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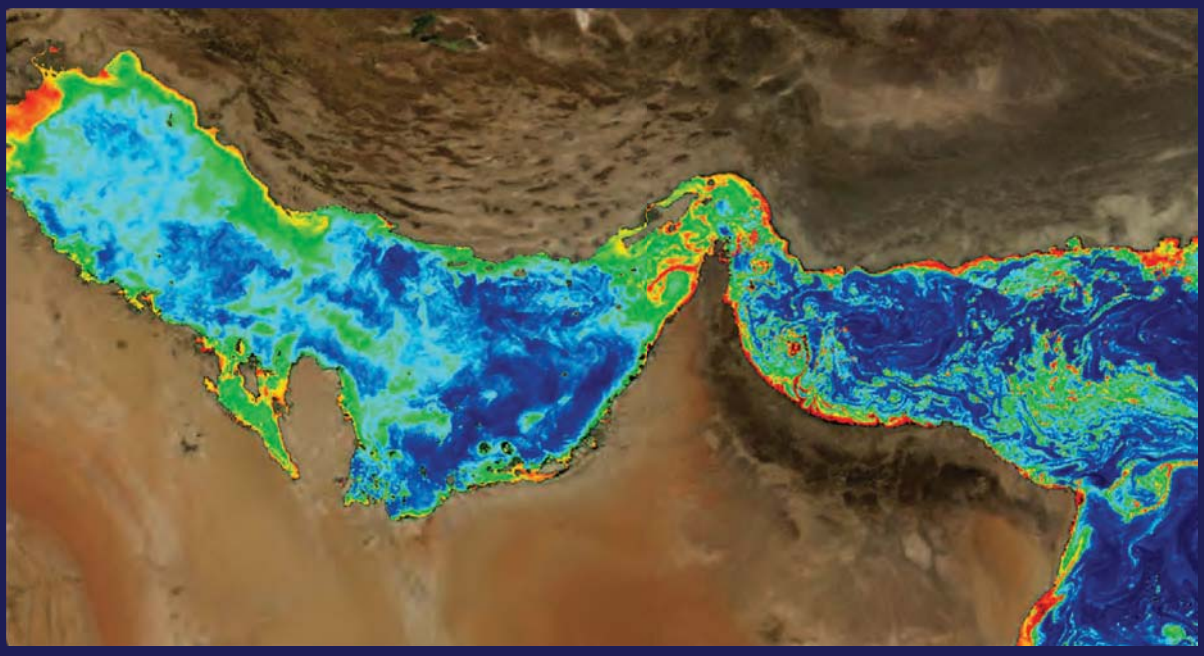
Harmful Algal Blooms (HABs) and Desalination: A Guide to Impacts, Monitoring, and Management



Edited by:

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5 HARMFUL ALGAL BLOOM-RELATED WATER QUALITY MONITORING FOR DESALINATION DESIGN AND OPERATION

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5.1 INTAKE FEEDWATER CHARACTERIZATION AND WATER QUALITY MONITORING

Characterization of the raw seawater at plant intakes and monitoring to detect poor water quality events including harmful algal blooms (HABs) is critical throughout the lifetime of a desalination plant. HABs can result in a substantial increase in the organic and solids load in the seawater feed to be treated at a desalination plant. This may result in an increase in the clogging of granular media filters and accelerated particulate and/or (bio)fouling of pretreatment and reverse osmosis membranes (see Chapter 2). Other feedwater quality changes may be observed during or following a HAB event, such as a reduction in dissolved oxygen levels and continued high concentration of organics due to decomposition of algal matter by bacteria when the algal bloom degrades. Seawater in areas that are prone to algal blooms or silt inflow etc. may require additional pretreatment if events are frequent and/or of long duration (Chapter 9).

Depending on the project structure and site, an extensive seawater quality assessment study may be conducted prior to plant design to provide the raw seawater quality design envelope, select pretreatment and/or to obtain environmental permits. The study may include a review of historical seawater quality such as the frequency and severity of algal blooms, hydrodynamic conditions at the intake area and consider diffuse and point pollution sources

around the intake area which may impact water quality (e.g., ballast water exchange in port areas that may promote HABs).

Subsequently, during plant operation, water quality monitoring of the intake feedwater (online or through sampling) is essential for process control and contractual purposes to:

- confirm the influent seawater is within the raw water design envelope in which case the plant is required to meet production and product water quality specifications;
- allow analysis of data relative to baseline data collected prior to design to identify seasonal or diurnal trends and to detect poor water quality events such as HABs;
- optimize pretreatment processes in response to a deterioration in feedwater quality due to events such as a HAB in order to maintain production and water quality targets; and
- allow the operational performance of downstream plant unit processes to be assessed against the intake values e.g. dissolved air flotation (DAF), granular media filtration (GMF), seawater reverse osmosis (SWRO), residual handling.

During a HAB event, desalination plant operators require methods to measure the concentration of algae and algal organic matter (AOM), its fouling constituents, and any increases in membrane fouling potential and other HAB associated water quality changes in the raw water and treatment process streams. This allows operators to respond to a bloom in a timely manner to optimize plant operation to avoid disruption to supply.

This chapter examines the ability of conventional water quality parameters routinely used in desalination feedwater monitoring during design, piloting, and SWRO plant operation to detect HABs and characterize water quality during a bloom. Although the focus is on water quality parameters monitored at the intake, key parameters commonly used within SWRO desalination plants to assess the reduction in the particulate fouling potential (i.e. the Silt Density Index (SDI)) and organic load of the raw water (e.g. total organic carbon) through pretreatment are discussed. More sophisticated and lesser known techniques that are under development to directly measure AOM or assess the biofouling and/or particulate fouling potential of feedwater are presented to provide an overview to plant operators when evaluating additional tests during a HAB event. Applications of these techniques are presented to illustrate their use.

Methods which directly identify the presence of HAB species in the seawater feed through algal cell identification and enumeration or an increase in algal productivity (such as chlorophyll-*a* measurements or advance warning through remote sensing) are discussed in Chapters 3 and 4, respectively.

5.2 SUITABILITY OF CONVENTIONAL ONLINE WATER QUALITY PARAMETERS TO DETECT HABS

Online instrumentation typically installed at a SWRO desalination plant intake to continuously monitor feedwater quality may include temperature, conductivity, dissolved oxygen (DO), pH, turbidity, residual chlorine and dissolved hydrocarbons. These online parameters can be monitored, trended and viewed in the control room to assess raw feedwater quality and the impact of water quality changes on the efficiency of unit processes such as pretreatment and desalination. None of the aforementioned parameters are specific to algal blooms. Changes in the core physiochemical parameters monitored (temperature, conductivity, DO, pH, and turbidity) can be caused by other factors such as pollution events and/or marine hydrodynamics, thus the interpretation of these water quality variables can be

complex. At best they can indirectly indicate conditions that favor a bloom, the presence of algal blooms, or associated with the termination of a bloom, such as DO depletion as discussed below.

5.2.1 Temperature

Temperature, a key desalination water quality process parameter, is trended at almost all desalination plants. Some algal species are known to bloom under specific ranges of temperature, e.g., *Trichodesmium,* commonly responsible for red tide outbreaks in the Gulf, favors seawater temperatures ranging from 20 – 34˚C (Thangaraja et al. 2007 cited in Zhao and Ghedira 2014). Alternatively, changes in temperature may indicate downwelling or upwelling events that can bring nutrients or established blooms to the plant intake.

5.2.2 Salinity (conductivity)

Salinity at plant intakes is typically calculated from online conductivity measurements using a correlation of total dissolved solids (TDS) and conductivity.[1] Many algal species have a broad tolerance for salinity, particularly those endemic to estuarine regions. Nevertheless, there are salinity ranges that are optimal for a HAB, as well as those that are too high or low for rapid growth. A particular salinity range in combination with temperature may promote growth of a specific bloom-forming algal species or break the dormancy of an algal cyst (Chapter 1). Alternatively, a change in salinity outside the tolerance range of an algal species may result in the termination of a HAB or changes in the species assemblage in a bloom community. Hence, monitoring changes in salinity and temperature at a plant intake may be useful where an algal blooming species routinely occurs.

5.2.3 pH

Monitoring of pH to detect blooms is complex and typically not useful for the purposes of detecting or characterizing HABs. The pH of seawater is around 8.2 and does not normally vary substantially due to the vast buffering capacity of the seawater bicarbonate-carbonate system. As a result of estuarine input, however, pH may increase or decrease depending on the salinity and evaporative effects on the estuary. Dense algal blooms in shallow coastal areas with limited tidal exchange may also cause a local pH change – leading to both increases and decreases in pH. As algae consume carbon dioxide during photosynthesis during daylight hours, removing it from the water, less carbonic acid dissociates and a pH rise can occur. During the night, when there is no photosynthesis, CO_2 is released by respiring cells, leading to a decrease in pH. When the bloom ends and the algal biomass degrades, CO_2 is again released and pH decreases. Diurnal changes in pH may subsequently occur due to bacterial decomposition and aerobic respiration.

5.2.4 Dissolved oxygen

As with pH, diurnal changes in online DO may also reflect algal photosynthesis and respiration as well as tidal exchange, which can replenish DO levels. Elevated DO may be observed in the photic zone (or sunlight zone) through photosynthesis. In contrast, a rapid decrease in DO may occur in stratified coastal water due to the respiratory activity of a bloom, or to bacterial decomposition of algal biomass as blooms age and decay, sinking to the seabed and sometimes leading to hypoxic conditions (<0.5 mg/L) or even anoxia. Hence, a decline in online DO may be observed depending on the depth of the intake, and DO trends may be used to indicate a HAB. Anoxic events due to DO depletion were observed at the La Chimba SWRO desalination plant, leading to the presence of hydrogen sulphide in the

[1] Caution should be taken when comparing this salinity with that measured by conductivity, temperature, and depth (CTD) sensors at sea which calculate salinity using the Practical Salinity Scale (Boerlage 2012).

feedwater due to the proliferation of sulphate-reducing bacteria that prolifereate under low DO conditions (see Chapter 11, section 11.6). Low DO can also be caused by pollution events and therefore needs to be assessed in conjunction with other water quality testing such as SDI, total organic carbon, and cell counts.

5.2.5 Turbidity

Turbidity, based on the amount of visible light (400 – 700 nm) scattered by particles in solution, generally increases with a greater load of suspended solids. While turbidity provides some information on particle concentration and water clarity[2], measurements can be inaccurate at both high and low levels. Scattered light is the aggregate response for all particles; the physical properties of particles such as color, shape, size distribution and numbers all affect the light scattering properties of a solution. When particles are in the wavelength range of visible light, turbidity is at a maximum (Edzwald and Tobiason 2011). In contrast, turbidity meters have been reported to be insensitive to small colloidal particles - particles with a diameter less than half the wavelength of visible light (0.2 μm) will not produce significant scatter (Kremen and Tanner 1998). Therefore, turbidity will decrease for smaller particles due to poor light scattering, while if the total particle mass remains constant, turbidity will also decrease for larger particles due to the decreased number or concentration (Edzwald and Tobiason 2011). Moreover, as noted by Tabatabai (2014a), transparent exopolymer particles (TEP), a component of AOM, do not absorb visible light. In some cases, high chlorophyll correlates well with high turbidity, but this is not always the case, as suspended materials like sand or clay will have similar light-scattering properties as algal cells. Turbidity is thus only a general indicator of algal blooms and cannot be relied upon to detect a bloom or an increase in particles associated with a bloom. Other confirmatory measures are needed such as those provided by chlorophyll sensors, or through direct cell counts.

5.3 OVERVIEW OF PARAMETERS TO DETERMINE ORGANIC MATTER

Total organic carbon (TOC) and dissolved organic carbon (DOC) are common measures of the concentration of organics at desalination plant intakes and are used to assess the efficiency of pretreatment processes in removing organics. Ultraviolet absorption at 254 nm (UV_{254}) and the related specific ultraviolet absorbance (SUVA) are used to a lesser extent. The maximum, average, or median concentration of these parameters may be provided as part of the raw seawater design envelope to characterize the organic load in the seawater to be desalinated.

Standards from ASTM International and Standard Methods for the Examination of Water and Wastewater (APHA 2012) are often recommended by membrane manufacturers for the analysis of these aforementioned parameters. In addition, these protocols may be specified in design and/or operation and maintenance (O&M) contracts for analysis of the saline feed and desalination process streams (see Table 5.1). In general, these parameters can be quickly and reliably determined by laboratories experienced in the analysis of saline matrices with some parameters determined by on site laboratories. These parameters are routinely measured on a weekly or monthly basis at the seawater intake depending on the site (e.g. to monitor the potential for HABs and/or pollution or to check the feedwater is within design specifications). Monitoring may also occur upstream and downstream of pretreatment processes to assess performance or in the RO feedwater for compliance with membrane guarantees. The

[2] Secchi disks - another method to measure water clarity are discussed in Chapter 3.

frequency of monitoring may increase when a bloom event is forecast or during a bloom to adjust operating parameters for process steps accordingly.

The aforementioned techniques measure aggregate organic matter and therefore provide no specific information as to the composition or concentration of potential AOM foulants produced during an algal bloom. TOC measures both organic matter derived from natural processes such as HABs, bacteria, riverine flushing or through direct anthropogenic input. Therefore, spikes in feedwater TOC may be due to an algal bloom and/or pollution or other events. Moreover, increases in TOC are not always observed during a bloom event. Feedwater TOC increased significantly in the Red Sea off the coast of Saudi Arabia during an algal bloom (pers. com. N. Nada) and also in the source seawater during testing of Long Beach Water Department's demonstration seabed infiltration gallery during blooms (see Chapter 6 Section 6.4.1.6). Yet, in other cases, TOC has not significantly increased during a bloom. The latter may be attributed to underestimating TOC if floatable organics are not captured during sampling or sample homogenization (Table 5.1). Measuring TOC removal to assess the efficiency of pretreatment processes is also inaccurate due to the difficulties in measuring low-level TOC residuals in seawater process streams. In high temperature catalytic oxidation measurement of organic carbon in seawater, the high salt concentration (in the range of 30,000 to 45,000 mg/L) compared to a few mg/L of organic carbon, results in low accuracy and high limits of detection for TOC measurements. Consequently, TOC results are often interpreted in conjunction with chlorophyll-*a* and algal counts (where available) and other more standard plant water quality monitoring parameters such as SDI, turbidity, total suspended solids, and DO to assess the occurrence of algal blooms in the intake water.

Although, UV_{254} and TOC can be determined online, these instruments are not frequently installed at SWRO plants. As with TOC, UV_{254} is an aggregate parameter, but only for selected organic constituents such as lignin, humic acids, and various aromatic compounds which strongly absorb UV radiation (APHA 5910B). SUVA, the quotient of UV_{254} and DOC, provides an indication of dissolved natural organic matter measured by UV_{254} compared to the overall dissolved organic concentration and can be used to indicate whether the dissolved organic matter is primarily derived from natural processes occurring at the intake rather than anthropogenic sources. Algal organic matter may contain some UV-absorbing compounds, but their proportion among AOM components significantly varies among species releasing them. Moreover, carbohydrates (i.e., polysaccharides produced by algae and marine bacteria) do not absorb UV (APHA 5910B) and therefore UV_{254} cannot be relied upon to monitor or measure AOM in the raw water or treatment process streams.

More sophisticated techniques to characterize the composition and concentration of AOM in seawater have been developed or are under development such as liquid chromatography - organic carbon detection (LC-OCD) to determine biopolymers or measurement of TEP, (compounds demonstrated to promote fouling in SWRO and ultrafiltration (UF) – see Chapter 2) and other AOM components as shown in Figure 5.1. While these methods offer more targeted information (and higher sensitivity) of AOM constituents and potential foulants in a feedwater, the degree of difficulty and cost in determining them is correspondingly higher. As yet, samples need to be sent to specialized laboratories with experience in determining these parameters, which are limited in number, resulting in delays to obtain results. Hence, at present they cannot be employed directly as a trigger to alert a plant of a bloom in the incoming feedwater or to adjust process parameters during plant operation. Nonetheless, these parameters are expected to be a key factor in developing an understanding in controlling AOM fouling in seawater UF and RO systems as they allow quantification of specific foulant components of AOM not detectable by standard monitoring parameters, including those components which are likely to cause membrane fouling.

Table 5.1 provides a summary of conventional analytical techniques used in desalination to determine organic matter in seawater along with the more advanced techniques to determine natural organic matter (NOM) and AOM, comparing the principle of each method, interferences, organic matter fraction identified, and operator skill required for the test. The more advanced techniques are discussed in detail in the following sections.

It should be noted that all these methods were originally developed for characterization of NOM regardless of its origin (microbial or terrestrial input); however, during a HAB a significant fraction of NOM will be comprised of AOM. TEP present in seawater can be a mixture of those produced by bacteria, HABs, and shellfish. While there is no technique to distinguish TEP based on their origin, during a HAB most TEP will be generated by algae. Following the collapse of an algal bloom the succession of bacterial species which can thrive on decaying AOM may release organic matter extracellularly including TEP and contribute to the organic load in the source seawater.

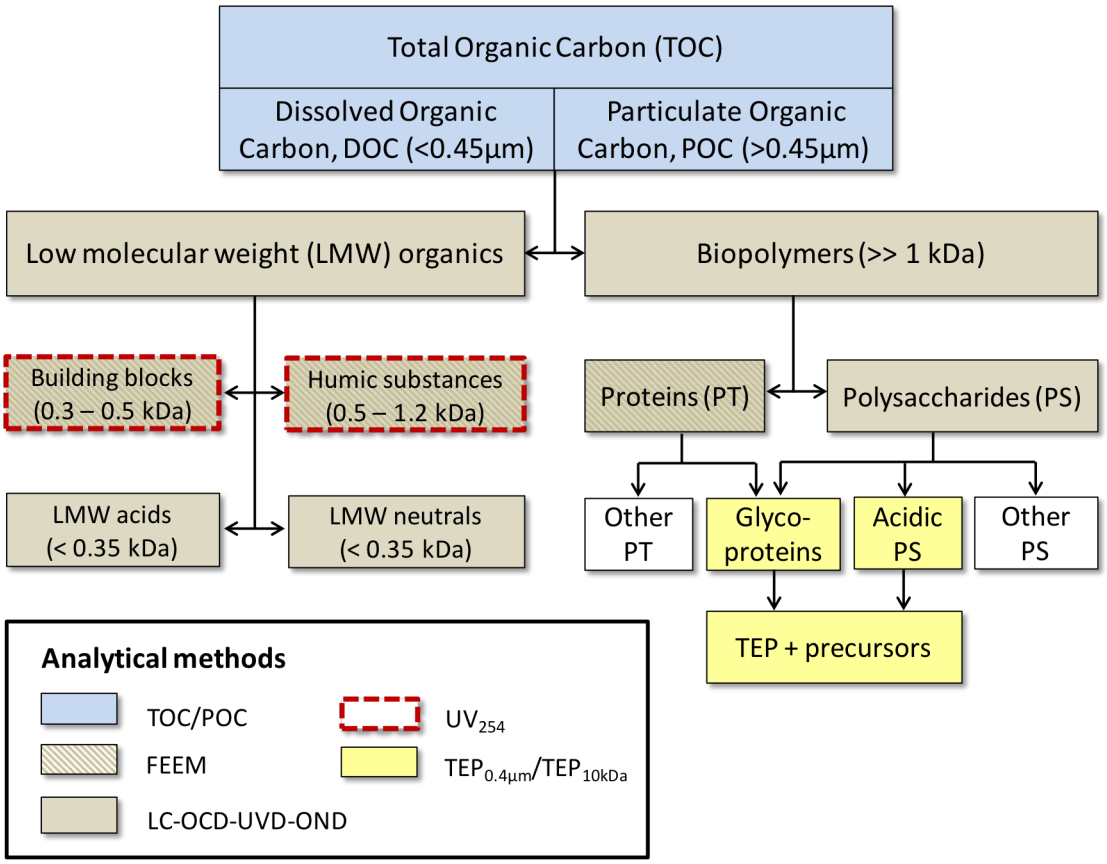

Figure 5.1. Major components of aquatic organic matter and corresponding analytical techniques for their identification and quantification. Legend: LC is liquid chromatography with inline detectors for organic carbon (OCD), UV absorbance at 254 nm (UVD,) and organic nitrogen (OND). FEEM is fluorescence excitation-emission matrices. TEP refers to transparent exopolymer particles measured with a 0.4 µm or 10 kDa membrane.

Table 5.1. Comparison of conventional and advanced parameters to measure organic matter in seawater and feedwater.

Parameter	Standard / Reference	Basis of Method	Organic matter (OM) identified	Interferences / Issues	Analysis time / Operator skill
Conventional water quality parameters					
Total organic matter (TOC) mg/L	ASTM D2579[a], D4129, D4839, APHA5310B, 5310C	Homogenize sample, acidify and sparge to remove inorganic carbon. Oxidation of organic matter by (i) high temperature combustion or (ii) persulfate-UV or heated-persulfate. Detection of CO_2 via NDIR[b] or conductivity. Limit of detection defined by instrument and method.	Aggregate parameter dissolved and particulate organic carbon. Non specific OM test. Natural and anthropogenic in origin.	510 B – potential loss of floating organic matter, particle size limited by injection syringe needle≈500µm 5310C – high turbidity, high chloride requires modification of method.	1-2 hours including preparation / routine inexpensive test. Standard test for most saline water laboratories.
Dissolved organic carbon (DOC) mg/L	As above	Filtration through 0.45 µm filter and analysis of filtrate as above.	Dissolved organic carbon <0.45µm. Non specific OM test. Natural and anthropogenic in origin.	5310C – high chloride requires modification of method.	As above.
Ultraviolet absorption at 254nm (UV_{254}) cm^{-1}	APHA 5910B	Filtration through 0.45µm. Absorbance at 254 nm measured with UV/Vis spectrophotometer.	Specific to aromatic organics. Carbohydrates (e.g. polysaccharides) and carboxylic acids do not absorb UV light and are not measured.	Turbidity, UV absorbing inorganics (ferrous iron, high bromide concentrations).	Less than one hour routine inexpensive test.
Specific ultraviolet absorbance (SUVA) L/mg.m	APHA 5910B/APHA5310	Calculated from UV_{254}/DOC		As above.	As per TOC test.

Table 5.1. *(Continued)*

Parameter	Standard / Reference	Basis of Method	Organic matter (OM) identified	Interferences / Issues	Analysis time / Operator skill
		Advanced organic matter (OM) characterization methods			
Liquid chromatography – organic carbon detection LC-OCD	Huber et al. 2011	Size-exclusion chromatography followed by in line detectors for (i) organic carbon, (ii) UV absorbance at 254 nm and (iii) organic nitrogen. Area integration of identified chromatogram peaks using customized software. Pre-filtration of sample through 0.45µm filter. Limit of detection is fraction specific and may be affected by water matrix.	Chromatographable hydrophilic DOC fractions such as biopolymers (proteins and polysaccharides), humic substances, building blocks, low molecular weight acids and neutrals.	Chromatographic columns may adsorb or trap hydrophobic and/or high molecular weight OM components (biopolymers). Particulate OM and large molecular TEP > 0.45 µm excluded due to inline filtration through 0.45 µm filter (the standard method for LC-OCD) or >2 µm without filtration. No standard method, nor calibration when bypassing the 0.45 µm filter.	Expensive technique which requires specialized equipment and high degree of operator skill; sample measurement and analysis time is up to 5 hours. Shipping of sample is location dependent.
Fluorescence excitation-emission matrices (F-EEM)	Coble et al. 1993	Sample is excited to a specific wavelength at which AOM fluorophores absorb light and subsequently emit the light at longer wavelength. This technique is performed using a spectrofluorometer across a spectrum of light wavelengths. The acquired data is then plotted in a 3D fluorescence contour for analysis.	Humic-like and protein-like compounds <0.45µm Fluorescence index (FI)c classification: FI = 1.7-2.0 (microbial origin); F = 1.3-1.4 (terrestrial origin)	Samples should be diluted below 1 mg C/L. Very sensitive to sample contamination. Does not detect non-fluorophore OM components. In principle, it covers only humic and fulvic-like components, part of biopolymers (proteins) and part of TEP (glycoproteins).	Inexpensive technique that requires specialized equipment and medium degree of operator skill; 0.5-1 hour of analysis time.

Table 5.1. *(Continued)*

Parameter	Standard / Reference	Basis of Method	Organic matter (OM) identified	Interferences / Issues	Analysis time / Operator skill
Advanced organic matter (OM) characterization methods *(continued)*					
Transparent exopolymer particles ($TEP_{0.4\mu m}$)	Passow and Alldredge 1995	Retention on 0.4-µm filter, staining with Alcian blue (pH 2.5), sulfuric acid digestion and absorbance measurement at 787 nm. Calibration with Xanthan gum.	TEP (>0.4µm)	Overestimation of results due to interference of dissolved ions. Exclusion of the colloidal components (TEP precursors). A proposed modification for salinity control by rinsing with ultrapure water has been introduced (Villacorte et al. 2015c).	Medium degree of operator skill and standard lab equipment required, risk during concentrated acid handling, 2-3 hours of analysis time. Calibration performed for every batch of dye solution takes 4-5 hours.
TEP_{10kDa}	Villacorte et al. 2015c	Retention on 10 kDa membrane, resuspension in ultrapure water by sonication, Alcian blue (AB) staining, removal of precipitates through 0.1-µm filter and absorbance measurement of residual AB in the filtrate at 610 nm. TEP concentration is based on reduction of AB absorbance and calibration with Xanthan gum standard.	TEP (>0.4 µm) and their precursors (10kDa-0.4µm)	Overestimation of results due to release of intracellular AOM during the sonication step. Such release may vary significantly with species of algae.	Medium degree of operator skill and specific lab equipment required. 3-4 hours of analysis time. Calibration performed for every batch of dye solution takes 4-5 hours.

[a] Historical method remains in use but withdrawn from ASTM
[b] NDIR - non dispersive infrared analyzer
[c] Fluorescence index (FI) = ratio of fluorescence intensity at emission wavelength of 450 nm to that at 500 nm obtained at excitation wavelength of 370 nm.

It should be noted that a loss in concentration due to adsorption of AOM components to sample bottle walls and/or degradation by bacteria can be an issue for all the analytical methods mentioned in Table 5.1 (TOC, UV, LC-OCD, FEEM, TEP). Therefore, samples should be cooled (typically at 5°C) and analyzed as soon as possible after collection. Concentration loss may vary from sample to sample. It is generally acceptable to follow the standard protocol for preservation and transport for DOC/TOC samples for all these analytical methods.

5.3.1 Advanced methods to determine algal organic matter

Advanced methods to determine NOM include FEEM, LC-OCD and TEP; the latter two can provide more information on the composition and concentration of fouling AOM compounds produced during a bloom. FEEM analysis provides insight into the presence and concentration of humic-like, fulvic-like and protein-like organic matter. As such, only a fraction of AOM, i.e. (glyco)proteins, can be determined by FEEM analysis resulting in an underestimation of the concentration and composition of organic matter during a HAB (see Figure 5.1 and Table 5.1). In contrast LC-OCD covers a wider range of NOM (and consequently AOM) fractions in terms of molecular weight, aromaticity and protein content, while TEP methods provide more information on a subset of biopolymers i.e. glycoproteins and acidic polysaccharides.

5.3.1.1 Liquid chromatography – organic carbon detection (LC-OCD)

Liquid chromatography-organic carbon detection (LC-OCD) is a semi-quantitative technique for identifying and measuring different components of NOM in aquatic environments. The LC-OCD technique combines the physical separation capabilities of liquid chromatography with mass balancing on the basis of chromatographable dissolved organic carbon (CDOC) for identification and measurement of various fractions of NOM of different molecular weight. Figure 5.2 shows where the LC-OCD technique stands in the suite of analytical tools available for characterization of NOM. The technique was developed by Huber and co-workers based on the Gräntzel thin film reactor for high sensitivity carbon detection in the early 1990s (Huber and Frimmel 1991).

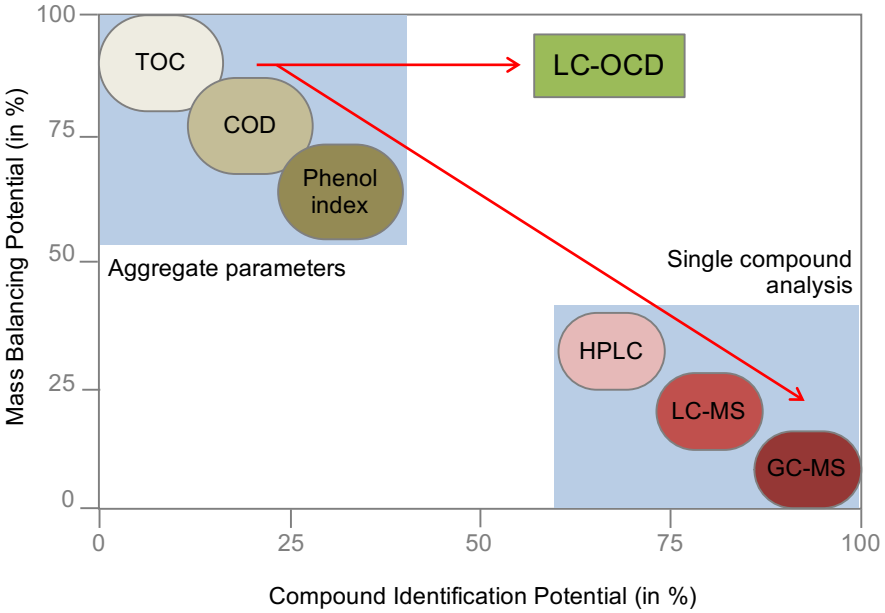

Figure 5.2. Position of LC-OCD in the suite of analytical tools for natural organic matter characterization (modified from www.doc-labor.de). Legend: HPLC is high performance liquid chromatography, LC-MS is liquid chromatography coupled with mass spectrometry and GC-MS is gas chromatography coupled with mass spectrometry.

Further developments of this technique have led to substantial reduction in footprint of the instrument (60 x 60 cm) and the introduction of a multi-detector system.

Current generations of LC-OCD utilize size-exclusion chroma-tography (SEC) and inline organic carbon detection, UV_{254}

detection and organic nitrogen detection (Huber et al. 2011). The detectors measure signal response of organic carbon, UV and organic nitrogen as a function of retention time of the organic component in the chromatographic column. DOC is determined using a bypass mode on the instrument.

Separation is achieved by differential exclusion of organic matter fractions through diffusion of hydrophilic dissolved organic carbon molecules (with 0.45 μm prefiltration) into resin pores of the column beads. In principle, larger molecules elute first as they cannot penetrate deep into the pores of the beads, while smaller molecules diffuse into the pores and elute later. Consequently, low molecular weight organics have higher retention time than compounds with high molecular weights. A customized software program (CHROMCalc) is used for data processing. Concentrations of organic carbon and organic nitrogen for different fractions is obtained by area integration of the chromatograms and with reference to calibration with standard organic compounds (International Humic Substances Society standards- Humic and Fulvic acids) (Huber et al. 2011). An example of a chromatogram is given in Figure 5.3 for North Sea water. Chromatographable dissolved organic matter is fractionated based on molecular weight, and to some extent in terms of major functional groups based on UV_{254} absorbance into five classes of compounds. The high molecular weight fraction (>>1 kDa) comprises non-UV absorbing biopolymers such as proteins and polysaccharides. The low molecular weight fractions (<1.2 kDa) comprise UV-absorbing humic substances and building blocks as well as biogenic substances such as low molecular weight organic acids and neutrals. A description of chromatographable dissolved organic matter fractions resolved by LC-OCD is presented in Table 5.2. Hydrophobic compounds e.g., natural hydrocarbons and sparingly soluble humics, do not elute from the column and are therefore excluded from the chromatograms and are referred to as non chromatographable hydrophobic organic carbon (HOC). HOC is determined as the difference between DOC and CDOC.

Table 5.2. Description of dissolved organic matter fractions measured by LC-OCD (DOC-Labor; Huber et al. 2011)

Organic fraction	Typical size range (Da)	Typical composition
Biopolymers	> 20,000	Very high in MW, hydrophilic, not UV-absorbing; typically polysaccharides, but may also contain proteins, amino sugars, polypetides (quantified on basis of OND), and aminosugars
Humic substances (HS)	500 – 1200	Humic and fulvic acids
Building blocks	300 – 500	Sub-units of HS and considered to be natural breakdown products of humics through weathering and oxidation
LMW neutrals	< 350	Low molecular weight, weakly or uncharged hydrophilic or slightly hydrophobic (amphiphilic) compounds appear in this fraction, e.g., mono-oligosaccharides, alcohols, aldehydes, ketones, amino acids
LMW acids	< 350	Aliphatic, LMW monoprotic organic acids co-elute due to an ion chromatographic effect. A small amount of HS may fall into this fraction and is subtracted on the basis of SUVA ratios

LMW is low molecular weight

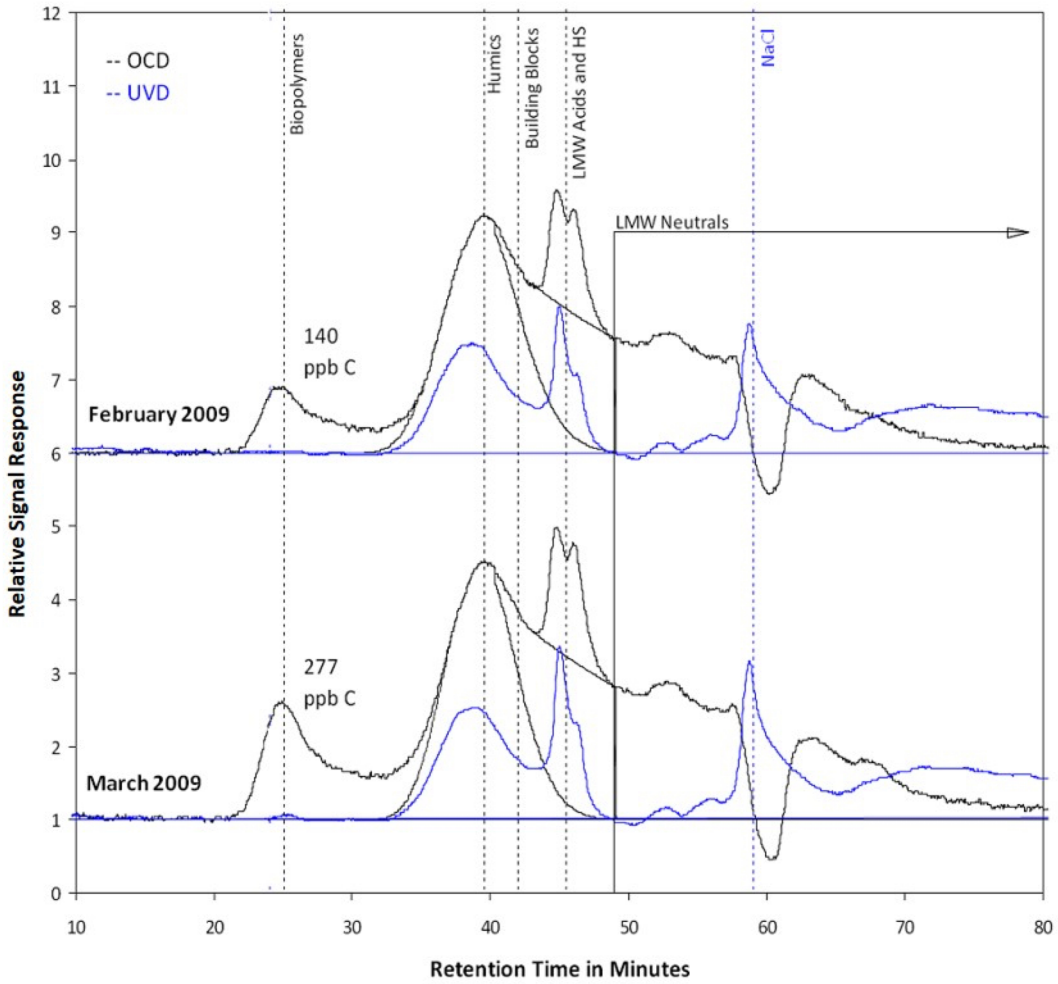

Figure 5.3. Typical signal responses generated by organic carbon detector (OCD) and UV_{254nm} detector (UVD) in coastal North Sea water samples and the assignment of the different organic matter fractions. The dip in OCD chromatogram within the LMW neutrals fraction is due to salinity, typical in seawater samples. Adapted from Villacorte et al. 2010.

High resolution LC-OCD, a recent development of DOC-Labor, provides better separation of biopolymers from humic substances using two columns instead of one. The first is only used to separate humic substances and low molecular weight compounds, whereas the separation of high molecular weight material is done on the second column. This gives semi-quantitative information on the molecular weight distribution of biopolymers into four fractions namely, 1000 kDa – 2 μm, 100-1000 kDa, 10-100 kDa, and < 10 kDa. Fractions are quantified based on area integration (area boundaries are defined by pullulan[3] standards). However, resolution is poor for the fraction < 10 kDa, as this fraction is superimposed by the building blocks and low molecular weight acids fractions. For this fraction the quantification is rather arbitrary and bias may well exceed 50%.

LC-OCD has been used to fractionate NOM in feedwater, brine and RO permeate and can be used to characterize and quantify AOM released during blooms in freshwater and seawater. Outside algal bloom periods, NOM in coastal seawater is mainly composed of low molecular weight aromatic compounds (e.g., humic substances) (Jeong et al. 2013). Algal-derived organic matter mainly comprises high molecular weight, hydrophilic, non-UV absorbing compounds, i.e., polysaccharides and proteins (Tabatabai 2014a; Villacorte et al. 2015a). A

[3] Pullulans are non-ionic extracellular polysaccharides excreted by the fungus *Aureobasidium pullulans*.

substantial increase in the biopolymer fraction is observed during severe algal blooms as shown in Figure 5.3 where an increase in biopolymer concentration was observed; from 140 ppb C in February 2009 outside of a bloom to 277 ppb C during a spring bloom in March 2009. Considering that high molecular weight AOM has been shown to cause irreversible fouling of low pressure membranes (microfiltration and ultrafiltration) and is likely to deposit and/or accumulate on SWRO membranes, monitoring the biopolymer fraction of organic matter in seawater is a promising indicator of organic and biological fouling potential of algal bloom-impacted waters.

The amount of proteins and polysaccharides in algal biopolymers can be estimated using LC-OCD. The organic carbon concentration of protein can be estimated based on the organic nitrogen content of the biopolymer fraction. Protein concentration is calculated by assuming that all organic nitrogen detected by the organic nitrogen detector between 25 and 42 minutes retention time are bound to proteinaceous compounds. Typically, proteins contain 14.5 - 17.5% nitrogen and 49.7 - 55.3 % carbon (Rouwenhorst et al. 1991). Hence, the C:N ratio of the protein fraction of biopolymers can be estimated as 3:1. The estimated protein concentration in mg C/L is calculated by multiplying the organic nitrogen concentration (in mg N/L) by 3. From there, the polysaccharide concentration is calculated by subtracting the organic carbon concentration of protein from that of the biopolymer concentration.

Since AOM may comprise large macromolecules (e.g., TEPs), LC-OCD analyses should be preferably performed without 0.45 μm inline filtration of samples – a standard pretreatment protocol for LC-OCD analysis (Villacorte et al. 2015b): however, removing the pretreatment step has been shown to cause clogging issues in the size exclusion columns. The theoretical maximum size when performing chromatography without sample pre-filtration is 2 μm, which is based on the pore size of the frit at the column entrance (S. Huber pers. com.).

5.3.1.2 Transparent exopolymer particles (TEP)

Since the discovery of TEPs more than two decades ago, various quantification methods have been developed, all of which are based on staining with cationic Alcian blue (AB) dye. This particular dye is known to be highly selective and forms insoluble complexes with TEP that cannot be easily reversed by subsequent treatment. In aqueous solutions without extra electrolytes, AB specifically binds with functional components such as acidic polysaccharides, glycoproteins and proteoglycans, resulting in the formation of neutral precipitates (Ramus 1977). AB does not react with nucleic acids and neutral biopolymers. The staining ability of AB depends on the type and density of anionic functional groups associated with TEP in the sample and to a large extent on the pH and ionic strength of the sample solution (Horobin 1988). In high ionic strength solutions, AB molecules spontaneously precipitate due to interactions with dissolved salts resulting in the formation of flocs not associated with TEP. This is considered the main drawback of the application of AB staining for TEP measurements in seawater. To minimize measurement artifacts due to coagulation, AB staining solutions should always be pre-filtered and should not be directly applied to solutions with high salinity.

So far, five methods have been developed to quantify TEP and their precursors. The first TEP method is based on optical microscopic enumeration. This method provides useful information on the size-frequency distribution of TEP in seawater (Alldredge et al. 1993), but it is laborious, complicated, time consuming and is not always feasible, especially for samples with low concentration and smaller size range (<2 μm) of TEP. All the succeeding methods based on semi-quantitative spectrophotometric techniques were able to address these issues. The method by Passow and Alldredge (1995), referred hereafter as $TEP_{0.4\mu m}$, has been widely used in various scientific investigations, but additional time-consuming pretreatment

techniques (e.g., bubble adsorption, laminar shear) are needed to measure TEP precursors (Zhou et al. 1998; Passow 2000). Further modification of this method using smaller pore size filters (e.g., $TEP_{0.1\mu m}$ or $TEP_{0.05\mu m}$) was later introduced to measure part of the TEP precursors (Villacorte et al. 2009; 2010). The alternative methods introduced by Arruda-Fatibello et al. (2004) and Thornton et al. (2007) are capable of measuring both TEP and their precursors in one single analysis; however, the former is only applicable in freshwater samples while the latter requires a dialysis step (performed for a couple of days) for saline samples. Furthermore, the method introduced by Thornton et al. (2007) is only accurate for samples with high concentration of TEP and their precursors.

The latest method, referred hereafter as TEP_{10kDa}, developed by Villacorte et al. (2015c) specifically for desalination applications aims to address the major practical issues associated with the previous methods (e.g., salinity, exclusion of TEP precursors), but also allows measurement of low concentration of TEP through the introduction of a concentration step (i.e., filtration through 10 kDa membrane). As such, it allows analyses of samples with a wide range of TEP + precursors concentrations (down to <0.1 mg X_{eq}/L) in seawater. In principle, this method also enables size fractionation of TEPs in seawater by making use of membranes with different pore sizes during the extraction step.

As discussed above, some of the TEP methods may not be suitable for seawater application due to potential artefacts formed with high salinity. Although TEP has been identified as a likely cause or initiator of biofouling in SWRO membranes during algal blooms (See Chapter 2), TEP monitoring is still not widely conducted in SWRO plants. Nevertheless, as TEP is gaining increasing attention in this regard, there is a clear need for a reliable method to measure these substances in seawater. The two methods considered to be most feasible for SWRO applications (i.e., $TEP_{0.4\mu m}$, TEP_{10kDa}) are described in detail in Appendix 3.

From the perspective of HAB monitoring in SWRO plants, the TEP_{10kDa} method is complimentary to the more established and widely accepted $TEP_{0.4\mu m}$ method. $TEP_{0.4\mu m}$ measures TEP while TEP_{10kDa} can measure both TEP and most (if not all) of their precursors. $TEP_{0.4\mu m}$ is a more rapid and less laborious method than TEP_{10kDa}, which means it is ideal for routine or high frequency TEP monitoring in intake seawater. This was demonstrated in the Jacobahaven demonstration plant in the Netherlands where $TEP_{0.4\mu m}$ was monitored for three years and a correlation between TEP and fouling rates in the UF pretreatment system was observed (see Chapter 11.10 Table 11.10.4).

To assess the removal of TEP and their precursors over the treatment processes, TEP_{10kDa} measurement is more appropriate because it covers the wider size spectrum of TEP. This was illustrated when both $TEP_{0.4\mu m}$ and TEP_{10kDa} testing was conducted along with biopolymer measurements (LC-OCD analysis) during a summer algal bloom (dominated by green algae) at a low salinity lake water desalination plant with extensive pretreatment. Measurements were taken of the raw water at the intake and after various pretreatment processes, microstrainer, coagulation, sedimentation and rapid sand filtration, granular activated carbon filtration and ultrafiltration and in the RO permeate. The concentration of TEP_{10kDa} was very high during the bloom in the raw lake water (see Figure 5.4) demonstrating that the test could be used to detect a HAB while quantifying the fouling AOM component in the bloom. Furthermore, the results illustrate the importance of measuring both TEP and their precursors when evaluating the efficiency of the pretreatment systems in removing algal-derived foulants from the RO feedwater. It revealed that TEP precursors were the dominant fraction as compared to TEP. While coagulation-sedimentation-sand filtration proved successful in almost completely removing the large TEP ($TEP_{0.4\mu m}$) component, TEP precursors (TEP_{10kDa}) and smaller biopolymers remained in the water. A substantial fraction of TEP precursors and

biopolymers were also removed by UF. Although substantially reduced, some of these potential foulants might still reach the SWRO system, even after advanced pretreatment. In general, both $TEP_{0.4\mu m}$ and TEP_{10kDa} concentrations demonstrated significant correlations with biopolymer concentration. In combination with particulate fouling indices (to be described in Section 5.5) and LC-OCD (Section 5.3.1.1), the application of at least one of these TEP methods can be crucial in developing strategies to minimize fouling issues in SWRO plants during HABs.

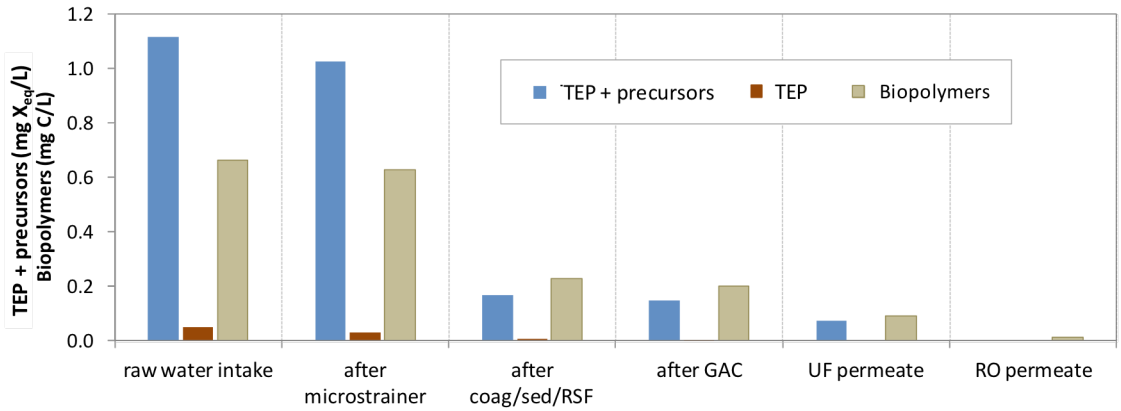

Figure 5.4. TEP ($TEP_{0.4\mu m}$), TEP + precursor (TEP_{10kDa}) and biopolymer concentrations measured in samples collected over the treatment processes of an RO plant treating lake water suffering from algal blooms. Legend: coag = coagulation + flocculation; sed = sedimentation; RSF = rapid sand filtration. Source: Villacorte et al. 2015c.

5.4 MEASURING BIOFOULING POTENTIAL

Biofouling refers to the growth of a biofilm on a membrane and/or feed spacers due to the attachment of microorganisms, principally bacteria and subsequent growth with the release of biopolymers as a result of microbial activity. The biofilm can lead to a decline in normalized permeate flux or increased differential pressure across membrane elements. As a result of this fouling, operating pressures need to be increased to maintain production and/or ultimately membranes will need to be cleaned to restore permeability, all of which will increase operating costs. If the membranes cannot be cleaned, membrane replacement will be required which is both costly and time consuming and will result in loss of production.

The TEP component of AOM can in particular potentially initiate and enhance biofouling in RO systems (Berman and Holenberg 2005). Due its sticky nature, TEP can adhere and accumulate on the surface of RO membranes and spacers. As TEP accumulate Bar-Zeev et al. 2012 proposed the TEP may serve as a "conditioning layer" - a platform for effective attachment and initial colonization by bacteria - which may then accelerate biofilm formation in RO membranes. As with assimilable organic carbon compounds (AOC - the easily biodegradable portion of TOC), TEP may be partially degradable and may later serve as a substrate for bacterial growth (Alldredge et al. 1993). The biodegradability of organic matter in a SWRO feedwater may therefore increase due to AOM produced during a HAB or through oxidation of AOM or other organic matter in the seawater by chlorination. The addition of some antiscalants which are designed to be biodegradable to minimize impacts of the RO brine discharge can also cause an increase in AOC (Boerlage 2001; Weinrich et al. 2015).

Biofouling remains the least understood of the RO fouling mechanisms, in part because simple, reliable and fast tests are not readily available to measure the biofouling potential of

RO feedwater (Schneider et al. 2012). Tests to determine the biofouling potential could be used to assess the increase in the biofouling potential of seawater from AOM and the efficiency of pretreatment to reduce it. For instance, the presence of trace AOCs in seawater can promote biofouling so by measuring AOC treatment plant operators would gain insight for managing pretreatment in terms of biofouling potential (Weinrich et al. 2016). To support this effort, an AOC test specifically for seawater was developed and later used for monitoring pretreatment effects on biofouling potential in full scale RO systems with both subsurface (beach well) and open intake seawater feed (Schneider et al. 2012; Weinrich et al. 2015). Only limited data are available for the correlation between growth potential levels and biofouling rate in full scale plants during algal blooms. This is mainly due to the relatively recent development of appropriate AOC assays for use in seawater studies. Moreover these tests require sophisticated equipment and are not currently deployed as an online test which could offer immediate results. In order to gain an understanding of the fouling potential of a feedwater without using a bioassay such as the AOC test, the Membrane Fouling Simulator (MFS) test was developed (Vrouwenvelder et al. 2006). In this test, fouling in a spiral wound element is simulated and monitored by the development of the head loss across the spacer. The AOC and MFS tests are discussed further below.

5.4.1 Assimilable organic carbon

5.4.1.1 AOC method development

A test was developed to determine the biofilm regrowth formation potential of drinking water in water distribution networks according to the growth response of a bacterial inoculum to the amount of easily assimilable organic carbon (AOC) (van der Kooij 1978; van der Kooij et al. 1982). Initially, the test was based on the growth of the bacterial *Pseudomonas fluorescence* strain P17 in a sample with the AOC concentration expressed as µg acetate-C/L, since the test is calibrated with sodium acetate solutions of different concentrations. The strain *P. fluorescence* P17 is capable of utilizing a variety of easily biodegradable compounds. As some compounds formed by oxidation in the water treatment process such as ozonation cannot be degraded by P17, the *Spirilium spp*. strain NOX was added to the inoculum (van der Kooij et al. 1982) and more recently, a special test making use of *Flavobacterium johnsoniae* has been developed to take into account less biodegradable organic compounds e.g. biopolymers (Sack et al. 2011). Further improvements to the AOC test include increasing the incubation test temperature from 15°C to 25°C and the inoculum from 500 to 10^4 CFU/mL (LeChevallier et al. 1993). Both of these adjustments reduced the time for the culture to reach stationary phase which was generally between two to four days. Other attempts to simplify the method used adenosine triphosphate (ATP) instead of determining plate counts (LeChevallier et al. 1993), but problems with commercial ATP measurement reagents discouraged adoption of this technique (Haddix et al. 2003). Nonetheless, both plate count and ATP methods are complex requiring weeks of turnaround time before results are available. In addition, the methods are costly because of the technical labor involved in assaying ATP levels from filter-concentrated cells or in spread plating samples and determining plate CFU counts.

A novel approach to simplify the method was achieved by producing bioluminescent strains of P-17 and NOX test bacteria through mutagenesis with luxCDABE operon fusion and inducible transposons (Haddix et al. 2004), and that method was further developed to include the use of a high sensitivity 96-microtiter plate luminometer (Weinrich et al. 2009). Using luminescence for bacterial growth estimation instead of the traditional plate counts reduces labor for preparing media and turnaround time to two days, which was an improvement on traditional methods taking three weeks or more. Moreover, the method provides information

regarding the kinetics of substrate utilization as well as the AOC concentration, in acetate carbon equivalent units which is consistent with previous methods. The bioluminescent fresh water method has been used for numerous projects that investigate biological filtration effectiveness and distribution system biological stability in both drinking water and reclaimed water matrices (Evans et al. 2013, Weinrich et al. 2010). Evaluations conducted previously indicate that the genetically modified P17 and NOX-strains tolerate salinity up to 5,000 mg/L TDS in the freshwater bioluminescent-AOC test, and are therefore not useful for seawater monitoring. Researchers have been developing methods for seawater application to address the need for managing biofouling and mitigating its costly consequences. The following sections describe tests suitable for seawater desalination plants.

5.4.1.2 Seawater AOC tests

An AOC test for seawater is used to assess the microbial growth potential in SWRO plants. Since P17 and NOX strains cannot survive in water with salinity greater than that of reclaimed water or brackish water (<5,000 mg/L TDS), luminescence assays have been developed using *Vibrio* bacteria.

The genus *Vibrio* contains biofilm-forming species that have been detected on a biologically-fouled SWRO membrane (Zhang et al. 2011). Weinrich et al. (2011) developed a seawater AOC test using a naturally occurring bioluminescent marine organism, *Vibrio harveyi* (ATCC®, 700106™). The *V. harveyi* seawater AOC is applicable to salinities between 20,000 – 35,000 mg/L TDS but has been applied in seawater with higher salinity from the Gulf and the Gulf of Oman. Briefly, the seawater AOC test consists of inoculating the sample with *V. harveyi* (from an overnight culture prepared at 30˚C). The inoculated samples are then transferred to a 96-well microtiter plate and a sensitive microtiter plate-luminometer is programmed to read the plate every two to four hours. The growth profile is monitored until the stationary phase (N_{max}) in which all substrate has been consumed by the test bacteria. The rate of utilization (μ_{max}) can be determined using Monod kinetics. Typically, the test duration with *V. harveyi* is about one day. Maximum luminescence measured at the stationary phase is converted into an AOC concentration with a 10 – 500 µg-C/L standard curve of acetate carbon equivalents. A full description is published in Weinrich et al. 2011, and Schneider et al. 2012. The AOC test for *V. harveyi* in seawater has been applied to monitor biofouling potential at bench scale and full scale SWRO plants for pretreatment monitoring, (Section 5.4.1.3) as well as in HAB events (see Chapter 11 Section 11.9).

Another AOC test based on the direct measurement of bioluminescence using *Vibrio fisheri MJ-1* was developed by Jeong et al. (2013) and is reported to estimate the AOC concentration within one hour. It is similar to the *V. harveyi* test described above but estimates AOC concentration with a 10 – 100 µg-C standard curve of glucose for *V. fischeri*. Recent research studies have been published using this method for monitoring AOC removal in SWRO pretreatment using granular activated carbon deep bed filtration (Jeong et al. 2013), and submerged membrane adsorption bioreactors which were operated with 2.4 – 8.0 g of powdered activated carbon per cubic meter of seawater (Jeong et al. 2014). The latter was shown to reduce biofouling for SWRO by adsorption and biodegradation of AOC and low molecular weight organic matter.

While these bioluminescence AOC tests using specific bacteria are faster, they may not measure high molecular weight biopolymers generated during a HAB. *Vibrio harveyi* utilizes compounds in the 100 - 350 Da range including disaccharides trehalose and cellobiose (Baumann et al. 1984) and low molecular weight monosaccharides, amino and carboxylic acids, alcohols and aldehydes (Weinrich et al. 2011). Biopolymers have much higher molecular weights and have been defined by size exclusion to be greater than 1 kDa (see

Figure 5.1) and in the range of 10 kDa defined by the TEP_{10kDa} method or 20 kDa (Huber et al., 2011 in LC-OCD). Under the conditions defined in the seawater AOC test, the test organism is unlikely to assimilate high molecular weight biopolymers. Specifically for SWRO treatment, biopolymers create conditions that enable bacterial attachment and increase biofouling potential. Therefore, knowing the AOC concentration would provide guidance on whether nutrients are present for the bacteria to proliferate and lead to biological fouling.

The luminescent AOC tests also require equipment that may not be typically used in a water quality lab and would need to be purchased, such as a luminometer for measuring bacterial growth, a water bath for temperature control, and an autoclave for sterilizing media. Consumables for the test such as test tubes, microtiter plates, and filters are inexpensive. Glassware used for AOC tests must be carefully prepared to minimize cross contamination of trace amounts of organic carbon. Alternatively, glassware is commercially available that claims to be AOC-free. Bacterial contamination is also a concern for AOC assays; however, salinity conditions in the seawater test would deter contamination from bacteria common in the human environment that are not halophilic or halotolerant. Assay samples should be analyzed as soon as possible after collection because of the highly biodegradable nature of the organic matter to be measured. If samples are to be shipped to the laboratory, then they should be cooled and shipped on ice overnight to inhibit biological activity in the sample during transit.

5.4.1.3 Application of seawater AOC test

Recently, the biofouling potential in numerous full-scale SWRO plants worldwide and extensively at the Tampa Bay Seawater Desalination Plant (TBSDP) was examined using the *V. harveyi* seawater AOC method. The AOC test was also used to assess feedwater quality to the plant, the impacts of pretreatment, and the biofouling potential in the SWRO feed.

The first study was at TBSDP when a non-toxic HAB contributed to periodic operational challenges. AOC at TBSDP has been investigated during normal operation and during a period of algal growth. The plant experienced foaming in the pretreatment basins, shortened diatomaceous earth (precoat) run times and reduced production capacity. The algal species *Ceratium furca* and *Phaeocystis* sp. were found in filter backwash media and were thought to contribute to the operational issues. At the same time, TOC was 7.6 mg/L at the plant influent and average AOC (from three consecutive days) was 360 ± 180 µg acetate C per L. AOC was also measured after chlorine dioxide treatment and increased by 65% compared to the raw water. TOC levels in TBSDP raw water were generally between 4-6 mg/L at the intake and are variable. During normal operation, AOC has been determined to be less than 30 µg/L (Weinrich et al. 2015) and up to 225 µg/L (Schneider et al. 2012). While the AOC test may not measure high molecular weight biopolymers as discussed earlier, the AOC increase may have occurred through shear of algal cells and release of low molecular weight AOM or from bacterial oxidation of organic matter into easily biodegradable low molecular weight compounds. In this case, the AOC test may measure the additional nutrients during a HAB which can be utilized by bacteria in a biofilm on the RO membrane. The results are further discussed in Chapter 11 Section 11.9.2. The plant has demonstrated AOC removal by the diatomaceous earth filters in the same studies.

In another study, plant personnel at the Al Zawrah plant in UAE described evidence of an algal bloom in May 2012 when the raw water pH decreased from the pH 8.1, normally observed, to pH 7.5. This was accompanied by elevated organic matter measured in the raw water as AOC (220 µg/L) and TOC (2.9 mg/L). During two other sampling events with reportedly normal conditions, the concentration of organics in the raw seawater was below

detection for AOC (<10 µg/L) and 60% less for TOC at 1.2 ± 0.04 mg/L in two sampling events from July and November 2012 (Weinrich et al. 2015).

These results demonstrate that AOC can increase at the seawater intake during algal bloom periods compared to periods when water quality and algae levels are normal. The seawater intake type also has important impacts on AOC levels. Organic matter measured as AOC and TOC was found to be lower in plants that have subsurface intakes (e.g. beach wells) compared to plants having surface intakes. Figure 5.5 shows AOC and TOC levels measured between 2009-2010 at various desalination plants (adapted from Schneider et al. 2012). AOC varied from 75 – 221 µg/L in surface intakes compared to <10 µg/L to 22 µg/L for beach well intakes measured during that study (Schneider et al. 2012). Hypotheses predicting that AOC was linked to biofouling of RO membranes in previous studies (including Franks et al. 2006, Fujiwara and Matsuyama 2008) were substantiated in recent evaluations of AOC concentrations near 50 µg/L in the RO feed that was linked with biofouling, increases in RO differential pressure and decreases in specific flux (Weinrich et al. 2015). Furthermore, pretreatment chemicals such as antiscalants and some oxidants increase AOC within the pretreatment process as mentioned previously, thereby, increasing the biofouling potential of RO feedwater (Weinrich et al. 2015, Weinrich et al. 2011, Schneider et al. 2012, Vrouwenvelder et al. 2000). An example is shown in Figure 5.5 for the Fujairah 1 SWRO desalination plant in the UAE which dosed antiscalant to the SWRO membrane feed. Antiscalants may contribute to AOC directly, or when dosed in pretreated water carrying a chlorine residual. Sequential addition of antiscalant followed by cartridge filtration and then sodium bisulfite (to reduce the oxidation reduction potential) presents an opportunity for chlorine to react with the antiscalant. In this scenario, byproducts such as AOC may be formed, or may be present as impurities in the antiscalant itself (Weinrich et al. 2015).

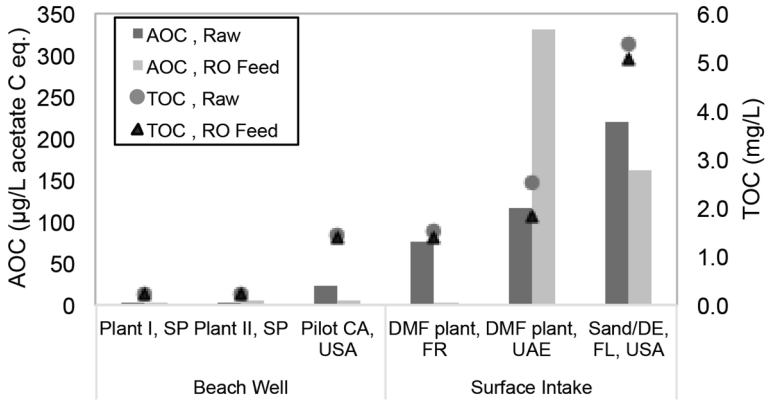

Figure 5.5. Organic carbon in raw and SWRO feedwater from SWRO plants in Spain (SP), France (FR), the United Arab Emirates (UAE) and United States of America (USA) measured as TOC and AOC (adapted from Schneider et al. 2012). DMF refers to dual media filtration and DE diatomaceous earth.

By measuring AOC during an algal bloom, the bio-fouling potential could be observed and quantified for operating records; both at the intake and at pre-treatment locations (e.g. after oxidation, before and after filtration). Assessing the impact of chemical, pressurization or mechanical forces on AOC and the availability of AOC would quantify biofouling potential. There is a risk that shear forces from feed pumps and valves could lyse algal cells and release soluble, intracellular organic matter (Ladner et al. 2010) but the risk is reduced if low shear valves are selected. Lysing algal cells (either through oxidation, pressurization or mechanical shear) is likely to release low molecular weight algal toxins (depending on the species) as well as organic matter that is highly biodegradable. For the latter issue, this release would create conditions sufficient for bacterial proliferation on RO membranes thereby increasing biofouling potential.

HABs would be best managed by SWRO plants that can effectively minimize nutrients during routine (non-HAB) operations. Nutrient limitation begins with identifying nutrient sources by testing antiscalants and other dechlorinating chemicals for impurities such as AOC or phosphate. While costly capital improvements could be an option (e.g. changing the intake source, installation of granular media filters and coagulation, conversion to biological filtration), modifying the chlorination strategy may be an effective solution for reducing biodegradable byproducts and bacterial growth. Plant operators need more specific water quality information for pretreatment optimization and biofouling reduction outside of typical bulk organic measurements or SDI. Monitoring AOC regularly and balancing pretreatment may be one solution; another would be sidestream piloting using the Membrane Fouling Simulator Test (see section 5.4.2). Granular media-based biological filtration is generally effective in drinking water applications and could be an option for SWRO as discussed in Chapter 9.6. Limiting AOC and removing it during pretreatment through biodegradation mechanisms on filter media and by coagulation would lower the biofouling potential of the RO feedwater carried to RO membranes. Removing this source of biological fouling material, measured as AOC, would reduce the potential for microbial growth or at least delay it on the RO membranes and associated operational impacts of biological fouling. Future work needed at SWRO plants would be to identify the increase of AOC caused by blooms of specific algal species in order to gain an understanding of their contribution to biofouling potential.

5.4.2 Membrane fouling simulator

Biofouling in spiral wound RO elements usually manifests in increasing head loss across the spacer. In full scale plants, the head loss across the first stage is commonly monitored with pressure sensors, since biofouling tends to occur primarily in the first 10 to 20 cm of the first element. It is possible to monitor the head loss across the first element in order to modify the pretreatment process and as a criterion for chemical cleaning.

In pilot tests, monitoring the increase of differential pressure along the feed channel over time as an index is very useful in testing different pretreatment schemes and conditions. It is, however, very costly due to the length of operations and/or the need for several pilot plants. For this reason the MFS was developed (Vrouwenvelder et al. 2006). In a MFS, biofouling along the feed channel is simulated. This device is constructed of two stainless steel plates containing sample coupons of membrane, feed and product spacer. It is equipped with connectors for feed and brine flow and sometimes for product flow as well. Head loss development is accurately monitored using pressure sensors.

Villacorte (2014) demonstrated, by making use of the MFS, that AOM produced by laboratory cultivated marine algae (*Chaetoceros affinis* in synthetic seawater) accelerated biofilm growth and resulted in a rapid increase in the feed channel pressure drop. The tests were performed by running two MFS in parallel, one initially with a RO membrane slightly pre-fouled with AOM and another one with a clean membrane (control). Both MFS were fed with 100,000 cells/L of marine bacteria *Vibrio harveyi* for about 24 hours and then fed with synthetic seawater spiked with dissolved nutrients (0.1 mg acetate-C/L, 0.02 mg N/L and 0.01 P/L) for 10 to 21 days. An exponential increase of pressure drop was observed for MFS pre-fouled with AOM with up to 1000% increase in only a span of 6 days. In comparison, the control membrane only showed 250% increase in a span of 17 days.

While the MFS allows the biofouling potential of feedwater to be measured quite accurately it remains a lengthy test. Therefore, the development of quick AOC tests that incorporate biopolymers into the AOC measurements would be of great value to plant operators to optimize pretreatment during a HAB.

5.5 FOULING INDICES TO MEASURE PARTICULATE FOULING POTENTIAL

The deposition of algal particulates (e.g. TEP and TEP precursors) on RO membranes during a bloom, along with inorganic and organic colloids, bacteria and other materials, can lead to a decline in normalized permeate flux and an increase in head loss across spacers (or membrane bundles). This type of fouling, often referred to as particulate fouling, may exacerbate other types of fouling (e.g. biofouling). Reliable methods to predict the particulate fouling potential of feedwater are important in preventing and diagnosing fouling at the design stage and for monitoring pre-treatment performance during full-scale plant operation. Turbidity and the Silt Density Index (SDI) are universally applied for this purpose as they often form the basis of RO membrane guarantees. Turbidity however, like particle counting, can only indicate the concentration or mass of particles in feedwater, but provides no information on the resistance of these particles when they deposit on a membrane. Similarly, measurements of total suspended solids (TSS), while important for solids loading in design and operation, will not provide any information on particulate fouling.

Fouling indices, of which the Silt Density Index is the most commonly used in practice, are designed as quick filtration tests to simulate RO membrane fouling and thereby, determine the particulate fouling propensity of a feedwater. The lesser known Modified Fouling Indices (MFI) are increasingly applied, in particular in research projects, pilot and lab/bench scale studies. While both indices are not specific for algal-related particulate material, an increase in the values above background may occur due to HABs at the intake. Table 5.3 provides a summary of the SDI and MFI indices, comparing the principle of each method, interferences, particulate fraction identified and operator skill required for the test. The fundamental background of the SDI and MFI fouling indices is provided in subsequent sections. Applications of the indices in measuring algal-laden feedwater are given to illustrate advantages and limitations of these indices. The performance of parameters such as turbidity and chlorophyll-*a* to compliment and interpret SDI measured at the seawater intake are also discussed.

5.5.1 Silt Density Index

The SDI, developed by the Du Pont Company at the request of the Bureau of Reclamation (Du Pont 1972), has been universally applied in the desalination industry for the last 40 years to assess the particulate fouling tendency of feedwater. ASTM International standardized the test protocol in 1995 as ASTM D4189, reapproving it most recently in 2014 (ASTM D4189-07(2014)).

The SDI test consists of passing a feedwater through a 0.45µm microfiltration membrane in dead-end flow at a constant pressure (207 kPa) and determining the membrane filter-plugging rate. The SDI_T [4]is calculated from Equation 1.

$$SDI_T\ (\%/\text{min}) = \frac{\%PF}{T} = \frac{\left[1 - \frac{t_i}{t_T}\right] 100}{T} \qquad (1)$$

where t_i is the time to collect an initial sample (normally 500 ml) filtered through the membrane, t_T is the time taken to collect a second sample after a total elapsed filtration time (T) of 5, 10 or 15 minutes, and %PF is the percentage plugging factor. The ASTM specifies the %PF should not exceed 75% when conducting the test. If so, the SDI should be

[4] The SDI means the percentage flux decline per minute. Dimensions of the SDI test are %/min; by convention the SDI is commonly reported as dimensionless.

Table 5.3. Comparison of Silt Density Index and Modified Fouling Indices to measure particulate fouling in seawater and feedwater.

Parameter	Standard / Reference	Basis of Method	Organic matter (OM) identified	Interferences / Issues	Analysis time / Operator skill
Silt Density Index (%/min)	ASTM D4189	Employs 47mm diameter flat 0.45µm microfiltration membrane. Measured in constant pressure mode. Measures filter plugging after 5, 10 or 15 minute interval.	>0.45 µm Not specific to HAB particulate material. Measurement will include algal cells and some algal debris.	Inaccurate at high particle concentration such as algae-rich seawater. Not based on a filtration mechanism. Not linear with particle concentration. No standard correction method for temperature, pressure or membrane related properties. Not applicable for UF permeate.	5 – 15 minutes. Simple routine inexpensive test.
Modified Fouling Index-0.45 (s/L^2)	ASTM D8002	Employs 47 mm diameter flat 0.45µm microfiltration membrane. Measured in constant pressure mode. MFI determined from cake filtration region in t/v vs V graph. MFI-0.45 corrected to standard reference conditions of temperature, pressure and membrane area.	>0.45 µm Not specific to HAB particulate material. Measurement will include algal cells and some algal debris.	Not applicable for UF permeate.	30 – 60 minutes. More complex to calculate MFI-0.45.
Modified Fouling Index-UF (s/L^2)	Not an ASTM standard	Employs 25mm diameter flat sheet ultrafiltration membranes of 10 – 100 kDa MWCO[1]. Measured in constant flux mode at 10 – 300 L/m^2h (Salinas 2011) or constant pressure mode. MFI-UF corrected for temperature, pressure and membrane area in both modes. For the MFI-UF in constant flux mode – the recommended test flux is the same as target MF/UF plant. For RO plants a flux correction method is under development. Alternatively, the same flux as for TEP measurements (60 L/m^2h) could be applied.	Not specific to HAB particulate material. Measurement will include algal cells and some algal debris. Depending on MWCO of test membrane, may include TEP and TEP precursors.		Test duration dependent on test flux in constant flux mode. 30 minutes at 250 L/m^2h and several hours at 15 L/m^2h (Salinas-Rodriguez 2011). Longer in constant pressure mode. More complex to calculate MFI-UF.

[1] molecular weight cut off (MWCO)

determined after 10 or 5 minutes. If the PF still exceeds 75% after only 5 minutes of filtration, the ASTM recommends another method be employed to analyze for particulate matter.

SDI is one of the key parameters to assess the particulate fouling potential of raw water and monitor the efficiency of RO pretreatment processes over time in design and operation of SWRO desalination plants. In some cases SDI may be provided in the raw seawater quality design envelope. For plant operation, SDI_{15} limits are often specified for RO feedwater in RO membrane guarantees (e.g. the SDI_{15} will not exceed 5, and be below 3 (or 4) for 90% of the time) and other plant performance contracts. These limits may be linked to turbidity monitoring in contracts as turbidity can be continuously monitored online. Automatic online SDI analyzers (not continuous) are available which can be input into plant control systems so SDI can be routinely monitored in the control room with SDI alerts and alarms allowing operators to respond to changes in influent water quality, including HAB events.

Despite the well-documented limitations of the SDI (Schippers and Verdouw 1980; Kremen and Tanner 1998; Boerlage et al. 2000; Boerlage 2008), it remains a mainstay in the desalination industry due to its simplicity. Key limitations summarized in Table 5.3, include that the SDI is not based on a filtration mechanism and therefore cannot be used as the basis of a model to predict pressure increase in RO systems. This was again recently demonstrated in practice by Jin et al. (2017) in a one year study measuring the SDI of RO feedwater which included algal bloom events at a full scale SWRO plant employing DAF and UF pretreatment. No correlation was found between the SDI and differential pressure increments in the RO systems.

Nonetheless, increasing SDI values may be the first sign of a HAB at an intake in the absence of changes in other parameters such as turbidity and chlorophyll-*a*. The increase in SDI is due in part to the retention of marine algal cells by the smaller pores (0.45µm) of the test membrane through size exclusion. For instance, *Cochlodinium polykrikoides*, the dominant species present in the notorious 2008 bloom in the Gulf, is 20 - 40 µm in size for individual cells, but forms chains that are much longer. Smaller algal related matter such as algal detritus from ruptured cells comprising cell walls, flagella, organelles, dissolved and particulate intra- or extracellular AOM may also be captured to some extent through a variety of mechanisms resulting in higher SDI values. Partial blocking of membrane pores can reduce the effective pore size of the test membrane. Smaller particles may also be trapped in the cake formed on the test membrane where the cake has smaller interstices than the SDI membrane pores. However, smaller pore size membranes are required to measure the more fouling colloidal particles such as TEP and TEP precursors.

Turbidity may not register an increase during a bloom due to the deficiencies of turbidity measurements in detecting HAB cells and small colloidal particles as discussed previously in Section 5.2.5. In particular, particle sizes smaller than 0.2 µm may not be measured due to limited light scattering (Kremen and Tanner 1998). Moreover, very small AOM-related particles such as TEP are transparent and are therefore "invisible" to turbidity meters.

Results trialing chlorophyll-*a* measurement using fluorescence as a proxy for algal biomass to compliment SDI and online water quality testing at the seawater intake have been mixed. As with turbidity, spikes in SDI may not coincide with an increase in chlorophyll-*a*. There are reports of no significant increase in chlorophyll-*a* above background being observed, despite elevated algal cell concentrations up to 5 million cells/L accompanying the observed increase in SDI. This is consistent with the discussion in Chapter 3 which describes limitations to measuring chlorophyll-*a* to estimate biomass using fluorescence. The relationship between chlorophyll-*a* fluorescence and cell biomass is not constant across all phytoplankton species, nutritional conditions, and times of sampling. The large *Noctiluca*

scintillans dinoflagellate is a notable example; it ranges up to 2 mm in size and while it releases ammonia into seawater and therefore can be harmful, it lacks chloroplasts and therefore its chlorophyll content is low (Pool et al. 2015). In this instance, SDI may increase along with ammonia concentrations (if measured) in the intake seawater, while chlorophyll would show no change. Other factors influencing chlorophyll-*a* include nutrients, and light history, with limitations often resulting in lower chlorophyll-*a* content than the same cells under more favorable conditions (see Chapter 3). If chlorophyll-*a* is measured then it is recommended that only the night time data be used, as nocturnal chlorophyll-*a* fluorescence is more consistent.

Other options that could be used in conjunction with SDI are regular microscopic examination and counting of cells, or some of the newer automated phytoplankton-identifying instruments, such as the Imaging FlowCytobot or FlowCam (see Chapter 3). They can also be automated, and provide more information about species and cell numbers. Routine, online use of these automated biosensors would allow operators to generate a long-term, high-resolution database of algal species and concentrations that are associated with plant disruptions, and an associated record of which pretreatment strategies worked or failed.

Visual examination of the SDI test membrane may provide additional information on feedwater constituents and indicate changes in quality such as an unusual color of the deposit on the SDI membrane e.g. a red filter deposit from red blooming algae. Closer examination of membranes by electron microscopy may be used in combination with algal counting to identify species or bloom types. This is illustrated in electron micrographs of SDI test membranes of raw water off the coast of Chile where diatoms and coccoliths are visible in Figure 5.6 (left) and an intact coccolithopore (*Emiliania huxleyi*) cell in Figure 5.6 (right) (Petry et al. 2007).

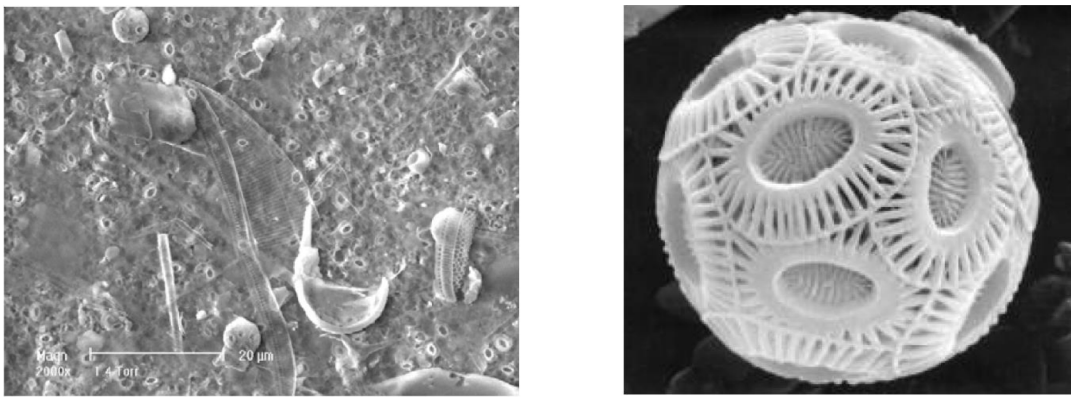

Figure 5.6. Electron microscopy of SDI test membranes showing the presence of algae and algal particulate debris (left) and close up (right) of a coccolithopore cell. Photo: Petry 2007.

Severe HAB events can significantly increase the fouling potential of seawater at open intakes due to the increase in algal biomass to the point that the SDI may not be measurable due to rapid plugging of the SDI test membrane. During the prolonged 2008 HAB event in the Gulf, algal cell counts of 11 to 21 million cells/L were recorded in surface waters near Fujairah (Richlen et al. 2010). As a result, TSS increased to 30 mg/L on occasion, compared to the median TSS of 5 mg/L; the SDI test was not informative, as it is limited to low fouling feedwater. Despite the ASTM recommendation that the SDI is only employed for low turbidity water (< 1 NTU) and for water that will not result in a %PF of > 75%, these guidelines are widely ignored in practice. Furthermore, raw seawater SDI_5 values often

exceed 75% PF and the industry then often measures the SDI_3 (not a specified ASTM SDI test interval).

Not surprisingly, even the SDI_3 was reported to spike above 25 (75% PF limit) on several occasions during the 2008 bloom in the seawater around Fujairah (see Chapter 11 Section 11.2). While these high SDI_3 can be useful in indicating the possible presence of a bloom in the incoming feedwater when trended against typical feedwater data, operators should be aware these SDI values will underestimate the fouling potential of the raw water as the SDI is not linear with particle concentration. Instead, the SDI is limited mathematically to a maximum value of 6.7, 10 and 20 for a filtration time of 15, 10 or 5 minutes, respectively. Using the ASTM criterion of 75% maximal plugging, the values are 5, 7.5 and 15 respectively. The asymptotic behavior of SDI with increasing particle concentration as it approaches these limits was demonstrated experimentally by Schippers and Verdouw (1980) by measuring SDI_T for a series of diluted formazine (a model colloid) solutions. Figure 5.7 shows SDI_{15} as a function of formazine with the accompanying %PF, and ASTM-recommended 75%PF limit and SDI_{15} test limit. As the SDI approaches its limit, it is obviously easier to obtain repeatable SDI results but the SDI will underestimate fouling and become increasingly inaccurate at higher %PF (Boerlage 2008). Hence, the typical SDI_{15} limit set by membrane manufacturers is < 3 to 4 depending on the feedwater source, which is equivalent to <5 to 60% PF and is in the more linear range of Figure 5.7.

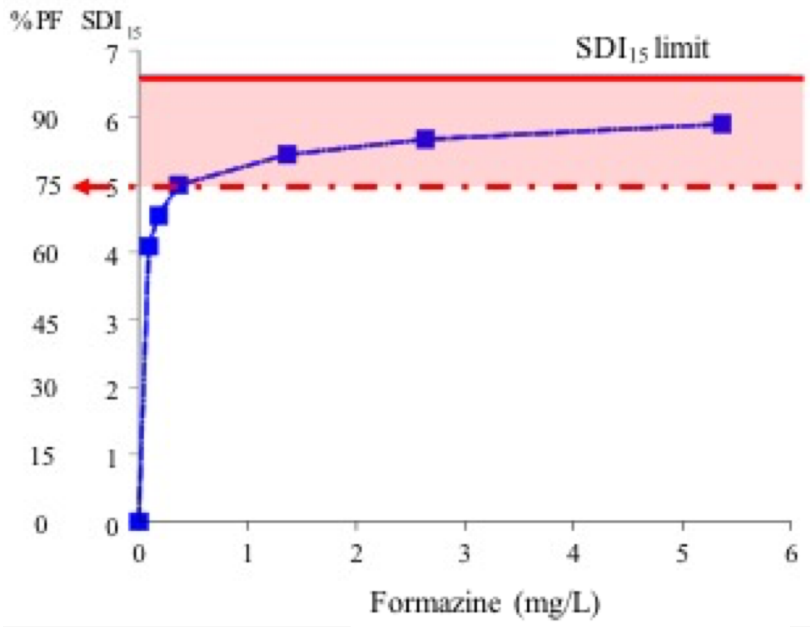

Figure 5.7. SDI_{15} and %PF of diluted formazine solution demonstrating the non linearity of SDI with colloidal concentration. SDI_{15} and 75% PF limits indicated (SDI data from Schippers and Verdouw 1980).

In summary, increases in SDI_5 (or SDI_3) can indicate the presence of HABs at the intake, while increases in SDI_{15} downstream can indicate the failure of pretreatment steps and that operator action is required; however, high SDI_3 and SDI_{15} values such as those observed during the 2008 Gulf bloom would have increasingly underestimated the fouling potential of these desalination process streams. Moreover, when assessing process performance it should be remembered that the SDI cannot be directly compared for different filtration intervals e.g. SDI_5 for raw water and SDI_{15} after pretreatment or when measured at different temperatures (the SDI test applies no temperature correction for differing feedwater temperature). Other factors which influence the SDI such as test membrane porosity etc. are discussed in Boerlage (2008).

5.5.2 Modified Fouling Indices

5.5.2.1 Modified Fouling Index-0.45

The MFI-0.45 was developed by Schippers to overcome the limitations of the SDI (Schippers and Verdouw 1980) and thus has the potential to be of value in detecting a HAB at an intake and optimizing the efficiency of pretreatment processes. The MFI-0.45 has recently been approved by ASTM International as a standard (D8002-15) to indicate the fouling potential of feedwater due to particular matter. Automatic analyzers are commercially available that can simultaneously measure MFI-0.45 and SDI online, but they are not as widely used as the SDI analyzers.

Unlike the SDI, the MFI-0.45 is based on a filtration mechanism (cake filtration) and is linear with particle concentration. As with the SDI, the MFI-0.45 is determined in dead-end flow under constant pressure using similar equipment as the SDI. The MFI-0.45 is determined in a plot of t/V vs V (where V is filtrate volume and t filtration time) from the gradient of the linear region of minimum slope where cake filtration occurs (refer to Schippers and Verdouw 1980 for more information). Schippers defined the MFI at reference pressure and temperature values of 2 bar (ΔP_o) and 20°C ($\eta_{20°}$), respectively and for the area of the 0.45 μm membrane (A_o=13.8×10^{-4} m^2). Incorporating the Carman-Kozeny relationship for *idealized* spherical particles to calculate the specific resistance of the cake deposited on the MFI-0.45 membrane yields the following equation for the MFI-0.45 at standard reference conditions:

$$MFI = \frac{\eta_{20^\circ C}\, 90(1-\varepsilon) C_b}{\rho_p d_p^2\, \varepsilon^3 \Delta P_o\, A_0^{\,2}} \qquad (2)$$

where (C_b) is the concentration of particles in the feedwater, (ρ_p) is the density of particles forming the cake, (ε) cake porosity and (d_p) particle diameter. From this equation the pronounced effect of decreasing particle size in increasing the MFI can be seen.

The MFI can be used as an index to characterize the fouling potential of a feedwater containing particles, as it is a function of the dimension and nature of the particles forming a cake on the membrane, and is directly correlated to particle concentration in a feedwater. For feedwater containing algae, the MFI-0.45 could provide information about the difference in net fouling potential (cake permeability) due to differing algal cell size (d_p) and cell abundance (C_b) of bloom species that can vary significantly. For instance, two algal bloom-forming species found in the Gulf and Gulf of Oman are *Cochlodinium polykrikoides* (with a size range of 20 – 40 μm and a maximum abundance up to 20 million cells/L in the 2008 HAB) compared to the much larger *Noctiluca scintillans* dinoflagellate which formed less dense blooms with only up to 68,500 cells/L measured during HAB events in the Gulf (Al Shehhi et al. 2014). The MFI-0.45 is expected to be higher for the smaller *Cochlodinium polykrikoides* as the MFI is inversely proportional to particle diameter squared (see equation 2).

A clear advantage of the MFI-0.45 is that it could be used to measure the fouling potential of low and high fouling feedwater and therefore assess the efficiency of pretreatment processes during a HAB. Data available from the Jacobahaven SWRO demonstration plant (see Case Study 11.10 for more information), where both the MFI-0.45 and SDI_{15} were measured during an algal bloom pre- and post-UF are shown in Figure 5.8 (from Al Hadidi 2011). Both

the SDI_{15} and MFI-0.45 values of the UF permeate are below one following ferric coagulation and filtration through the 150 kDa UF membranes. However, the SDI_{15} of the UF feed was highly fouling with the 75% PF exceeded on both days. In fact, the plugging of the SDI test membrane was reported to be so rapid that even the 75% PF was exceeded when measuring SDI_3. Therefore, the fouling potential of the UF feed is underestimated and the performance of the UF step cannot be accurately determined by the SDI test. In comparison the MFI-0.45 is not limited to low turbidity or low fouling feedwater. While the ASTM MFI-0.45 standard does not recommend the test is used for UF permeate it can measure the efficiency of the UF step in removing fouling particles captured by the 0.45 µm test membrane during the bloom. In this study Al Hadidi estimated a particle removal of 99.947± 0.053% based on the average MFI-0.45.

Assuming that cake filtration is the dominant mechanism in RO membrane fouling, a MFI model was developed to predict flux decline or pressure increase to maintain constant capacity in RO systems. However, the predicted rate of fouling based on MFI-0.45 measurements was much lower than observed in practice. For instance, given a MFI of 1 s/L^2, a fouling rate of 15% was predicted to occur within several hundreds of years. It was

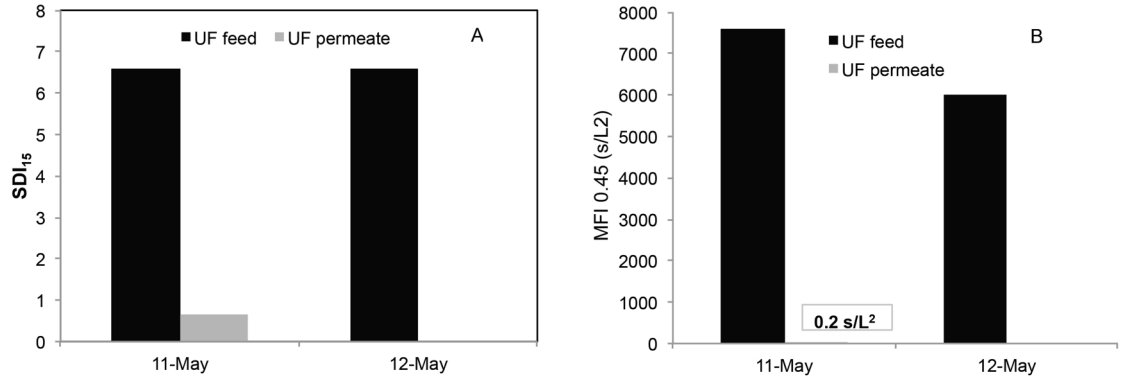

Figure 5.8. SDI_{15} (A) and MFI-0.45 (B) measurements at the Jacobahaven SWRO Plant in May 2010 of the UF feed (seawater filtered through 50 µm screens with ferric coagulant added) and post filtration through 150 kDa UF membranes (data from Al Hadidi 2011).

concluded that particles smaller than those captured by the MFI-0.45 (and SDI) test membranes were responsible for the fouling observed in RO due to their much higher cake resistance (Schippers and Verdouw 1980).

5.5.2.2 Modified Fouling Index-UF

The MFI-UF was initially developed to include smaller particles using a reference ultrafiltration membrane of 13 000 Da (13 kDa) molecular weight cut off in both constant flux and constant pressure modes (Boerlage et al. 2000, 2002, 2004). Much higher MFI-UF values were measured as predicted. By employing UF membranes the MFI test could be extended to measure UF permeate. However, more accurate fouling prediction is expected with the MFI-UF measured in constant flux mode. In this case, the MFI is determined from the linear region, where cake filtration occurs, in a plot of applied transmembrane pressure over time (see Boerlage (2004) for derivation of the MFI in constant flux mode). Salinas–Rodriguez et al. (2011; 2015) further developed the MFI-UF test in constant flux mode to use smaller disposable UF test membranes (25 mm) with variable MWCO (10-100 kDa) where filtration flux can range between 10 L/m^2h to 300 L/m^2h. Research efforts trialling the MFI-UF on seawater during algal blooms or in laboratory studies with AOM for various purposes are described below.

The use of lower MWCO membranes means that smaller fouling TEP and TEP precursors present in an algal bloom could be included in the MFI measurement as well as larger algal cells and detritus. Villacorte (2014) calculated the theoretical MFI-UF for several bloom-forming algal species, based on their cell size and concentration, and found that it was significantly lower than that measured in natural seawater by the MFI-UF using 150 kDa test membranes. The substantial difference was attributed mainly to the presence of TEP precursors and TEP in seawater retained by the test membranes and which are not considered when calculating the theoretical MFI-UF. Furthermore, the TEP precursors (measured by TEP_{10kDa}) were found to be the dominant fraction of TEP during a bloom (see Figure 5.4). As discussed by Villacorte (2014) TEP are gel-like and capable of squeezing through the interstitial voids between algal cells accumulated on the MFI-UF membrane, resulting in a more-fouling cake layer due to the higher resistance. Therefore, smaller MWCO MFI-UF test membranes on the order of 10 kDa would capture these TEP precursors and their associated fouling potential. This is depicted in Figure 5.9 which shows an electron micrograph of the pores of the earlier 13 kDa MFI-UF reference membrane, which were around 1000 times smaller than the pores of the MFI-0.45 membrane. Some of the TEP precursors (ranging in size from a few nm up to 0.4 µm) as well as TEP (0.4 µm up to 1000 µm) which cause fouling on both UF and RO (refer Chapter 2) should now be captured in the MFI-UF test for similar small MWCO test membranes.

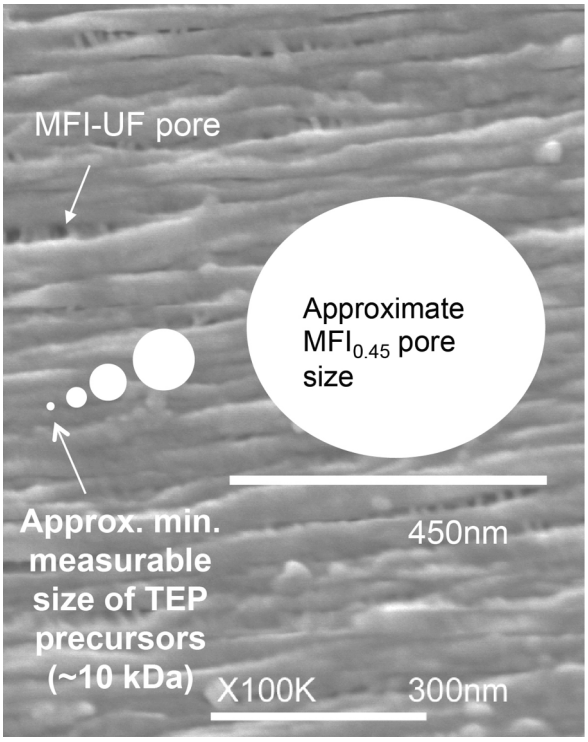

Figure 5.9. Scanning electron micrograph of the MFI-UF PAN 13 kDa membrane showing pore size comparison to MFI-0.45 membrane pore. Tight UF membranes in the MFI test will capture some of the fouling TEP precursors (< 400 nm) in size in addition to larger TEP. Modified from Boerlage 2008.

Villacorte (2014) therefore trialed the MFI-UF (in constant flux) using the smaller 10 kDa MWCO membrane to measure the fouling potential of the raw water during algal blooms at five different RO plants desalinating water of various salinities, including lake, river, and seawater and after pretreatment processes (Figure 5.10). The relationship between the MF-UF and the concentration of fouling AOM constituents ($TEP_{0.4\mu m}$, TEP_{10kDa} and biopolymers) determined in the treatment process stream was examined. Results showed a higher correlation between MFI-UF and the TEP_{10kDa} component (R^2>0.65) of AOM than between the MFI-UF and concentration of biopolymers or the larger AOM components measured by $TEP_{0.4\mu m}$. This demonstrated that the MFI-UF could be used to measure the fouling constituents of AOM during HABs and that the TEP precursors can most likely influence the fouling propensity of the water more than other types of organic matter.

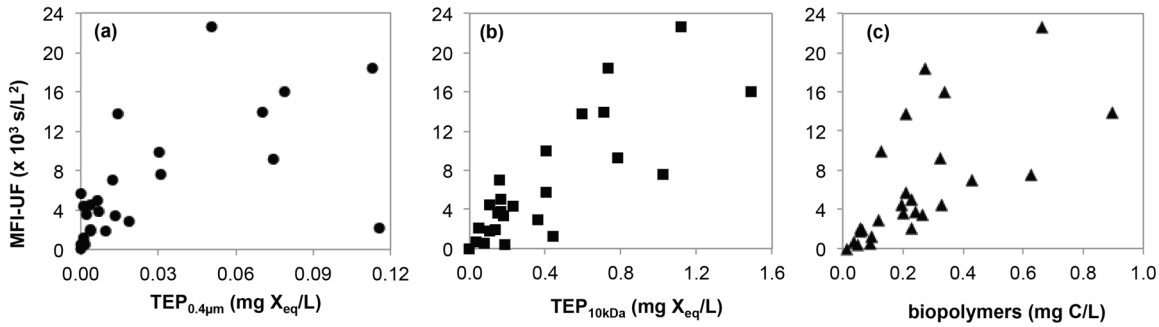

Figure 5.10. The membrane-fouling potential (MFI-UF_{10kDa}) of 26 water samples collected during the treatment processes of five plants (lake, river, reservoir and seawater sources) plotted against (a) $TEP_{0.4\mu m}$, (b) TEP_{10kDa} and (c) biopolymer concentrations, respectively. Modified from Villacorte 2014.

In another study, pretreatment efficiency was assessed using a range of MWCO membranes in the MFI-UF test (constant flux) at the Jacobahaven SWRO demonstration plant (see Chapter 11.10) which routinely experiences seasonal algal blooms in the European spring (Salinas-Rodriguez 2015). Initially, in the spring and summer of 2009, MFI-UF measurements were conducted only using the larger MWCO test membrane of 100 kDa. Subsequently, in spring 2010 additional MFI-UF measurements were conducted across the plant using smaller MWCO test membranes of 50 and 10 kDa. The MFI-UF fouling potential measured using the larger 100 kDa membranes is summarized in Table 5.4. Chlorophyll-*a* measurements at the plant intake close to the time of the MFI-UF tests are included in Table 5.4 (from Figure 11.10.6 in Chapter 11.10).

Table 5.4. Membrane fouling potential based on MFI-UF measurements with 100 kDa test membranes (data from Salinas-Rodriguez (2015) and chlorophyll-*a* (data from Fig 11.10.6 in Chapter 11.10 courtesy of R. Schurer) for the raw source water at the Jacobahaven SWRO Demonstration Plant.

	MFI-UF (s/L^2)	**Chlorophyll-*a* (µg/L)**
23 April 2009	4310	3.4
28 April 2009	4840	6.3
16 June 2009	3800	1.0
2 July 2009	2950	1.0
6 July 2009	2840	1.0
10 May 2010	25,340	3.9

For the Jacobahaven plant, spikes in chlorophyll-*a* generally indicated algal blooms at the intake. However, the fouling potential of the seawater in spring 2010 was very high based on the MFI-UF, more than five times that measured during a previous bloom in April 2009. This was not mirrored by a similarly high chlorophyll-*a* measurement in the raw feedwater. Algal speciation varied during blooms (see Chapter 11, section 11.10) and as discussed above, the chlorophyll-*a* concentration varies with a myriad of factors including the bloom species and cell size. Hence, while MFI-UF measurements are not specific to algal particulate matter, they can provide operators with more reliable information as to the potential fouling impact of an algal bloom at the intake.

When Salinas-Rodriguez (2015) used the smaller MWCO test membrane of 10 kDa, thereby potentially capturing the smaller algal-derived biopolymers (TEP precursors) as suggested by Villacorte (2014), the fouling potential of the raw water in May 2010 more than doubled relative to the MFI-UF with 100 kDa membrane (Figure 5.11). MFI-UF results for the three

different MWCO membranes across the plant allow the removal efficiency of pretreatment processes for particles of various sizes, captured by the different test membranes, to be assessed. For example, the fouling potential of the seawater during the May 2010 algal bloom was reduced following coagulation and ultrafiltration (nominal MWCO of 150 kDa) by 94%, 93%, and 88% for 100, 50, and 10 kDa MFI-UF test membranes, respectively. As biopolymers can vary upward of 1 – 20 kDa some will pass through the UF membrane with a much larger MWCO. This is reflected in the lower reduction in fouling potential for the smaller 10 kDa membrane. This means that some of the more fouling AOM such as TEP precursors may reach the RO membranes.

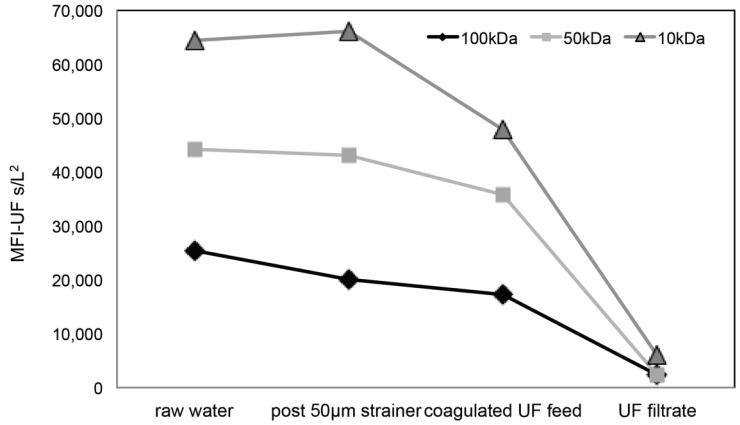

Figure 5.11. Effect of pretreatment on MFI-UF at the Jacobahaven demonstration plant using test membranes of 100, 50 and 10 kDa size at 250 L/m^{2}h (data from Salinas-Rodriguez 2015).

The MFI-UF was also trialed to determine the optimal coagulant dose to reduce the fouling potential of seawater containing AOM. Tabatabai (2014b) conducted MFI-UF experiments in constant flux using a larger 150 kDa MWCO test membrane in laboratory experiments for seawater solutions containing algal organic matter (0.5 mg/L as biopolymers). MFI-UF measurements showed the addition of 5 mg/L Fe reduced the fouling potential seven fold in the seawater with no measureable reduction when the coagulant dose was doubled (see Chapter 9 for further information). It would be worthwhile to repeat such an experiment using a 10 kDa membrane in the MFI-UF test to assess the optimal coagulant dose for the more fouling TEP precursors.

As there is currently no ASTM standard for the MFI-UF test, it has been applied in the field in both constant pressure and constant flux mode and for membranes of varying MWCO. Jin et al. (2017) evaluated multiple MFI-0.45/MFI-UF tests for RO feedwater in a one year study which included algal bloom events at a full scale SWRO plant employing DAF and UF pretreatment. The MFI tests were conducted in constant pressure mode with decreasing MWCO membranes in series to interpret fouling potential through size fractionation; MFI-0.45, MFI-UF 100 kDa and MFI-UF 10 kDa and results correlated to RO differential pressure. During algal blooms, all MFI values significantly increased and generally reflected the variation in differential pressure with the MFI 100 kDa more closely related to differential pressured variation (Jin et al. 2017).

In conclusion, the above MFI-UF results to monitor the particulate fouling potential of feedwater and assess pretreatment for removal of smaller fouling particles (including TEP precursors) have so far proved promising. Moreover, the MFI-UF can be used in combination with other MFI-UF tests of varying MWCO either in series or in parallel to compare the efficiency of pretreatment processes or pretreatment trains for the removal of selected particle sizes.

5.6 SUMMARY

HABs can result in a substantial increase in the organic and solids load in the raw source water to be treated at a desalination plant and may lead to overloading of pretreatment

systems and membrane fouling. SWRO designers and operators therefore require methods to determine the concentration of AOM, its fouling constituents, and any increases in the particulate and biofouling fouling potential or other HAB-associated water quality changes. Such methods allow HABs to be monitored and detected in the raw water so that treatment processes can be optimized during a bloom event to maintain plant production and water quality targets.

Temperature, conductivity, pH and turbidity are often continuously monitored at plant intakes, in addition to analysis of SDI, TOC and TSS to characterize feedwater quality. None of the conventional online parameters can definitively detect HABs as they are not specific to algal blooms. Changes can be caused by other factors such as pollution events and/or marine hydrodynamics. The interpretation of a water quality variable can thus be complex. Nonetheless, these measurements may indicate conditions that promote a bloom, such as temperature and salinity or indirect impacts from HABs such as low DO following decomposition of a dense bloom. In conjunction with other conventional water quality tests such as SDI, the standard online water quality parameters can be useful in indicating a deterioration in feedwater quality due to HAB events, and can provide timely and valuable information that action is required.

Measuring TOC to detect AOM and for process control is generally unreliable. Spikes in TOC may be derived from both natural processes such as HABs and/or through anthropogenic input. Measuring TOC removal to assess the efficiency of pretreatment processes is also inaccurate due to the difficulties in measuring low level TOC residuals in seawater process streams. Of the conventional water quality parameters used in desalination, the SDI, despite its well known limitations, has proven useful in detecting algal blooms at the intake compared to other parameters including turbidity and chlorophyll-*a* (determined via fluorescence). Notwithstanding, care should be taken in interpreting results, as the SDI test was not designed for high fouling feedwater such as algae-laden seawater. As a result, it can underestimate the fouling potential of feedwater. Moreover, it does not include the smaller, more fouling AOM produced during a bloom.

Recently, more sophisticated tests have been developed to determine constituents of AOM which may better indicate the biofouling and particulate fouling potential of seawater and process streams during a bloom. Villacorte (2014) demonstrated that algal-derived TEP and biopolymers can promote fouling of both pretreatment and SWRO membranes and developed tests to measure the concentration of larger TEP ($TEP_{0.4\mu m}$) and smaller TEP precursors (TEP_{10kDa}) in seawater. Applications of both tests showed the smaller and more fouling TEP precursors dominated AOM during a bloom and allowed the differences in the efficiency of pretreatment in removing these algal-derived foulants to be distinguished. For instance, UF was found to be superior in removing TEP precursors in comparison to conventional coagulation-sedimentation-sand filtration.

AOM generated during a HAB may lead to an increase in the biodegradability of organic matter in seawater and serve as a substrate for bacterial growth causing biofouling. A recently developed AOC test, based on luminescence, to measure the biofouling potential of seawater using *Vibrio harveyi* which utilizes low molecular weight organics, demonstrated an increase in AOC during a HAB event compared to normal operating conditions. Other AOC tests are under development to incorporate high molecular weight organic compounds such as biopolymers generated during a bloom. As with AOC, the determination of TEP and the MFI-UF have both proven valuable in laboratory and field trials. They offer distinct advantages over the SDI. The MFI-UF has been applied to optimize coagulant dose to reduce the fouling potential of feedwater containing AOM and to investigate pretreatment efficiency

during a bloom. Promising results were found when using a 10 kDa membrane in the MFI-UF test. A high correlation was found between the MFI-UF and TEP_{10kDa}, indicating the $MFI\text{-}UF_{10kDa}$ could be used to investigate the fouling potential of feedwater containing the smaller high fouling TEP precursors across a plant during a bloom.

While the AOC, TEP and MFI-UF tests offer more targeted information on AOM constituents and the potential biofouling and particulate fouling potential of a feedwater during a bloom than conventional parameters used in the industry, the degree of difficulty in determining them is correspondingly higher. The tests require skilled analysts and specialized equipment. At present, TEP, AOC and MFI-UF cannot be directly employed as a trigger to alert a plant of a bloom in the incoming feedwater or to adjust process parameters during plant operation. Nonetheless, these parameters are expected to be key factors in developing our understanding of AOM fouling in seawater UF and RO systems, and therefore in efforts to control them.

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