of the intake water, given most desalination plants operate at under 50% recovery. While the concentration of toxin in the immediate vicinity of the outfall may be more than in the intake water, this will be diluted quickly to background levels, especially in modern desalination plants where mixing is designed to occur rapidly. Impacts greater than that already experienced naturally due to the bloom, if any, would be in the immediate vicinity of the outfall.

## 10.7 SLUDGE TREATMENT AND BACKWASH DISPOSAL

At the time of publication, no literature was available discussing sludge concentrations of toxins and taste and odors in SWRO plants; however, freshwater literature was available. Cell lysis has been documented to occur in the clarifier sludge, releasing intracellular toxins (Drikas et al. 2001). This becomes a problem during clarification processes in conventional drinking water plants, especially if long sludge retention times are evident in sedimentation tanks, or sludge blanket clarifiers, and in particular where recycling of the supernatant from the sludge to the head of the WTP is practiced.

Once confined in sludge, fresh water cyanobacteria may lose viability, die, and release metabolites into the surrounding water (Newcombe et al. 2010). This can occur within one day of treatment for some cyanobacteria, and could potentially result in very high dissolved concentrations of algal metabolites. Similarly, algal cells carried onto sand filters, in flocs or individually, could rapidly lose viability. As a result, where cyanobacteria (or marine HABs) are potentially toxic, all sludge and sludge supernatant should be isolated from the plant until the toxins have degraded sufficiently, wherever this is possible. Microcystins are readily biodegradable (Newcombe et al. 2010) so this process should take 1-4 weeks. Cylindrospermopsin appears to be slower to degrade and the biological degradation of saxitoxins has not yet been studied; however, the latter are known to be stable for prolonged periods (greater than 4 weeks) in source water, so caution is recommended. Intracellular geosmin and MIB may also be released in sedimentation tanks and sludge treatment facilities. This could result in increased taste and odor levels through the plant, or in the sludge supernatant which, if it is returned to the head of the plant, could contribute significantly to the levels entering the treatment plant (Newcombe et al. 2010). The possibility of this occurring in individual treatment plants should be the focus of regular in-plant sampling.

## 10.8 TOXIN REMOVAL IN THERMAL DESALINATION PLANTS

While HABs do not have major operational impacts on thermal desalination plants as discussed in Chapter 2, some water supply authorities have expressed concern related to the removal of marine toxins by thermal desalination during toxic blooms. The removal of algal toxins by thermal desalination processes has not been well researched. The study by Laycock et al. (2012) experimentally determined the removal of marine toxins in the dissolved form, i.e. extracellular in synthetic seawater using a bench scale micro distillation system. Boerlage and Nada 2014 reviewed this work and examined the physical and chemical properties of the four major classes of marine toxins that might be present at plant intakes to determine their fate in thermal (and SWRO) desalination plant processes and the potential (residual) risk in desalinated drinking water. Barriers to remove intracellular toxins in intact algal cells and extracellular toxins from ruptured cells were identified. The following section is a summary of Boerlage and Nada (2014).

### 10.8.1 Chemical and physical properties of marine HAB toxins

Four of the most potent and well characterized groups of marine toxins which could appear at desalination plant intakes include saxitoxin, domoic acid, okadaic acid and brevetoxin. As discussed in Chapter 2, the toxins have been classified based upon the poisoning syndromes the toxins elicit. Physical and chemical properties of these toxins are summarized in Table 10.2. Algal toxins are structurally and functionally diverse, with varying charge, polarity, and size, and many being derived from unique synthetic pathways (Wang 2008). Most of the marine toxins that have high molecular weights are acid stable and non-volatile. Brevetoxins, for example, are reported to withstand heat up to 300 ºC.

**Table 10.2.** Physico-chemical properties of common marine toxins (http://www.chemspider.com/ 2016; http://www.latoxan.com/ 2016).

| Toxin | Human poisoning syndrome | Solubility | Molecular weight (Da) | Melting/Boiling Point (ºC) | Vapor Pressure (mmHg at 25ºC) |
|---|---|---|---|---|---|
| Saxitoxin | Paralytic shellfish poisoning (PSP) | Water soluble at pH <7; stable | 299 | BP 549-575 | 0 |
| Brevetoxin 1 | Neurotoxic shellfish poisoning (NSP) | Fat soluble (liposoluble) | 867 | BP 197-199 | NA |
| Brevetoxin 2 | | | 895 | MP 265- 270 | |
| Brevetoxin 3 | | | 897 | BP 291 - 293 | |
| Brevetoxin 9 | | | 899 | MP 289 - 293 | |
| Domoic acid | Amnesic shellfish poisoning (ASP) | Water soluble at pH <7 | 311 | BP 607 | 0 |
| Okadaic acid | Diarrhetic shellfish poisoning (DSP) | Slightly water soluble | 805 | BP 921.6 | 0 |

### 10.8.2 Toxin barriers in thermal desalination plants

Thermal desalination systems are quite robust in terms of source water quality. Therefore, pretreatment is limited prior to MSF and MED plants, and typically comprised of feedwater chlorination, screening, and chemical addition to prevent scaling and foaming. Feedwater is screened to remove coarse debris to prevent equipment erosion by suspended solids and prevent equipment from becoming blocked. For MSF, the allowable particle size for seawater entering the tubes varying between 5- 15 mm (Gille 2003). On the other hand, MED needs finer filtration, with the allowable particle size for seawater going through the spray nozzles being < 0.5 mm.

Open intake screening commonly consists of coarse bar screening (75 to 150 mm) to remove large debris and flotsam followed by mechanical fine screening (6-9.5 mm), e.g. travelling band screens and drum screens to remove finer material and protect downstream processes. Alternatively, only wedge wire screen may be employed with apertures ranging between 0.5 to 10 mm. Dinoflagellate and diatom cells can easily pass through these screens; for example, *Alexandrium* spp. (the potent saxitoxin producers) are typically 15 to 48 µm in size. Hence, screening will not serve as a barrier for algal cells, unless the screen is blinded, nor for extracellular toxins. Instead shear forces during intake pumping and screening may break down algal cell walls, particularly unarmoured cells like *Karenia brevis* whose cell walls are fragile, releasing toxins into the seawater. Brevetoxins produced by *K. brevis* could become aerosolized around onshore screens and could pose a respiratory risk to plant personnel if not enclosed.

Chemical conditioning is utilized in thermal desalination in two treatment streams: the seawater cooling water component and the seawater makeup water (used within the desalination process). An oxidizing 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 antiscalant (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 oxidize organic matter. Antifoam agents may have an effect on organic compounds associated with algal blooms, but are not expected to degrade the toxin itself.

Most thermal desalination plants practice continuous chlorination at the seawater intake to provide a residual chlorine concentration of approximately 0.15 – 0.3 mg/L to prevent fouling marine growth in piping and biofilm formation on heat exchange surfaces. Chlorination has also been proven to detoxify some marine toxins, with domoic acid the most sensitive to chlorine - requiring only 1 ppm hypochlorite. Exposure to ≥ 4 ppm hypochlorite for 10 min at 37 ºC completely destroyed saxitoxin and okadic acid (Laycock et al. 2012); however, brevetoxin (3 and 300 µg/L concentration) was unaffected by exposure to hypochlorite up to 30 ppm for one hour. Hence, chlorination is not a barrier for all marine toxins. The experiments of Laycock et al. (2012) were in synthetic seawater with toxins isolated from laboratory cultures. In practice the higher organics present during a bloom will exert a chlorine demand, thereby reducing the efficiency of toxin degradation by chlorination, potentially rendering it impractical as a degradation strategy. It is unlikely that continuous chlorination of intake seawater can be applied at 4 ppm hypochlorite in thermal desalination 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 and the guarantee values of various equipment may be exceeded. Finally, as discussed earlier in this chapter, chlorine can result in the lysis of algal cells, thereby releasing intracellular toxins into solution. Hence, chlorination should be avoided during a HAB when possible.

In thermal desalination systems, volatile and semi-volatile organics with boiling points lower than water's boiling point may carry over in the steam to contaminate the distillate 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, but this can sometimes be erroneous. This is because the evaporation of organics from seawater and their condensation into distillates is governed by a multitude of factors such as the temperature and pressure of the MSF stage or MED effect and the concentration, vapor pressure, latent heat of condensation of the individual compounds (Kutty et al. 1994).

The four major toxins presented in Table 10.2 are all reported to be heat stable, have low vapor 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 boiling point of brevetoxin is higher than that of water. These factors would suggest that the toxins will not carry over in thermal desalination systems or co-distill, but instead will remain in the flashing brine.

The results of Laycock et al. (2012) support high removal of toxins in the MSF and MED desalination processes. The maximum temperature in that study was 104 ºC which is approaching the top brine temperature of MSF (90 to 112 °C), but above MED (60 and 64°C). 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 with a synthetic seawater base, salinity 37 . Algal cell walls may be broken down under the varying temperature and pressure conditions of MSF and MED (if not already damaged by shear forces of pumps at screens). Therefore the majority of toxins are expected to be extracellular, justifying the approach of using dissolved toxins in these laboratory studies. Distillation results from Laycock et al. (2012) showed 99.5 to 99.9% removal of the three extracellular toxins. Removal of the fourth toxin, brevetoxin, was conducted in a separate series of tests, with the removal of that toxin somewhat lower than for the other toxins, but still high at 98.3% removal. Similar to the other toxins, the test concentration of brevetoxin (900 µg/L) is considered unusually high for natural bloom conditions in the marine environment. Laycock et al. (2012) suggested that due to the aerosolization nature of brevetoxin, it 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 work of Laycock et al. (2012) demonstrated that thermal desalination is an effective barrier for the removal of these marine toxins, assuming no leaks in the system. 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. Nonetheless, 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.

## 10.9 CHLORINATION PRIOR TO THE DISTRIBUTION SYSTEM

Following remineralization 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. This provides a further barrier for some toxin removal after RO. The study of Laycock et al. (2012) showed chlorination (in seawater) was ineffective in degrading brevetoxin. Above1 ppm chlorination was effective in degrading domoic acid while saxitoxin and okadic acid required 4 ppm or more. Zamyadi et al. (2010) showed that at pH 6.8-8, saxitoxin at a concentration of 1.5 µg/L was degraded to less than 0.1ug/L after a contact time (CT) value of 15 – 20 mg.min/L (Figure 10.4). Thus when product water is chlorinated at 3 ppm, saxitoxin is degraded in five minutes. As desalination plants regularly have transfer pipelines to transport water to the distribution system, ample chlorination time is usually available for saxitoxin degradation.

The STX congeners (e.g., GTX 2&3 and C1&2) behaved similarly to the parent compound during chlorination (Zamyadi et al. 2010). The longest required CT value was 35 mg.min/L or 11.7 min at 3 ppm of chlorine (Figure 10.4). Operators have the potential to maximize the speed of degradation of saxitoxin by increasing chlorine dose, as long as no other related factors are detrimentally affected (such as production of disinfection by-products in distribution systems where water is blended with surface water).

While chlorine is not normally dosed in drinking water at 4 ppm due to the objectionable taste, chlorination in the distribution system may be an effective final barrier for toxin removal in the treatment train. While it may not be required in practice, chlorination could be used to form another layer of treatment to provide confidence for operators and water authorities during toxic blooms.

Taste and odor compounds like geosmin are not degraded by chlorination. Geosmin is very well detected by smell and taste, at around 10 ng/L, but is not toxic. It is therefore regularly detected by customers of river and reservoir water. It will be removed moderately well by RO (80-95%) (Dixon et al. 2010, 2011a) and more so by a full two pass RO. Typical bloom concentration in river and reservoir sources can be as high as 100 ng/L. The instrument detection limit for GC/MS is 4 ng/L and a full two pass system will approximately produce a permeate concentration of this value given a worst-case scenario, if geosmin is allowed to stay intracellular for best removal during pretreatment.

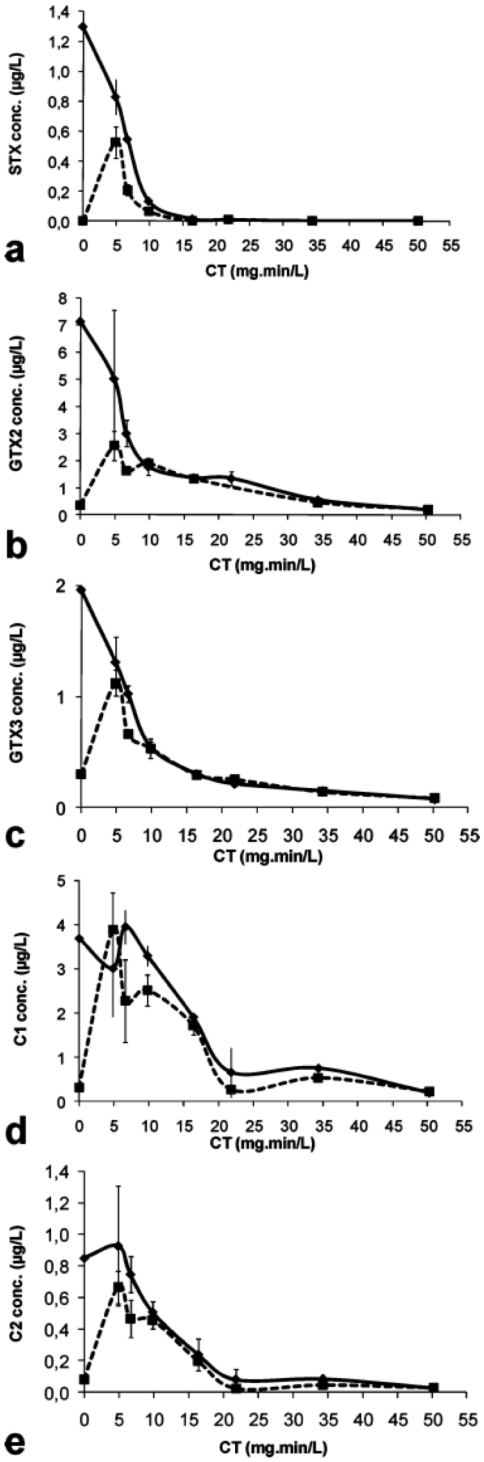



**Figure 10.4.** Toxin oxidation in Myponga Reservoir water at pH 8 with 3 mg/L (solid line) chlorine dose (a) STX, (b) GTX2 (c) GTX3 (d) C1 and (e) C2. (Dashed line represents chlorination at 2 mg/L) (modified from Zamyadi et al. 2010)

Operators may consider chlorination experiments on remineralized distillate/permeate to see whether chlorination is effective in fresh water and whether a lower dose than that used by Laycock et al. (2012) might be effective in degrading saxitoxin and okadic acid. As degradation of toxins is pH dependent, this would need to be investigated in these experiments. Given the current status of research on the effect of chlorination in degrading marine toxins, further work is clearly required for greater confidence in chlorination as a final barrier to all common HAB toxins.

## 10.10 SUMMARY

This chapter describes the process steps within SWRO and thermal desalination that specifically remove HAB toxin and taste and odor compounds and the limitations of each process step. The general principle for HAB toxin and taste and odor compound removal is to ensure toxin remains intracellular to maximize the removal efficiency of each pretreatment step. By avoiding chlorination of the intake or any shock chlorinations during a HAB bloom, cells will not be ruptured and release toxin. In SWRO plants, extracellular toxin is difficult for the downstream processes to remove, apart from the RO process. DAF will effectively remove intact cells to approximately greater than 90%, thus removing intracellular toxin along with the cells. GMF will remove similar percentages of intracellular toxins to DAF.

UF/MF will remove greater than 99% of HAB cells and associated intracellular toxins, although some minor leakage of toxins from the cells may occur due to shear and pressure in the unit process. RO is the major toxin removal step and removes greater than 99% of extracellular toxin. A two pass system will remove another 99% of the remaining 1% extracellular toxin, although operators should take care to assess a partial split two pass system. Taste and odor compounds are difficult to remove when extracellular. Should off taste and odor occur with the HAB bloom, pretreatment will remove intracellular compounds to greater than 90% (similar to removal of toxins), while each full RO pass will remove 60-80% of the extracellular taste and odor. Chlorination will not remove taste and odor compounds. As common HAB tase and odor compounds can be detected at around 10ng/L, single pass RO systems may experience customer complaints. Any sludge produced from pretreatment will still contain toxin and care must be taken when considering any supernatant return to the plant or disposal of the sludge. Removal of toxins from thermal systems should be in the order of 99%, and toxin should exit the plant in the brine. As an additional barrier to toxin removal, some toxins are denatured by chlorination, for example saxitoxin (STX) will be removed with a CT of 15 µg.min/L. Thus the inherent multiple barrier approach to seawater desalination systems creates an effective removal system for HAB toxin with built in redundancy.

## 10.11 REFERENCES

Azanza, M. P. V., Azanza, R. V., Gedaria, A. I., Sententa, H. G., and Idjao, M. V. 2001. Decimal reduction times of *Pyrodinium bahamense* var. compressum and *Escherichia coli* in chlorine- and ultraviolet-treated seawater. *Letters in Applied Microbiology* 33(5), 371-376.

Bellona, C., Drewes, J. E., Xu, P., and Amy, G. 2004. Factor affecting the rejection of during NF/RO treatment - a literature review. *Water Research* 38, 2795-2809.

Boerlage, S. F. E., and Nada, N. 2014. Algal toxin removal in seawater desalination processes, In: *Proceedings of European Desalination Society*, Cyprus.

Campinas, M., and Rosa, M. J. 2010. Evaluation of cyanobacterial cells removal and lysis by ultrafiltration. *Separation and Purification Technology* 70, 345-353.

Chemspider. 2016. www.chemspider.com. Royal Society of Chemistry, Accessed 13 Feb 2016.

Chow, C. W. K., Drikas, M., House, J., Burch, M. D., and Velzeboer, R. M. A. 1999. The impact of conventional water treatment processes on cells of the cyanobacterium *Microcystis aeruginosa*. *Water Research* 33(15), 3253–3262.

Chow, C.W.K., House, J., Velzeboer, R.M.A., 1998. The effect of ferric chloride flocculation on cyanobacterial cells. *Water Research* 32, 808–814.

Chow, C. W. K., Panglish, S., House, J., Drikas, M., Burch, M. D., and Gimbel, R. 1997. A study of membrane filtration for the removal of cyanobacterial cells. *Aqua,* 46(6), 324–334.

Daly, R. I., Ho, L., and Brookes, J. D. 2007. Effect of chlorination on *Microcystis aeruginosa* cell integrity and subsequent microcystin release and degradation. *Environmental Science and Technology* 41(12), 4447-4453.

DesalData. 2015. Worldwide desalination inventory (MS Excel Format), downloaded from DesalData.com (GWI/IDA) 2015.

Desormeaux, E. D., Meyerhofer, P. F., and Luckenbach, H. 2009. Results from nine investigations assessing Pacific Ocean seawater desalination in Santa Cruz, California. Proceedings of the IDA World Congress, Dubai, UAE, November 2009.

Desormeaux, E. D., Meyerhofer, P. F., Luckenbach, H., and Kudela, R. M. 2011. Pilot-testing multiple pretreatment systems for seawater desalination. *IDA Journal of Desalination and Reuse* 3(1), 42-52.

Dixon, M. B. 2014. Removal of toxin and taste & odor compounds using membranes and associated processes. Proceedings of the Middle East Desalination Research Centre's HABs and Desalination workshop, Muscat, Oman, April 2014.

Dixon, M. B., Churman, H., and Henthorne, L. 2015. Harmful algae blooms and desalination: a cells journey from sea to SWRO. *Proceedings of the IDA World Congress*, San Diego, California, Sept 2015.

Dixon, M. B., Falconet, C., Ho, L., Chow, C. W. K., O'Neil, B., and Newcombe, G. 2010. Nanofiltration for the removal of algal metabolites and the effects of fouling. *Water Science and Technology* 61, 1189–1199.

Dixon, M. B., Falconet, C., Ho, L., Chow, C. W. K., O'Neil, B. and Newcombe, G. 2011a. Removal of cyanobacterial metabolites by nanofiltration from two treated waters. *Journal of Hazardous Materials* 188(1), 288–295.

Dixon M. B., Ho, L., Chow, C., Newcombe, G., Croue, J-P., Buisson, H., Cigana, J., and Treuger, R. 2012. Water Research Foundation Report #4016: Evaluation of integrated membranes for taste and odour and algal toxin control, Published by Water Research Foundation, Denver, Colorado, USA.

Dixon, M. B., Richard, Y., Ho, L., Chow, C. W. K., O'Neil, B. and Newcombe, G. 2011b. A coagulation-powdered activated carbon-ultrafiltration – Multiple barrier approach for removing toxins from two Australian cyanobacterial blooms. *Journal of Hazardous Materials* 186(2), 1553–1559.

Dixon, M. B., Richard, Y., Ho, L., Chow, C. W. K., O'Neil, B., and Newcombe, G. 2011c. Integrated membrane systems incorporating coagulation, activated carbon and ultrafiltration for the removal of toxic cyanobacterial metabolites from *Anabaena circinalis*. *Water Science and Technology* 63(7), 1405-1411.

Drikas, M., Chow, C. W. K., House, J. and Burch, M. D. 2001. Using coagulation, flocculation, and settling to remove toxic cyanobacteria. *Journal American Water Works Association* 93, 100–111.

Fujioka, T., Tu, K. L., Khan, S. J., McDonald, J. A., Roux, A., Poussade, Y., Drewes, J. E., and Nghiem. L .D. 2014. Rejection of small solutes by reverse osmosis membranes for water reuse applications: a pilot-scale study. *Desalination* 350, 28-34.

Gille, D. 2003. Seawater intakes for desalination plants. *Desalination* 156(1), 249-256.

Kutty P. C. M., Nomani, A. A. and Thankachan,T. S. 1994. Carry over of some high molecular weight organics from seawater to MSF distillates SWCC RDC 25 Technical Report.

Ladner, D. A. 2009. Effects of bloom-forming algae on fouling of integrated membrane systems in seawater desalination. PhD dissertation, University of Illinois at Urbana-Champaign.

Laycock, M. V., Anderson, D. M., Naar, J., Goodman, A., Easy, D. J., Donovan, M. A., Li, A., Quilliam, M. A., Al Jamali, E., and Alshihi, R. 2012. Laboratory desalination experiments with some algal toxins. *Desalination* 293, 1-6.

Lefebvre, K. A., Bill, B. D., Costa, P. R., Nance, S., Erickson, A., Trainer, V. L., and Baugh, K. A. 2008. Characterization of intracellular and extracellular saxitoxin levels in both field and cultured *Alexandrium* spp. samples from Sequim Bay, Washington. *Marine Drugs* 6(2), 103-116.

McDowall, B. 2008. Removal of geosmin and 2-methylisoborneol from drinking water through biologically active sand filters. PhD Thesis, The University of Adelaide.

Newcombe, G. 2011. Personal Communication.

Newcombe, G., House, J., Ho, L., Baker, P., and Burch, M. 2010. Management strategies for cyanobacteria (blue-greenalgae): a guide for water utilities: cooperative research centre for water quality and treatment research report #74.

Pierce, R. H., Henry, M. S., Higham, C. J., Blum, P., Sengco, M. R. and Anderson, D. M. 2004. Removal of harmful algal cells (*Karenia brevis*) and toxins from seawater culture by clay flocculation. *Harmful Algae* 3(2), 141–148.

Qian, F., Dixon, D. R., Newcombe, G., Ho, L., Dreyfus, J. and Scales, P. J. 2014. The effect of pH on the release of metabolites by cyanobacteria in conventional water treatment processes. *Harmful Algae* 39, 253-258.

Resosudarmo, A. Ye, Y. Le-Clech, P.. amd Chen, V. 2014. UF pretreatment for desalination during algal blooms: Negative effects of stress and benefits of hybridised systems. Proceedings of the HABs and Desalination Worksop, Muscat, Oman April 2014.

Schaefer, A., Akanyeti, I., and Semiao, A. J. C. 2011. Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens. *Advances in Colloid and Interface Science* 164(1–2), 100-117.

Schoonenberg Kegel, F., Rietman, B. M., and Verliefde, A. R. D. 2010. Reverse osmosis followed by activated carbon filtration for efficient removal of organic micropollutants from river bank filtrate. *Water Science and Technology* 61(10), 2603-2610.

Seubert, E. L., Trussell, S., Eagleton, J., Schnetzer, A., Cetinic, I., Lauri, P., Jones, B. H., and Caron, D. A. 2012. Algal toxins and reverse osmosis desalination operations: laboratory bench testing and field monitoring of domoic acid, saxitoxin, brevetoxin and okadaic acid. *Water Research* 46(19), 6563-6573.

Smith, J. L., Tong, M., Fux, E., and Anderson D. M. 2012. Toxin production, retention, and extracellular release by Dinophysis acuminate during extended stationary phase and culture decline. *Harmful Algae* 19, 125–132.

Teixeira, M. R., Sousa, V., and Rosa, M. J. 2010. Investigating dissolved air flotation performance with cyanobacterial cells and filaments. *Water Research* 44(11), 3337-3344.

Teixeira, M. R. and Rosa, M. J. 2006. Comparing dissolved air flotation and conventional sedimentation to remove cyanobacterial cells of *Microcystis aeruginosa*. Part I: The key operating conditions. *Separation and Purification Technology* 52(1), 84-94.

Teixeira, M. R. and Rosa, M. J. 2007. Comparing dissolved air flotation and conventional sedimentation to remove cyanobacterial cells of *Microcystis aeruginosa*. Part II. The effect of water background organics. *Separation and Purification Technology* 53(1), 126-134.

Verliefde, A. R. D., Cornelissen, E. R., Amy, G., Van der Bruggen, B., and Van Dijk, H. 2007. Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration. *Environmental Pollution* 146(1), 281-289.

Verliefde, A. R. D., Cornelissen, E. R., Heijman, S. G. J., Verberk, J. Q. J. C. and Amy, G. L. 2009. Construction and validation of a full-scale model for rejection of organic micropollutants by NF membranes. *Journal of Membrane Science* 339(1), 10-20.

Velzeboer, R., Drikas, M., Donati, C., Burch, M., and Steffensen, D. 1995. Release of geosmin by *Anabaena circinalis* following treatment with aluminium sulphate. *Water Science and Technology* 31, 187–194.

Villacorte, L. O. Algal Blooms and Membrane Based Desalination Technology, UNESCO-IHE PhD Thesis Dissertation, May 20 2014.

Wiley, R. 2014. Proceeding of the American Membrane Technology Membrane Technology Conference, March 2014, Las Vegas, NV.

Wang D.-Z. 2008. Neurotoxins from marine dinoflagellates: a brief review. *Marine Drugs* 6(2): 349-371.

www.latoxan.com. Natural Active ingredients, Accessed 13 Feb 2016.

Zamyadi, A., Ho, L., Newcombe, G., Daly, R. I., Burch, M., and Baker, P. 2010. Release and oxidation of cell-bound saxitoxins during chlorination of *Anabaena circinalis* cells. *Environmental Science and Technology* 44(23), 9055-61.

Zhu, I. X. and Bates, B. 2012. Seawater desalination pretreatment for harmful algae blooms using dissolved air flotation. *IDA Journal of Desalination and Water Reuse* 4(1), 34-37.

Zhu, I. X., Bates, B. J. and Anderson, D. M. 2014. Removal of *Prorocentrum minimum* from seawater using dissolved air flotation. *Journal of Applied Water Engineering and Research* 2(1), 47-56.