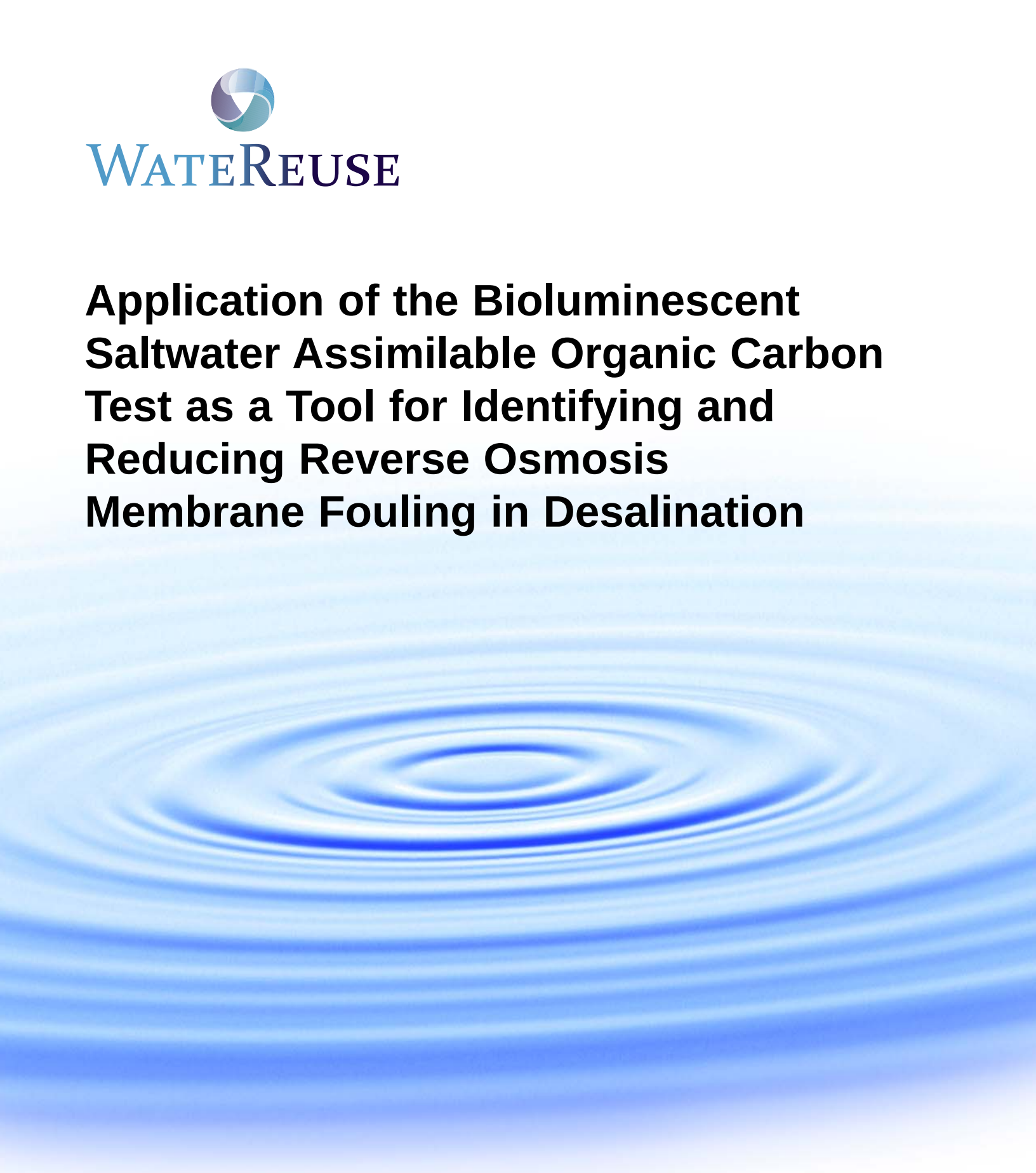
WATEREUSE

Application of the Bioluminescent Saltwater Assimilable Organic Carbon Test as a Tool for Identifying and Reducing Reverse Osmosis Membrane Fouling in Desalination



WateReuse Research Foundation

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About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water for various uses through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, reduction of energy requirements, concentrate management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of providing a reliable, safe product for its intended use.

The Foundation's funding partners include the supporters of the California Direct Potable Reuse Initiative, Water Services Association of Australia, Pentair Foundation, and Bureau of Reclamation. Funding is also provided by the Foundation's subscribers, water and wastewater agencies, and other interested organizations.

Application of the Bioluminescent Saltwater Assimilable Organic Carbon Test as a Tool for Identifying and Reducing Reverse Osmosis Membrane Fouling in Desalination

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Abbreviations and Acronyms

ACS	American Chemical Society
AOC	assimilable organic carbon
AOM	algogenic (algae-derived) organic matter
AOP	advanced oxidation processes
BOM	biodegradable organic matter
CAS	Chemical Abstract Service
DMF	dual media filter
DOC	dissolved organic carbon
DOM	dissolved organic matter
DPD	N,N-diethyl-p-phenylenediamine
MF	microfiltration
MSDS	material safety data sheet
O&M	operation and maintenance
ORP	oxidation reduction potential
RO	reverse osmosis
SBS	sodium bisulfite
SDI	silt density index
SEM	scanning electron microscopy
SWRO	seawater reverse osmosis
TBSDP	Tampa Bay Seawater Desalination Plant
TOC	total organic carbon
UF	ultrafiltration
WBMWD	West Basin Municipal Water District

Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide sustainable sources of high quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse and desalination research topics, including:

- Defining and addressing emerging contaminants, including chemicals and pathogens
- Determining effective and efficient treatment technologies to create "fit for purpose" water
- Understanding public perceptions and increasing acceptance of water reuse
- Enhancing management practices related to direct and indirect potable reuse
- Managing concentrate resulting from desalination and potable reuse operations
- Demonstrating the feasibility and safety of direct potable reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project to provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

Biological fouling on seawater reverse osmosis membranes results in high operating expenses and inhibits efficient treatment. In this study, a test that measures easily assimilable organic carbon (AOC) was investigated for its usefulness in predicting biofouling potential. The novel seawater AOC test uses a naturally occurring, bioluminescent marine organism, *Vibrio harveyi*. Correlations between AOC and operational changes (membrane differential pressure, specific flux) were investigated in full-scale facilities that experienced biological fouling problems and in bench- and pilot-scale configurations. Pretreatment chemicals were evaluated for their potential to increase the biodegradability of seawater and included oxidizing, antiscaling, cleaning, and dechlorinating agents. This report contains evidence that AOC is a useful tool for understanding the impact of pretreatment on biological fouling at bench-, pilot-, and full-scale desalination plants.

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Executive Summary

Desalination using seawater reverse osmosis (SWRO) membranes is a sustainable solution for meeting drinking water needs, and its application continues to expand globally. Although SWRO desalination can be a costly alternative, advances in membrane technology and performance, market demand, and energy recovery have driven costs down in the past few decades. However, SWRO still faces expensive challenges from membrane fouling. Biological growth and deposition of bacteria on the reverse osmosis (RO) membranes (i.e., biological fouling) continues to be difficult to prevent or control.

Assisting the SWRO industry in overcoming the operational challenges caused by biological fouling, specifically through identifying aspects related to prediction, prevention, and, when possible, removal, was the motive for this research. Biological growth occurs when bacteria and nutrients are present under favorable treatment conditions. Disinfection at the plant intake has not been a successful tactic for reducing biological fouling on the membranes because variable treatment, loss of residual, and creation of biodegradable organic matter (BOM) establish conditions in which bacteria can attach to and proliferate on the RO membrane. A measurement for BOM, specifically assimilable organic carbon (AOC), was developed for applications in seawater and uses naturally occurring marine bacteria *Vibrio harveyi*. The test measures an organism's growth response to the nutrients available in a particular water sample. This seawater AOC test can be used as a surrogate measurement for biofouling potential and was evaluated in this project for its predictive capability.
The results contained in this report address changes to AOC formation and removal and the resulting impacts on SWRO membrane conditions. The objectives in this study are the following:

- Identify relationships between biofouling potential, chemical dosing, operational data, and AOC in full-scale SWRO treatment plants.
- Evaluate organic carbon changes and AOC formation from three commonly used oxidants: chlorine, chlorine dioxide, and ozone.
- Evaluate pretreatment chemicals, including antiscaling, membrane cleaning, and dechlorinating agents for organic carbon content and AOC formation after reaction with chlorine.
- Determine the influence of AOC on biological fouling in bench- and pilot-scale RO membrane testing.

SWRO Plant Performance

Water quality from three full-scale SWRO plants was evaluated for changes to organic carbon during pretreatment and to AOC in the RO feed. The plants were selected because they are geographically diverse but experience biological fouling and use surface water intakes. The three plants were Tampa Bay Seawater Desalination Plant (TBSDP), the demonstration plant in California's West Basin Municipal Water Department (WBMWD), and the Al Zawrah facility located in the United Arab Emirates on the Arabian Sea. Grab samples were collected throughout the pretreatment process and indicated that total organic carbon (TOC) removal was poor (<10%); in some cases, the TOC increased at the final step before the RO feed. AOC often changed throughout pretreatment but increased at the RO feed.

At TBSDP, AOC increased after addition of sodium bisulfite (SBS) in the RO feed. WBMWD also had poor organic carbon removal, but TOC at the intake was the lowest of the three plants at 1 mg/L. However, AOC at the WBMWD intake was variable. Numerous operational changes were made at the WBMWD plant during the testing period, and often AOC was higher at the end of the treatment process compared to the intake. In one such pretreatment adjustment, the oxidation reduction potential (ORP) of the water increased after disinfection prior to the RO membrane feed, and increased AOC was reflected in this change. Al Zawrah pretreatment removal of AOC was not consistent, and TOC was variable throughout the pretreatment process, which consisted of dual media filtration. Increases in ORP (measured at the cartridge filter) were correlated to AOC ($r = 0.98$, $p<0.01$) but not TOC ($r = -0.034$, $p = 0.82$).

Operational data were collected to observe changes to the membrane fouling rates during the sampling events at full-scale SWRO plants. The membrane fouling rate was assessed using the increases in membrane feed–brine differential pressure and decreases in permeate flux. At TBSDP, there are seven RO trains. Train 4 was used to determine the membrane fouling rate because that train was operated during the full sampling period in fall 2012. Other trains did not have a consistent data set during the period of interest because they were being cleaned or were offline for some other reason. The data from Train 4 provided a unique opportunity to compare chemical dosing, AOC, and other changes against the membrane fouling rate. The data showed statistically significant correlations ($p<0.01$) when AOC was used as a predictor variable for the increased differential pressure (4–8 psi from September–December 2012) and a 53% decrease in specific flux.

Role of Oxidants and Chemical Addition

Pretreatment changes frequently impacted AOC in the RO feed at the SWRO plants. To further investigate the effects, bench-scale studies evaluated changes to organic carbon in solutions with common pretreatment chemicals that included oxidizing, membrane cleaning, antiscaling, and dechlorinating agents. AOC was formed as a byproduct of reactions with chlorine, chlorine dioxide, and ozone, typical disinfectants used in water treatment. In many of the treatments, the biodegradability of the water increased; in full-scale applications these effects would generate conditions amenable to bacterial proliferation and subsequent biological fouling. AOC was increased by 70% in seawater with 1 mg/L humic acid and a chlorine dose of 0.5 mg/L Cl_2. Increases in biodegradability and AOC were often not accompanied by a significant change in TOC (TOC varied <3%). These and other results indicate that TOC is not an informative tool for the plant operators to predict biofouling potential, which is problematic because it is often the only organic carbon parameter used in SWRO water quality monitoring. For other chemicals, impurities in frequently used treatment chemicals were shown to increase AOC concentrations that were undetected by TOC.

Antiscalants used for the protection of RO membranes from inorganic fouling are generally composed of polyphosphates, polyphosphonates, and polycarboxylates (polymers). Antiscalants used in SWRO were tested for biodegradability in seawater. Polyphosphonates (n=4) and polymer-based antiscalants (n=6) in seawater contributed generally less than 30 µg/L AOC; however, phosphate-based antiscalants (n=2) increased AOC levels nearly 100 µg/L AOC. Depending on the active chemical or inherent impurities, antiscalants may increase the biofouling potential of the RO feed despite the targeted application for the control of inorganic fouling. Antiscalant is often dosed before the cartridge filter or in the pretreatment process where a disinfectant residual is present (i.e., prior to reducing ORP with a dechlorinating agent like SBS).

In this case, conditions facilitate contact time and subsequent reaction potential between the antiscalant and chlorine, and this study found that the byproducts include AOC and phosphate, which both would provide essential nutrients for biological growth. The byproducts would increase assimilable nutrient loading conducive to biological fouling and potentially decrease effectiveness of the antiscalant. Better operational practices, such as removing the chlorine residual prior to dosing the antiscalant, would alleviate the adverse effect of AOC byproduct production. Overdosing SBS as a control practice for ORP was observed at one of the study sites, but this practice increased AOC and led to decreased specific flux and increased differential pressure on the RO membranes.

Bench and Pilot Studies for AOC Modeling

Monitoring data at full-scale treatment plants showed significant correlations with AOC. RO membrane differential pressure increases, specific flux decreases, or both were correlated with AOC. Conducting experiments at the bench- and pilot-scale were required to further investigate the effects of AOC on biological fouling. Using a single membrane provided testing conditions that could be easily monitored and controlled. Therefore, a focused investigation of RO water quality, specifically AOC, was used to evaluate biological fouling and the resulting impact on differential pressure and specific flux. Two approaches examined these operational conditions: the first used a 500 gpd RO pilot that housed one 29 ft^2 membrane, and the second was a bench-scale test unit that housed one 0.0452 ft^2 membrane coupon.

In the latter testing, the coupon was used so that multiple tests could be conducted using baseline (30 µg/L) and elevated AOC (1000 µg/L) RO feed water. The extreme difference in AOC concentrations was used to increase the fouling occurrence and monitor the effect in a shorter time period. Permeate flux decline was associated with RO membrane biological fouling when AOC was elevated (1000 µg/L) and other conditions were constant, including operating pressure and water quality. Flux decline under the same operational conditions was greater in the test where the RO feed contained more AOC, most likely from biofilm formation and organic fouling. Fouling was detected on more portions of the membrane when AOC was higher. Biofilm and bacterial deposits were apparent from the scanning electron microscopy imaging.

Changes to differential pressure were monitored in pretreated TBSDP water under constant flux conditions in the RO pilot. Increased differential pressure was associated with RO membrane biological fouling when the naturally present median TBSDP AOC was 50 µg/L and permeate flux was constant. Even with a constant setting, flux decline occurred from biological fouling, and membrane pore blocking occurred from biofilm growth. AOC was more significant for predicting changes to differential pressure than TOC.

Conclusions and Recommendations

SWRO plant managers would benefit from investigating more efficient techniques for the removal of organic carbon during treatment. TOC removal efficiency is typically very poor, and pretreatment impacts on AOC levels should be controlled in SWRO plants that experience biological fouling problems on the RO membranes, the most critical component. Besides creating more effective organic carbon removal, minor pretreatment configurations may help control AOC levels in the RO feed. Managers and operators could better control

RO membrane biofouling by conducting studies that incorporate the following suggestions, as appropriate:

- Monitor the plant intake (raw) water quality through online or grab samples to determine or adjust pretreatment processes. Relevant parameters that would create a water quality profile for assessing the changing conditions and adjusting pretreatment processes would include AOC, ORP, inorganics (fluoride, nitrate, nitrite, ammonium, metals, phosphate, silicate), TOC/ultraviolet absorbance/organics, particles/modified fouling index, algae, dissolved oxygen, conductivity.
- Collaborate with local public or private institutions to track the occurrence of red tide or algal blooms and institute measuring and control strategies.
- Understand the unique aspects of SWRO plants and water quality to make appropriate choices of chemical type, dose, and maintenance and performance goals.
- Design a daily control sampling plan with sufficient samples to monitor the impacts from pretreatment changes.
- Install sample taps or sampling lines into an operator's lab for quick and convenient monitoring at various treatment steps.
- Monitor RO performance data (differential pressure, permeate flux, and salt passage) to determine the AOC threshold and the effect of pretreatment performance on the membrane; institute nutrient control strategies.
- Devise bench-scale testing approaches for evaluating parameters that lead to a loss in membrane performance or overall SWRO production performance.
- Administer proper chemical treatment in appropriate locations. Track impurities between manufacturers or batches; organic acids such as citric acid, used for membrane cleaning, are a direct source of AOC. Care should be taken to reduce the need for cleaning and clear the membranes of the chemical completely.
- Remove free chlorine residual before administering an antiscalant. Studies show that these chemicals react to produce byproducts such as AOC.
- Investigate other pretreatment management options (e.g., biological filtration) for minimizing or removing biodegradable byproducts (e.g., AOC) that lead to biological fouling.
- Train operators, maintenance staff, and technicians to use results from the sampling strategy to correlate operational changes to water quality fluctuations.
- Incorporate a flat sheet membrane test cell at the first pass of RO feed water for a simplified investigation of the fouling type and rate on the RO membrane and associated water quality.
- Evaluate the type and degree of fouling through membrane autopsies at the time of replacement or before.

Maintaining appropriate chemical doses would be a simple control measure for minimizing biofouling potential of the RO feed water. This report has shown that antiscaling, membrane cleaning, and dechlorinating (ORP control) agents could be wholly responsible for increasing AOC at the RO feed. AOC was shown to be a significant predictor variable for biological fouling impacts on increased differential pressure or permeate flux decline in bench-, pilot-,

and full-scale research from this SWRO study. Pretreatment applications have largely been focused on physical separation. Membrane pretreatment, for example using micro- or ultrafiltration membranes, can be effective for particulate removal and even some removal of TOC; however, low molecular weight organic molecules can readily pass through those membranes. These molecules typically compose the AOC fraction of organic matter; therefore, membrane pretreatment systems would not provide adequate protection against biological fouling of the RO membranes unless the AOC fraction is controlled. Thus, further development of biological treatment of source water to reduce nutrients in the RO feed seawater would be valuable.

Evaluating pretreatment impacts using new methods, including the bioluminescent AOC test, will facilitate control measures to optimize chemical addition and achieve reduced biodegradable nutrient loading and fouling rates. Additional focus on information collection for data modeling applications and real-time monitoring is recommended. Other quantitative and qualitative techniques for monitoring water quality and microbiology of seawater intakes during pretreatment will aid current and future SWRO applications. Additional SWRO research and development are crucial for the efficiency of this growing industry.

Recommendations from this study suggest that biological filtration and other pretreatment management options should be investigated for removal of biodegradable byproducts in order to minimize AOC and subsequent biological fouling. SWRO treatment plant personnel interested in minimizing adverse operational effects should, at a minimum, consider the following scenarios for understanding and mitigating biofouling occurrence on the RO membranes:

- Measuring the water quality at the intake and the RO feed would be a first step in determining the effectiveness of pretreatment on AOC removal.
- Systems that use oxidants (e.g., hypochlorite, chlorine dioxide) should monitor AOC after typical and extreme dosing scenarios.
- Systems should reduce the ORP first with a dechlorinating agent (e.g., SBS/sodium metabisulfite) before adding an antiscalant to maintain antiscalant effectiveness and minimize formation of AOC.
- Chemical dosing should be evaluated through bench-scale tests to minimize AOC, maximize desired outcome, and optimize the treatment process for better operational control.
- Fluctuating water quality at the intake should be tracked to correlate sources of AOC increases (algae, increased organic loading, rain events) so operations may be adjusted to account for changes in AOC and minimize the biofouling potential.

Future studies should be conducted at individual treatment plants to evaluate the maximum AOC threshold and thereby institute measures to control the nutrients entering the RO feed. Pretreatment adjustment by maximizing organic carbon removal or minimizing chemicals that may exacerbate the biodegradability of the RO feed would be most efficient. Identifying the locations during pretreatment in a specific system where AOC is formed or increased would be the first step to control biofouling occurrence and minimize biofouling potential and associated adverse effects on SWRO plant operations.

Chapter 1

Introduction

1.1 Background

Desalination using seawater reverse osmosis (SWRO) membranes is a drinking water solution that is not affected by increasing scarcity or pollution of freshwater resources, although this advantage is counterweighted by more costly operation compared to conventional drinking water treatment. In the United States, two-thirds of desalination capacity is used for municipal water supply (Carter, 2011). Desalination is on the rise, and the United States is currently the leader for reverse osmosis (RO) membrane desalination. The rise in desalination was forecast from the current level of 2324 MGD of contracted desalination capacity up to 3434 MGD by 2016 (Gasson et al., 2010). With this projection, it is more important than ever to address shortcomings in SWRO desalination operations and maintenance (O&M) and investigate approaches to optimize this process.

Although SWRO membrane desalination can be a costly alternative, advances in membrane technology and performance, market demand, and energy recovery have driven costs down in the past few decades (WateReuse Association, 2011). An essential component for increasing SWRO efficiency is to reduce the occurrence and impacts of membrane fouling, which continues to pose an expensive challenge for aspects related to prediction, prevention, and, when possible, removal.

Significant progress has been made in reducing and preventing inorganic and colloidal fouling, but the other two types of fouling, organic and biological, are not as well understood. Biofouling, caused by microbial growth on the membrane, is generally not well managed in SWRO. Biofouling causes costly O&M consequences that include increases in transmembrane pressure, reduction in permeate flux, changes to solute rejection efficiency, compromised membrane integrity, increased cleaning frequency, and process train downtime.

Previously, SWRO personnel lacked the necessary test capable of predicting the biofouling potential in seawater, specifically for measuring the biodegradable fraction of organic carbon, commonly referred to as easily assimilable organic carbon (AOC). The AOC bioassay is considered to be an indicator for the biological growth potential of a water sample (LeChevallier et al., 1993); similar application for SWRO treatment provides a tool for determining biofouling potential. The AOC test is a microbial assay (bioassay) that traditionally uses two strains of bacteria, P17 and *Spirillum* NOX. Bacterial growth is monitored over time in a pasteurized freshwater sample until maximum growth occurs (N_{max}). However, highly saline conditions are not conducive for growth, and previous attempts using traditional AOC strains have had to drastically alter the sample (Ong et al., 2002). Other attempts at AOC tests have not resulted in an appropriate reference organism and use plate counts for measuring biomass, which is time consuming, costly, and has a long turnaround time for results (Amy et al., 2011).

Using a naturally occurring, bioluminescent marine organism, *Vibrio harveyi*, a saltwater AOC test was developed and applied to environmental samples from seawater intake points and treatment points in full-scale SWRO desalination facilities (Schneider et al., 2011;

Weinrich et al., 2011). Unlike traditional spread plating techniques in bioassays, a photon-counting luminometer was used to measure bioluminescence and bacterial growth. Bioluminescence is the amount of light produced and is the key measurement for this bioassay. Standard curves produced linear relationships between maximum bioluminescence and acetate carbon equivalents. There are numerous advantages to this bioassay, including minimal consumables, short turnaround time, determining available substrate (AOC, N_{max}), and Monod kinetic model fitting to determine the bacterial rate of utilization (μ_{max}).

1.2 Fouling

Membrane fouling results from the accumulation of materials on, in, or near the membrane (Taylor and Weisner, 1999). The result of this accumulation has long been recognized as a major problem for RO facilities because it can result in a decline in water production over time for constant pressure operations or an increase in required feed pressures (Zhu and Elimelech, 1995). A successful future for membrane applications will be realized by having a clear understanding of fouling mechanisms and developing essential tools for quantification and prevention.

Fouling is generally documented as one of four types: scaling from precipitation of sparingly soluble salts, plugging caused by deposition of particulate matter, adsorption of organic matter, and biological fouling from growth of microorganisms on membrane surfaces (Zhu and Elimelech, 1995; Duranceau, 2007). Managing SWRO membrane fouling is further complicated because each type of fouling may not occur independently. Membrane fouling can occur through adsorption of organic matter onto the membrane surface. Once sorbed, removal is difficult and may lead to irreversible fouling. Colloidal aggregates package organic matter, making it more readily biologically utilizable. Colloidal interactions with natural organic matter (NOM) exacerbate fouling when the sorbed particles block membrane pores, form part of the membrane cake, or become biologically available.

Organic and biological fouling types are interrelated. Organic fouling was reported to be most common in SWRO desalination in the recent Water Research Foundation report by Veerapaneni et al. (2011). In addition, the study found that 40% of permeability decline in RO membranes is attributed to organic and biological fouling. Membrane foulants only compose a small fraction of NOM (Cai and Benjamin, 2011) when measured in freshwater. NOM can occur naturally in the source water or originate from anthropogenic sources, specifically wastewater or industrial or agricultural effluents. NOM present in seawater was reported to be 24% high molecular weight dissolved organic carbon (1–100 nm) and about 75% low molecular weight (<1 nm); the other 1% was identified as particulate organic carbon (Benner et al., 1997).

Ultrafiltration (UF) and microfiltration (MF) membrane pore sizes are from 0.01 to 0.05 µm and 0.1 to 0.5 µm, respectively. RO membrane pore size is near 0.0001 µm. Therefore, the opportunity for organic matter removal in RO feed is diminished by the inherent capacity of the membrane. Traditional approaches for predicting organic fouling potential include total organic carbon (TOC), ultraviolet (UV) absorbance, and color; however, the measured fouling rates for NOM in seawater do not correlate with these parameters (Amy et al., 2011). Discovering the link between potential and realistic fouling rates is critical, and additional understanding of organic matter behavior in high salinity (i.e., seawater) environments will be most useful for successful O&M applications at full-scale facilities. Opportunities exist for either breaking NOM down into smaller fractions that can be removed by biological pretreatment or some other combination of organic adsorption and removal.

1.3 Biological Fouling

Biofouling is neither well understood nor consistently prevented and continues to be a challenge in SWRO membrane separation processes (Griebe and Flemming, 1998; Vrouwenvelder et al., 2000; Vrouwenvelder and Van Der Kooij, 2001; Pang et al., 2005; Kumar et al., 2006). The growth of microorganisms into a biofilm on the membrane surface leads to cost increases in SWRO treatment. Decreasing permeate flux, increasing pressure drops in the RO modules, increasing salt passage, and irreversible damage to the RO membrane are all issues associated with biofouling. Extracellular polymeric substances (EPS) present in the biofilm (composed of marine microorganisms and extracellular substances generated by them) accounts for 50 to 90% of the biofilm TOC. Other naturally occurring or anthropogenic biopolymers as well as sources of AOC provide a food source that enables bacteria to proliferate. In addition, EPS provides another substrate for this unwanted proliferation.

Red tides are highly destructive algal bloom events that can occur when red-pigmented marine algae rapidly increase in concentration Blooms can significantly increase turbidity of seawater; however, the release of organic material from the algae is also a major concern. Intake pumps, pretreatment processes, and hydrodynamic shear forces in RO treatment can cause algal cell lysis and lead to release of intracellular organic matter, thereby increasing soluble and highly biodegradable algogenic (algae-derived) organic matter (AOM; Ladner et al., 2010). AOM is composed of acids, proteins, simple sugars, anionic polymers, and negatively charged and neutral polysaccharides (Edzwald and Haarhoff, 2011). It provides a rich substrate for bacterial growth, thereby exacerbating membrane biofouling by creating favorable conditions for bacterial attachment on the RO membrane (Ladner et al., 2010). In general, harmful algal blooms are increasingly recognized for their detrimental impacts on RO desalination facilities. Although pretreatment can prohibit algal cells from entering the RO membrane modules, cell destruction and AOM would still require control and removal to reduce the biofouling potential.

1.4 Pretreatment Effects on Biofouling

Chlorine and chlorine dioxide are typically applied at the seawater intake for control of biological growth. Operators have experienced incidences of RO biofouling despite this application and also after intensive shock chlorination. Shock chlorination involves elevated intermittent dosing of chlorine as opposed to continuous dosing. Most utilities monitor organic carbon in seawater sporadically, which has not been sufficient to understand the impact of disinfection on transforming organic matter into biodegradable organic matter (BOM) in a SWRO system. For instance, the measurement for TOC only quantifies carbon content in a given volume of water but provides no specificity of the biodegradable nature.

Biodegradability and impacts from pretreatment, including disinfection, should be considered in SWRO operations where microbial growth on the membranes is a problem. The drinking water industry often practices preoxidation as part of pretreatment, which creates biologically available organic carbon, or AOC. For example, ozone reacts with NOM to form aldehydes and low molecular weight organic acids (Miltner et al., 1992; Weinberg et al., 1993; Schechter and Singer, 1995; Siddiqui et al., 1997), which can then be removed by biological filtration to increase biological stability and decrease disinfection byproduct formation. Van der Kooij (1986) showed that AOC concentrations increased in water samples treated with increasing chlorine doses. In a similar study, Hambsch and Werner (1993) reported higher

biodegradability of humic substances (NOM) after chlorination. LeChevallier et al. (1992) found that chlorination can increase AOC depending on the point of chlorine application.

Increasing biodegradability and the effects of pretreatment have been extensively investigated in surface and groundwater matrices used for drinking water, but the effects of disinfection with specific regard to production of BOM and AOC are largely unknown in seawater and brackish water matrices used for RO desalination. It is unfortunate that there is no biofiltration research to this extent in desalination, yet there is significant interest in mitigating irreversible biofouling of the RO membranes. This issue has been clearly referenced by numerous authors (Flemming et al., 1997; Griebe and Flemming, 1998; Schneider et al., 2005; Fujiwara and Matsuyama, 2008; Voutchkov, 2010). The seawater bioluminescent AOC test provides a tool to better manage and mitigate fouling and measure BOM and RO biofouling potential for the purpose of increasing plant efficiency.

Other chemicals introduced into the treatment process, including impure acids or phosphate-based scale inhibitors, may also exacerbate biofouling (Vrouwenvelder et al., 2000; Weinrich et al., 2011). Chemicals are added prior to membrane separation to reduce the precipitation of sparingly soluble salts. The ability of a chemical to reduce scale formation is related to its chemical structure, molecular weight, active functional groups, and solution pH (Shih et al., 2004). The molecular weights of antiscalants are reported to range from 1000 to 11,000 and typically consist of polycarboxylates, polyacrylates, polyphosphonates, and polyphosphates. Phosphonates contain a carbon–phosphorus bond that must be broken for microbial assimilation, and bacterial degradation pathways have been studied in naturally occurring phosphonates. Pathways for cleaving the carbon–phosphate bond present in these chemicals have been investigated (Huang et al., 2005), and bacteria, including some *Vibrio* species, contain specific genes that are capable of this coding.

With the increasing use of artificial phosphonates in industry and their natural occurrence in the environment, phosphate-containing chemicals provide an essential nutrient supply. The presence of phosphate in waste streams and concentrates has impacts in areas of discharge that may be associated with algal blooms. Companies are developing environmentally friendly antiscalants to avoid this issue, some of which are free of phosphates (Musale et al., 2011). In desalination applications, the potential for microbial growth from the application of phosphonate, phosphate, and carboxylate chemicals requires additional research. This report helps to close the knowledge gap between increased biofouling potential, pretreatment chemicals, disinfectants, and the oxidation impacts on NOM in seawater using the saltwater bioluminescent AOC test (Weinrich et al., 2011).

1.5 Project Objectives

Biological growth and the resulting fouling on SWRO membranes continue to be costly challenges for efficient SWRO treatment. Determining the effect and extent of pretreatment processes on AOC levels has become an important focus for investigating ways to control the formation of AOC and ultimately limit adverse effects of SWRO membrane fouling. The results contained in this report address changes to AOC formation and removal and the resulting impacts on SWRO membrane conditions. The objectives in this study were to:

- Identify relationships among biofouling potential, chemical dosing, operational data, and AOC in full-scale SWRO treatment plants.
- Evaluate organic carbon changes and AOC formation from three commonly used oxidants: chlorine, chlorine dioxide, and ozone.

- Evaluate organic carbon changes and AOC formation from pretreatment chemicals and after reaction with chlorine.
- Determine the influence of AOC on biological fouling in bench- and pilot-scale RO membrane testing.

Chapter 2

Full-Scale SWRO Plant Performance

2.1 Objective and Methods

Water quality variation and organic carbon removal were examined at three full-scale SWRO desalination plants. Grab samples were collected from various points within the pretreatment process. The grab samples provided information on source water quality fluctuations and the effectiveness of treatment for removing organic carbon and AOC as related to biofouling potential. The treatment plants use seawater from surface intakes but have geographic variability and different pretreatment configurations. Organic carbon removal was determined through typical measurements such as TOC and UV absorbance at 254 nm (UV_{254}) as well as more specific determination of biodegradability using the seawater bioluminescent AOC test. Operational data were supplied by treatment plant personnel to supplement the grab sampling efforts and evaluate the plant's performance. Cleaning procedures, treatment changes, flow rates, membrane flux, and differential pressure data were used to correlate the significance of AOC as an indicator of biological fouling potential in the following treatment plants: Tampa Bay Seawater Desalination Plant (TBSDP), West Basin Municipal Water District (WBMWD) Ocean Water Desalination Demonstration Facility, and Al Zawrah.

2.1.1 Assimilable Organic Carbon

AOC was measured using the luminescence assay reported by Weinrich et al., 2011. All experimental and environmental samples (50 mL) were prepared in AOC-free glassware and pasteurized in a water bath for 30 min once the temperature of the proxy reached 70° C. Samples were then cooled in an ice bath. After pasteurization the cooled samples were inoculated with *V. harveyi* at approximately 10^3 colony forming units (cfu) per mL. *V. harveyi* was used because it is a naturally occurring marine organism.

The inherent bioluminescent characteristic of this organism facilitates the use of an automated photon-counting luminometer for monitoring proliferation in a water sample. Samples were gently swirled, and duplicate 300 µL aliquots were transferred into the microplate immediately after inoculation. A laminar flow hood (SterilGARD II; The Baker Co., Sanford, ME) was used to maintain sterility during sample handling, inoculation, and transfer to the microplate. The microplate was covered with adhesive film to minimize evaporation, and measurements were taken immediately and then at hourly intervals (generally 2–5 hours) until peak luminescence (or maximum growth, N_{max}) was reached. Additional methodology is located in the Appendix.

2.1.2 Total Organic Carbon

TOC was measured using a platinum-catalyst combustion TOC analyzer (TOC-V_{CSH}, Shimadzu Scientific Instruments, Inc., USA) with an autosampler according to Standard Method 5310 B. Samples were acidified using sulfuric acid to pH greater than 2 prior to analysis. Results shown are the average of triplicate injections.

2.1.3 Ultraviolet Absorbance at 254 nm and SUVA

UV_{254} was measured using a UV-Vis spectrophotometer (DR 5000, Hach, Co., USA) set at a single wavelength of 254 nm; water samples were filtered through Whatman GF/F glass fiber filters with a nominal 0.7 µm pore size and measured using a 1 cm quartz cuvette. The filtrate was also used for measuring dissolved organic carbon (DOC). Specific UV absorbance (SUVA) was calculated by dividing UV_{254} (m) by DOC in mg/L; units are L/mg/m.

2.2 Tampa Bay Seawater Desalination Plant

TBSDP is located on Tampa Bay in Gibsonton, FL. The plant is colocated with the Tampa Electric Company (TECO) coal-fired power plant and receives feed water from the plant's cooling loop; if the cooling water exceeds the temperature limits of the membranes, bay water can be mixed in. A process flow schematic of the plant is shown in Figure 2.1. The combined bay water and cooling water (i.e., raw water) was treated with chlorine dioxide (0.5–1.1 mg/L) and further treated with sodium hypochlorite, sulfuric acid, and ferric chloride in the coagulation step. The water is flocculated prior to the sand filters: upflow, deep bed, granular media filters with continuous backwash. From these filters, the water is sent to two parallel banks of diatomaceous earth (DE) filters. Any residual sediment from the DE filtrate is then removed in cartridge filters prior to the SWRO desalination membranes. Cartridge filters (Fulflo Durabond and Honeycomb Filters, Parker Hannifin Corporation, Oxnard, CA) are replaced once a year. Sodium bisulfite (SBS) is added at this step to control the oxidation reduction potential (ORP) of the water and prevent oxidative damage to the membranes. Additional information on the RO membranes at TBSDP is provided in Section 2.2.2.

Samples were collected from pretreatment locations at TBSDP on September 20 and October 24, 2012 and January 3, 2013 for the purpose of evaluating treatment effectiveness for AOC removal and comparing the biofouling potential (i.e., AOC content) of the RO membrane feed. The project team initially proposed to collect samples quarterly from TBSDP; however, because of the ongoing operational directives, the plant was online from August through December and had adjusted pretreatment in preparation for shutting down the plant in January. The plant was offline from January 7 through 24, 2013.

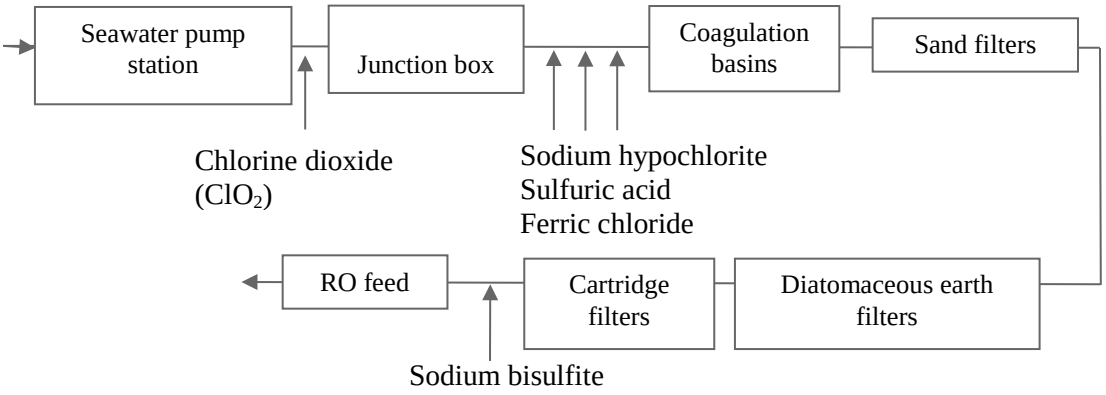

Figure 2.1. Tampa Bay Seawater Desalination Plant process flow diagram.

2.2.1 Pretreatment and Organic Carbon Removal

TOC removal throughout pretreatment between coagulation and cartridge filtration was 3% in September and 6% in October, which is consistent with the limited TOC removal at TBSDP reported previously (Schneider et al., 2011). This does not include organic removal before coagulation as the intake was not included as a result of sampling issues. AOC was generally below detection (<10 µg/L) after DE filtration. Although not directly investigated in this study, bioactivity in the DE may have been sufficient to reduce AOC after that treatment step. AOC was less than 10 µg/L following DE treatment, but after the cartridge filter AOC increased to 97±19 µg/L in September and 23±1 µg/L in October (Table 2.1). Chemical addition after the cartridge filter is limited only to SBS to remove the residual oxidant from sodium hypochlorite added prior to coagulation (Figure 2.1). The staff reported that SBS was typically dosed between 5 and 22 mg/L, but the records from August through December 2012 indicated that the range was 3 to 123 mg/L (specifically in Train 4) for controlling ORP. There were no other chemicals added at this treatment step; antiscalant was not used at TBSDP.

Table 2.1. TBSDP Organic Carbon Data

	Treatment Step	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
September	Coagulation	0.135	6.20	20
	Sand filter	0.133	6.38	60
	DE Filter East	0.127	6.29	1
	DE Filter West	0.128	6.12	8
	Cartridge filter	0.132	6.00	97
October	ClO_2	0.173	5.85	29
	Coagulation	0.131	5.49	2
	Sand filter	0.103	5.29	1
	DE Filter East	0.106	5.13	1
	DE Filter West	0.103	5.07	2
	Cartridge filter	0.110	5.17	23

Notes: AOC=assimilable organic carbon; DE=diatomaceous earth; TOC=total organic carbon; UV=ultraviolet.

2.2.2 Data Modeling Approach

TBSDP went online in August after new RO membranes were installed in Trains 1 and 7, which provided a unique opportunity for the research team to conduct an in-depth analysis on membrane changes caused by fouling. By capturing this time period immediately after restarting, the operational impacts from fouling on new membranes were investigated from August until December 2012, when the plant was online and operating. There are seven first-pass RO trains at TBSDP. Each train is preceded by a lift pump, cartridge filter, and high-pressure feed pump. There are two stages in each vessel separated by a block. The first stage contains Elements 1 through 3; after a block, permeate from the five Lag Elements 4 through 8 is sent to the second-pass RO for further treatment. In the performance tracking software, data are entered for the two stages separately.

The first three elements were selected for additional analysis because the incoming water from the cartridge filter would be the most representative RO feed for the purpose of investigating fouling effects. The flow rates, total flow, and differential pressure were used for further evaluation. The operating time was compared between the RO trains. Total flow (in billion gallons) for each of the seven trains during the time period of interest is listed in Table 2.2. Because of maintenance and variable production needs, not all of the trains were continuously operated; those that were operated the longest were suitable for further data analysis and comparison. Trains 1, 4, and 6 were operating for 68, 65, and 80 days, respectively. These trains also received the greatest volume of seawater compared to the other trains. The following section describes the preliminary analyses for the type of membranes, flux, and differential pressure associated with these trains.

Table 2.2. TBSDP Operating Time, Total Flow, and Average Specific Flux

Train and Membrane Type	Total Time in Operation (days)	Total Flow (billion gallons)	Average Sp. Flux ($gpm/ft^2/psi$)
1 SWC4-LD	68	11.5	0.000027
2 SW30HR	57	7.3	0.000021
3 SW30HR	22	1.1	0.000019
4 SW30HRLE	65	11.1	0.000033
5 SW30HR	32	2.4	0.000023
6 SW30HRLE	85	18.3	0.000028
7 SWC4-LD	60	8.5	0.000028

Notes: Normalized to 25° C; testing from August through December 2012; Sp=specific.

There were various membranes used during the time period of interest in 2012. Each train has 160 pressure vessels containing eight membranes. In August 2012, new Hydranautics SWC4-LD membranes were installed in Trains 1 and 7. The SWC4-LD membrane has 400 ft^2 of membrane area. Trains 2, 3, and 5 contained older SW30HR Filmtec membranes, each having an area of 380 ft^2. Trains 4 and 6 had newer SW30HRLE-370/34i Filmtec membranes with an area of 370 ft^2 each. The area of the three lead elements in each train was calculated to determine specific permeate flux from each membrane type. Specific flux was calculated from the permeate flow (gpm) from Elements 1 through 3 divided by the net driving pressure (psi) divided by the total area of the membranes used in that stage (Figure 2.2). For instance, in RO Train 1, flow from the three elements (400 ft^2 each) in the 160 vessels crosses 192,000 ft^2 of RO membrane surface. Therefore, at a flow of 1888 gpm and net driving pressure of 260 psi, the specific flux is 0.000038 gpm/ft^2/psi.

$$Specific\ flux = Q_p \div NDP \div A$$

where:

Q_p *is the permeate flow* (*gpm*)

NDP is the net driving pressure (*psi*)

and

A is the membrane area (*sq. ft.*)

Figure 2.2. Specific flux calculation.

Table 2.3. TBSDP RO Trains and Change in Specific Flux

Train and Membrane Type	Δ Specific Flux September	Decrease Based on Average (%)	Δ Specific Flux October	Decrease Based on Average (%)	Decrease August–December (%)
1 SWC4-LD	0.000005	19	0.000010	37	47
2 SW30HR	0.000003	14	ND	ND	39
3 SW30HR	ND	ND	ND	ND	ND
4 SW30HRLE	0.000000	1	0.000012	36	53
5 SW30HR	ND	ND	0.000008	33	36
6 SW30HRLE	0.000005	18	0.000008	28	49
7 SWC4-LD	0.000007	25	0.000012	44	45
Average	0.000004	16	0.000011	29	45

Notes: ND=no data, membranes were not in operation; operations started August 2012.

Changes to specific flux and differential pressure were monitored to determine the impact of fouling in each RO train. Decreased specific flux is observed when water passage is reduced by a fouling layer, pore blockage, or both. As an alternative, when additional force is needed to overcome osmotic pressure changes on membranes that had succumbed to fouling, the differential pressure increases. Membrane manufacturers typically set limits for differential pressure, and when the limits are reached a cleaning procedure is triggered at the plant. During the time period evaluated, Train 4 underwent a cleaning on November 18, and Train 6 was cleaned on December 14, 2012. Trains 1, 4, and 6 produced the majority of the water (Table 2.2) during September and October; overall trends indicate that specific flux decreased, and differential pressure increased. Specific flux decreased to a greater extent in October (Table 2.3). Most pronounced was the 53% decrease in specific flux in Train 4 prior to the cleaning on November 18, 2012.

2.2.3 Operational Performance and Data Modeling Results

Grab sample collection coincided with the period of operation for RO membranes in Train 4. Other trains were periodically offline for maintenance and therefore did not provide a complete data set for comparison with the water quality samples. Train 4 was operating for 47 days prior to the first cleaning on November 18, 2012. Figures 2.3 through 2.5 graphically depict the operational data beginning on September 22 for Train 4. Consistent trends were evident for decreasing specific flux (Figure 2.3) and increasing differential pressure (Figure 2.4); a strong correlation existed between the two data sets (r^2=0.89; Figure 2.5).

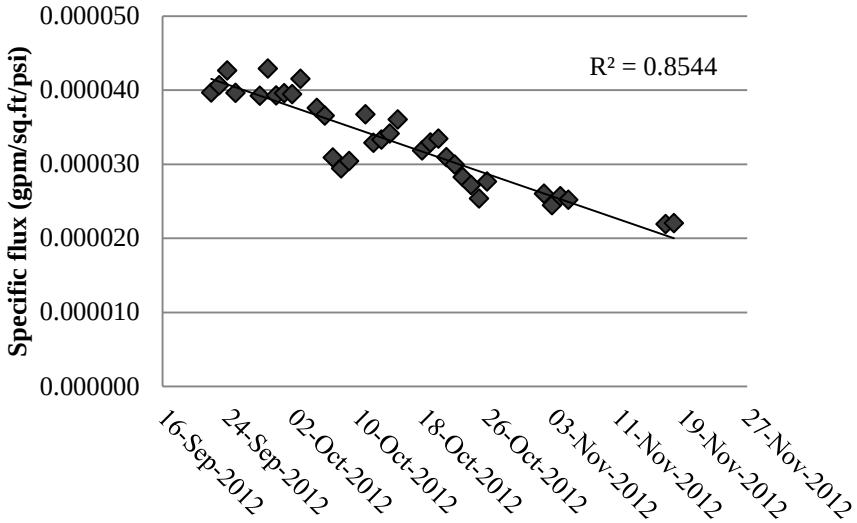

Figure 2.3. TBSDP: Specific flux of the first-pass RO membranes in Train 4.

Notes: September to November 2012 (n=35). New membranes were installed in August, and the train was online beginning September 22.

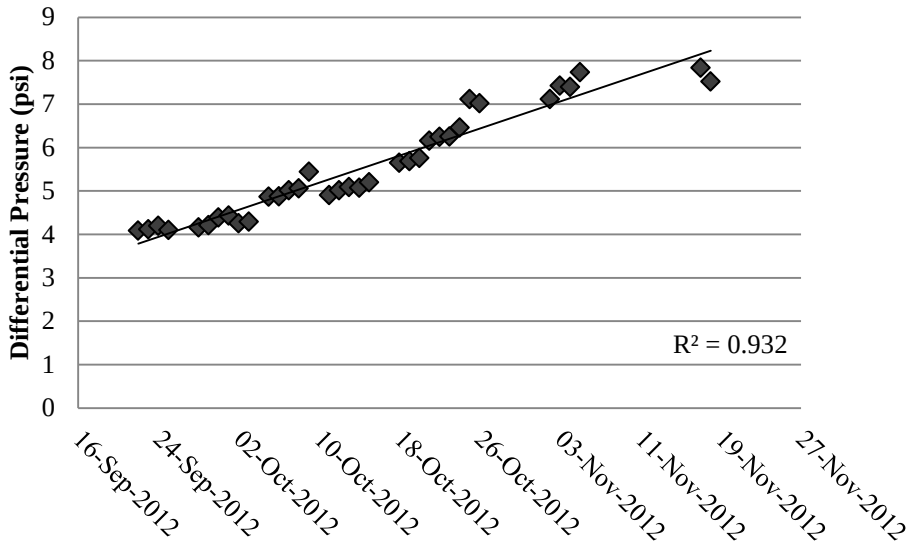

Figure 2.4. TBSDP: Differential pressure of the first-pass RO membranes in Train 4.

Notes: September to November 2012 (n=35). New membranes were installed in August, and the train was online beginning September 22.

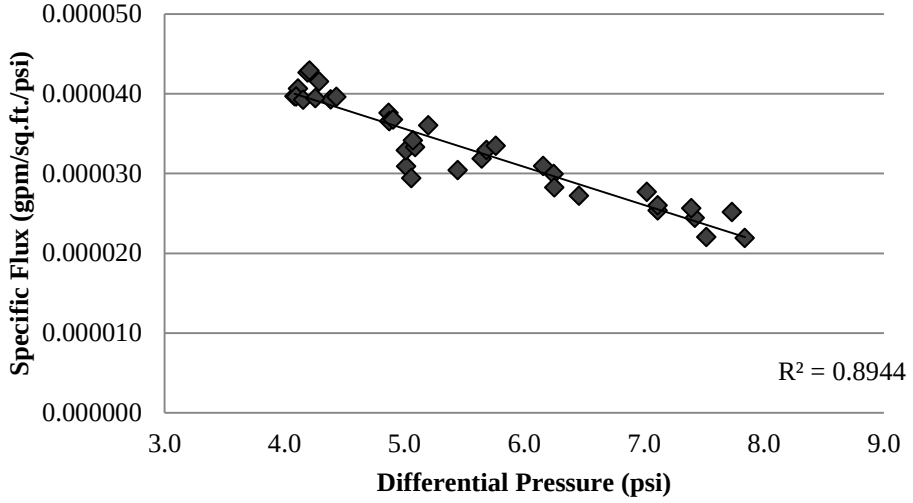

Figure 2.5. TBSDP: Correlation between specific flux and differential pressure in Train 4.

Note: n=35.

Organic loading and cartridge filter monitoring data were examined to evaluate whether the operational changes to the RO membranes (specific flux and differential pressure) were a result of biological fouling. A small dataset (n=16) for AOC, TOC, and UV_{254} suggested that organic content of the RO feed increased as specific flux decreased (r=0.933, n=16, p<0.01). To confirm this, a larger data set (n=120) using monitoring data at the cartridge filter was investigated to ascertain treatment impacts and operational effectiveness on organic carbon removal and the impact on RO fouling. Monitoring and chemical dosing data after the cartridge filters were used for an evaluation of the plant condition at this treatment step.

Cartridge filter monitoring data included differential pressure, turbidity, and silt density index (SDI) compiled from hard copy records at TBSDP for August through December 2012. Differential pressure increased at two intervals, with peaks on October 15 and November 18, 2012 (average 6.9 psi; range 4–35; n=120; Figure 2.6). During these same periods, SDI of the Train 4 cartridge filtrate averaged 3.9 (range 2.9–4.9; n=119; Figure 2.7). There was no significant relationship between differential pressure or specific flux and the predictor variable SDI (Table 2.4), which is not surprising; SDI is inadequate for addressing a range of fouling issues because the test is limited to only measuring particles and not the BOM that contributes to biofouling. Turbidity was generally low and stable below 0.5 NTU, in most instances less than 0.25 NTU (average 0.11; range 0.05–0.35; n=119; Figure 2.8). Turbidity had an inverse relationship to differential pressure (r=-0.45, $p<0.01$, n=34), and in the absence of a positive relationship depicted, the results suggest that the increases in differential pressure were not solely caused by particulate or colloidal fouling. Interpretation of the data would suggest that the fouling was biological from AOC loading after startup in August, the effects of which were observed through November.

SBS was applied to the cartridge filtrate to remove the chlorine residual and decrease ORP in the RO feed. The highest SBS doses from that quarter were applied in October and November (during the same periods in which differential pressure increased). From plant startup on August 14 until December 31, the average SBS dose was 8 mg/L and ranged from 3 to 123 mg/L. AOC concentrations in the RO feed were extrapolated from the SBS dose. SBS used at TBSDP was investigated in bench-scale testing (Chapter 3), and impurities in the solution increased AOC. In addition to bench-scale tests, SBS increased AOC at the RO feed during sample collection (Table 2.1). The reported concentrations represented more conservative estimates, in which average AOC was 150 µg/L (range 90–1830 µg/L; n=123) versus another model that predicted average AOC to be 190 µg/L (range 70–3020 µg/L; n=123).

Using the conservative approach, calculated AOC results were similar to the grab sample results; cartridge filter AOC was 97 µg/L in September, and the extrapolated AOC from SBS dosing was 98 µg/L. AOC in the RO feed for Train 4 during the period of investigation is depicted in Figure 2.9. AOC in the RO feed was evaluated as a variable for predicting fouling (observed from decreased specific flux and increased RO differential pressure; Table 2.4). Of the possible predictor variables for fouling, including cartridge filter differential pressure, SDI, cartridge filtrate turbidity, and RO feed AOC, the strongest correlation was with AOC (r=0.563, $p=0.001$, n=34; Table 2.4).

The relationships among TOC, UV_{254}, and AOC were evaluated to determine whether these parameters were significantly correlated ($p \leq 0.05$). TOC and UV_{254} were correlated (r=0.61, $p=0.05$); however, AOC showed no significant relationship at TBSDP with UV_{254} (r=0.36, $p=0.28$) or TOC (r=0.43, $p=0.19$). Given the lack of specificity for TOC and UV_{254} in measuring the biodegradability of organic carbon present, it is recommended that this utility track AOC for predicting pretreatment changes impacting the biofouling potential.

Table 2.4. Correlation and Significance of Predictor Variables at the TBSDP Cartridge Filter and RO Feed for Differential Pressure and Specific Flux

	Differential Pressure		Specific Flux	
	Pearson Correlation	***p* (2-tailed)**	**Pearson Correlation**	***p* (2-tailed)**
CF differential pressure (n=35)	0.187	0.282	-0.219	0.206
CF SDI (n=33)	-0.232	0.194	0.238	0.183
CF turbidity (n=34)	-0.450	0.008	0.397	0.020
AOC (n=34)	0.563	0.001	-0.495	0.003
Day (n=35)	0.965	0.000	-0.920	0.000

Notes: September to November 2012; AOC=assimilable organic carbon; CF=cartridge filter; SDI=silt density index.

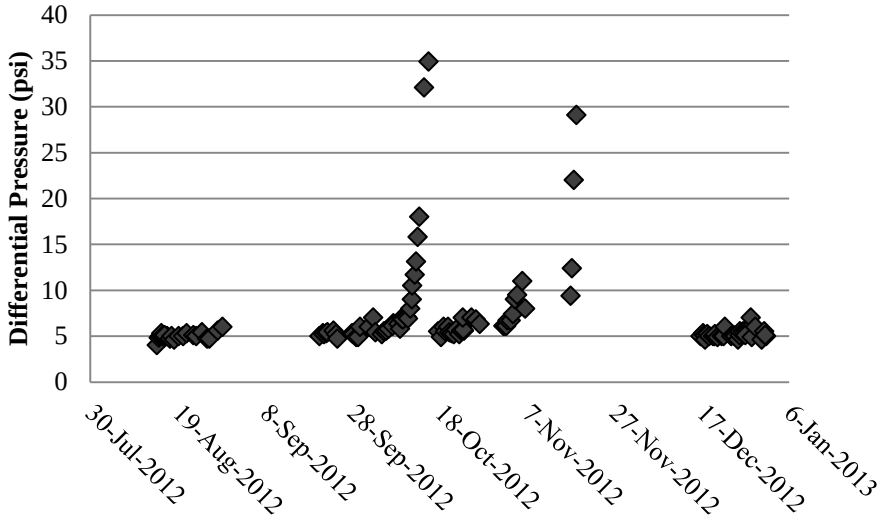

Figure 2.6. TBSDP cartridge filters Train 4: Differential pressure.

Notes: Peaks detected October 15 and November 18; average=6.9 psi (range 4–34.9; n=120).

The SBS dose (n=59, September–December) showed a positive relationship with differential pressure ($p<0.01$) and a negative relationship with specific flux ($p<0.01$). Increases in differential pressure and decreases to specific flux occurred because of fouling on the membranes during the periods investigated. TBSDP has experienced biofouling in the past on account of water quality issues at the intake and the high concentration of organic carbon in the RO feed. Pretreatment generally removes less than 10% of TOC, and sampling events indicate that AOC was increased in the postcartridge filter sampling point (i.e., RO feed). The only chemical addition at that point was SBS, and in conjunction with the bench-scale testing, operational records, and statistical evidence, the addition of SBS increased AOC in the RO feed. These conditions were conducive to biological growth on the RO membranes, and,

given the low potential for particulate fouling, chemical dosing and operational parameters suggest that the fouling was biological in nature.

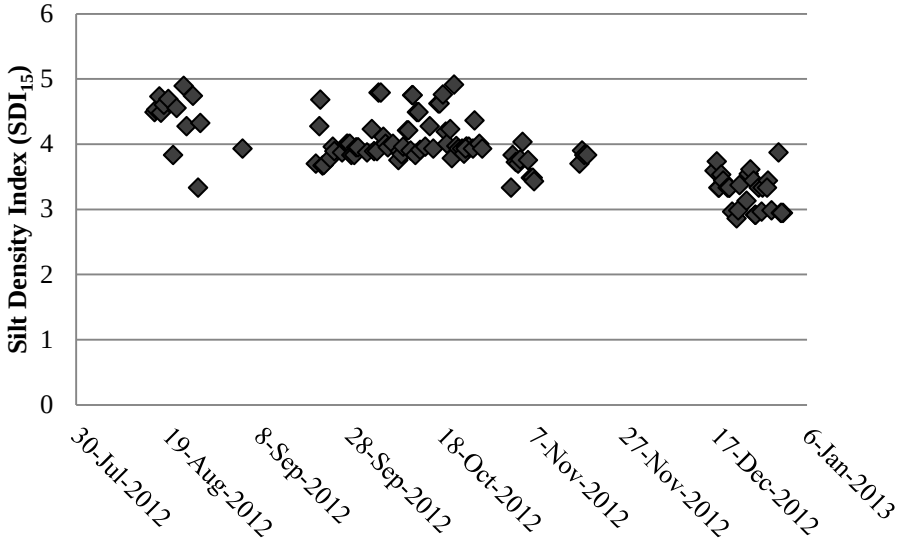

Figure 2.7. TBSDP cartridge filters Train 4: Silt density index.

Note: Average=3.9 (range 2.9–4.9; n=119).

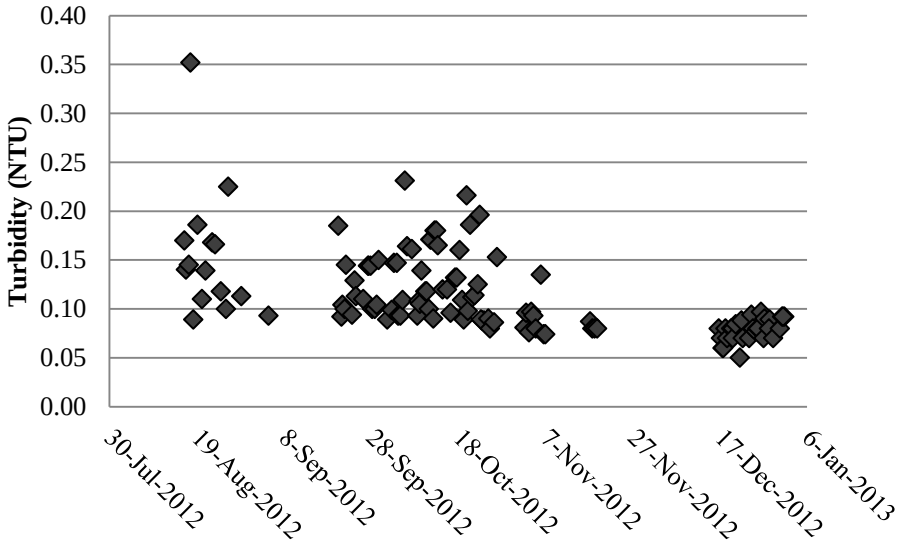

Figure 2.8. TBSDP cartridge filters Train 4: Turbidity.

Note: Average 0.11 NTU (range 0.05–0.35; n=119).

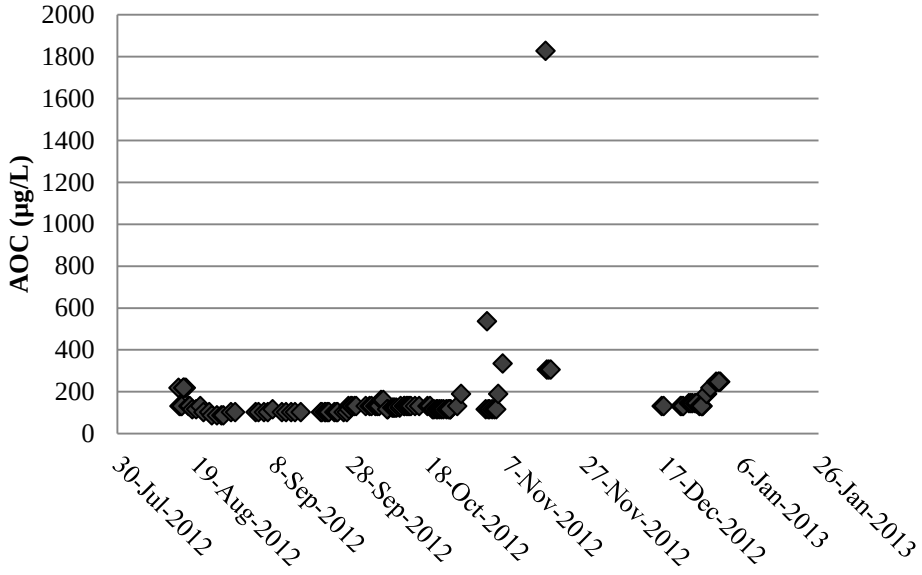

Figure 2.9. TBSDP Train 4: AOC in RO feed

Note: Average AOC 150 µg/L (range 90–1830 µg/L; n=123).

2.3 West Basin Municipal Water District Ocean Water Desalination Demonstration Facility

WBMWD is colocated with a natural gas power plant, and the seawater intake is located at Redondo Beach, CA, 0.5 mile into the Pacific Ocean and 30 feet below the surface. The plant was chosen because of its relatively low organic content (TOC~1 mg/L), reported challenges with biological fouling, and Pacific Ocean location. The desalination process consists of a 2 mm intake screen and 100 µm Arkal disk filters followed by UF and RO. UF membranes were ZeeWeed 1000 (GE, USA). Hypochlorite and citric acid were used for UF maintenance cleaning. There were two parallel RO pressure vessels, and each vessel contained seven membrane elements. RO membranes were from the QuantumFlux™ line by NanoH2O (California, USA). NanoH2O membranes used in the first-pass RO had a surface area of 400 ft^2, for a total surface area of 5600 ft^2.

2.3.1 Pretreatment and Organic Carbon Removal

Four sampling sets were collected from WBMWD for the purpose of evaluating the changes to organic carbon through the pretreatment process (Table 2.5). Samples were collected from pretreatment locations on June 5, July 31, November 29, and December 28, 2012, during which time the plant was producing about 0.05 MGD of desalinated water. The sampling locations included raw seawater (after intake screen and before Arkal filter pods), UF feed following Arkal screening and ferric chloride addition, UF filtrate, feed to the cartridge filter after chemical addition (when applied), and at the RO feed after the cartridge filters. A shipping issue during the November sampling resulted in a loss of the UF filtrate and RO feed samples.

Average TOC throughout the treatment train was 1.09±0.07 mg/L in June, 0.9±0.03 mg/L in July, and 0.7±0.05 mg/L in December. In the fall and winter sampling events, TOC was lower than in the summer but increased during pretreatment. During June and July, TOC was

only removed by 5% throughout pretreatment. Average AOC throughout treatment was also greatest in June, particularly before UF treatment. In June the water quality evidence from lower pH, higher ORP, higher AOC, TOC, and UV_{254} were all different from the other sampling events. Changes to organic carbon during pretreatment are graphically represented in Figure 2.10. In July, both AOC and UV_{254} were higher at the RO feed than in the intake, which was not reflected in the TOC data set. Average AOC from July was 55±30 µg/L, and in June it was 79±57 µg/L. In the June event, AOC was reduced between the intake and RO feed by 110 µg/L. In July, AOC at the intake was less than 30 µg/L but increased to 90 µg/L in the RO feed during the time in which preformed chloramine was dosed at 5 mg/L (ORP 468 mV). No other chemical addition was responsible for both the increase in AOC and UV_{254} in the cartridge filter and RO feeds.

AOC was incrementally higher at two pretreatment locations: after coagulation and after SBS dosing at the location before the cartridge filter. Chemical dosing at the plant accounted for the higher AOC levels upstream of the RO feed. Increased AOC from the presence of cleaning agent residuals and the addition of SBS was not reflected in the TOC levels.

The relationships among TOC, UV_{254}, and AOC were evaluated to determine whether these parameters were significantly correlated ($p \leq 0.05$). TOC did not have a significant relationship with UV_{254} ($r = -0.05$, $p = 0.75$) or AOC ($r = 0.01$, $p = 0.97$); however, AOC and UV_{254} are very strongly correlated at WBMWD ($r = 0.995$, $p < 0.001$). Through additional testing using long term correlations, it may be possible to track the biofouling potential using routine UV_{254} and AOC measurements.

Table 2.5. WBMWD Organic Carbon and Water Quality Data

	Treatment Step	TOC (mg/L)	AOC (µg/L)	UV_{254} (cm^{-1})	pH	ORP (mV)
June (18° C)	Raw seawater	1.08	131±24	0.014	7.9	311
	UF feed	1.16	145±2	0.017	7.9	305
	UF filtrate	1.01	33±9	0.013	7.9	301
	Cartridge filter feed	1.15	67±26	0.011	7.8	265
	RO feed	1.03	20±5	0.010	7.8	270
July (17° C)	Raw seawater	0.91	27±4	0.013	8.1	294
	UF feed	0.92	20±13	0.011	8.1	276
	UF filtrate	0.88	62±9	0.010	8.1	282
	Cartridge filter feed	0.91	79±20	0.042	8.1	463
	RO feed	0.86	89±20	0.040	8.1	468
November (16° C)	Raw seawater	0.88	8	0.009	8.1	270
	UF feed	0.87	3	0.007	8.1	228
	Cartridge filter feed	0.92	14	0.007	8.0	210
December (15° C)	Raw seawater	0.68	18±2	0.010	8.0	144
	UF feed	0.62	30±15	0.017	7.9	168
	UF no SBS	0.64	12±2	0.006	7.7	173
	UF SBS	0.63	63±9	0.007	6.5	123
	Cartridge filter feed	0.75	15±4	0.010	7.2	173
	RO feed	0.73	15±0	0.010	7.2	164

Notes: AOC=assimilable organic carbon; ORP=oxidation reduction potential; RO=reverse osmosis; SBS=sodium bisulfite; TOC=total organic carbon; UF=ultrafiltration.

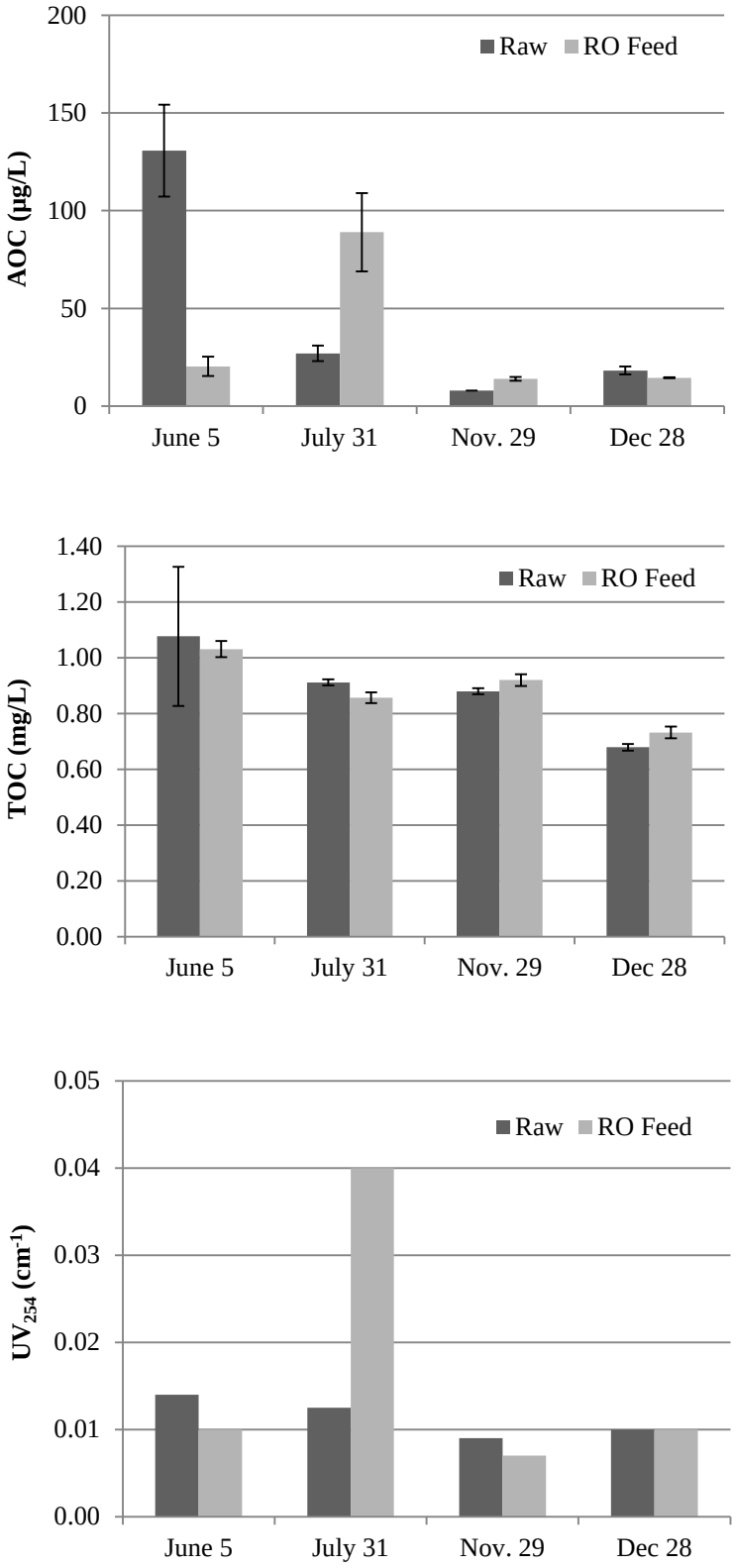

Figure 2.10. WBMWD: Organic carbon in raw seawater and RO feed.

2.3.2 Data Modeling Approach

Operational performance of the plant that coincided with the grab samples was tracked to identify changes that were indicative of biological fouling. To that end, RO operational monitoring data were collected for June through August and November through December 2012 and included flow (gpm), conductivity (mS), RO feed temperature (° C), differential pressure (difference between feed and concentrate pressure, psi), permeate flow from the front and tail, and conductivity from the front and tail permeate. Specific flux of the entire RO train was calculated from the permeate flow (sum of front and tail flows in gpd) divided by the net driving pressure (psi) and total area of the membranes (5600 ft^2).

Net driving pressure was calculated according to the equations provided by the consulting contractor for WBMWD (Figure 2.11). Daily averages were calculated from the 15 min increments, and outliers embedded in the data set were removed from the averages (loss of system correspondence or briefly offline). Observations of the data indicated major changes between July and November with regard to differential pressures and specific flux. From June through August, normal trends were apparent, but the November through December data were noticeably different (Figures 2.12 and 2.13). WBMWD confirmed that the changes were from ongoing testing of new membranes and hybrid configurations, which consisted of 21 separate runs using two models of membranes alone in the vessels and combined as hybrids.

P_{net}=NDP=Net Driving Pressure (psi)

$$P_{net}=P_{feed} - \Delta\pi - \frac{\Delta P}{n+1} - P_{Permeate}$$

where:

$\Delta\pi$=Average Osmotic Pressure Differential (psi)
$= 0.006 \times$ Average Feed/Brine Conductivity

n=Number of stages in Array

$$\text{Average Feed/Brine Conductivity}=\text{Conductivity of Feed} \times \left[\frac{\ln\left(\frac{1}{1-Y}\right)}{Y}\right]$$

where:

$$Y=\text{Recovery}=\frac{\text{Permeate Flow}}{\text{Concentrate Flow + Permeate Flow}}$$

ΔP=Feed Pressure-Concentrate Pressure (psi)

$P_{Permeate}$=Permeate pressure (psi)

Figure 2.11. Calculations for net driving pressure of the RO membranes.

The organic carbon results from the water quality sampling were incorporated into a 2 week period before and after the sampling date. Extending the values in this way followed the assumption that water quality changes would be minimal in the absence of major treatment changes or incoming water quality fluctuations otherwise not detected during the four periods in June, July, November, and December. The data were extended based on similar differential pressure and specific flux near the sampling dates. Water quality data were input for June 1 to 16, July 27 to August 9, November 17 to 25, and December 11 to 29. Because of a shipping issue during the November sampling event, the RO feed was not available, and therefore the water quality data from the cartridge filter feed were used. The data were analyzed using statistical software (SPSS19; IBM Corp.).

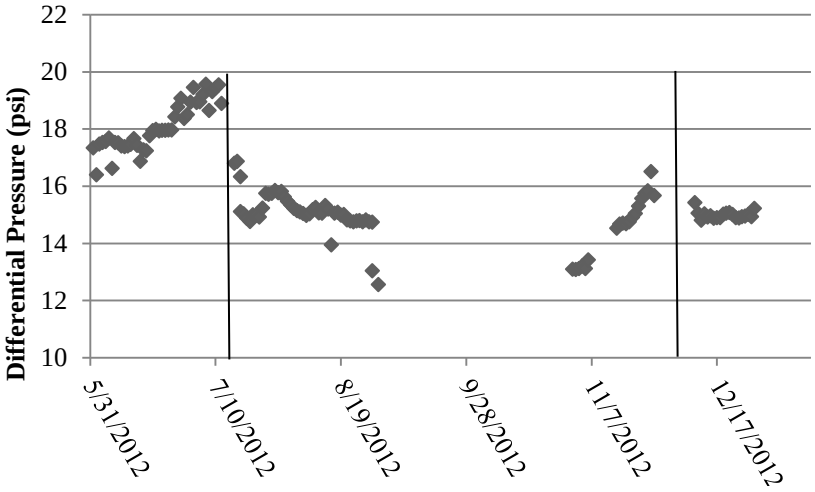

Figure 2.12. WBMWD: Differential pressure of the first-pass RO from June to December 2012

*Notes***:** (n=163). Data are reported for the months in which grab samples were collected (June, July, November, December). A clean in place(vertical lines) was conducted on the RO membranes on July 12 and December 6, 2012. Membrane configurations were changed during the duration of testing**.**

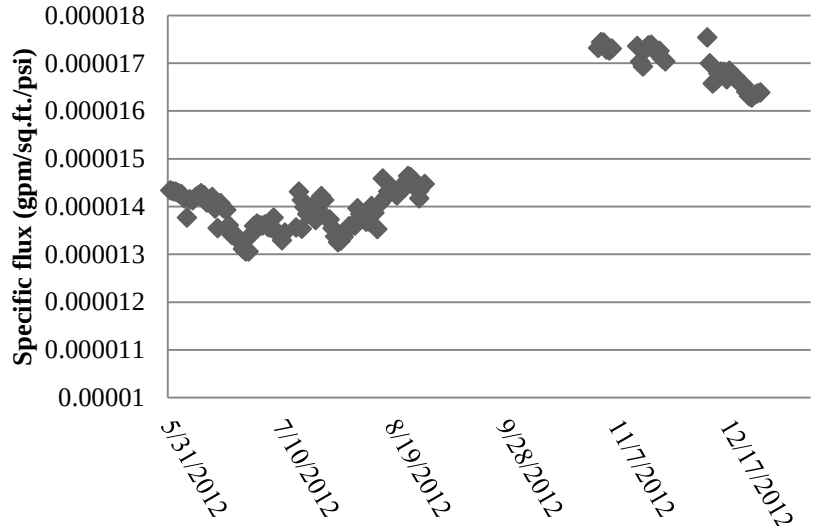

Figure 2.13. WBMWD: Specific flux of the first-pass RO from June to December 2012.

Notes: Data are reported for the months in which grab samples were collected (June, July, November, and December); n=163. Membrane configurations were changed during the duration of testing.

2.3.3 Operational Performance and Data Modeling Results

During the year in which this study was conducted, both chemical pretreatment and membrane types were varied at WBMWD. Membranes were changed between October 30 and November 15, 2012 and again between November 15 and December 31, 2012; other changes included adjustments to recoveries, flux, and feed flow. Because of the inherent variability, there was limited opportunity to evaluate meaningful relationships between the water quality of the seawater and long term operational impacts. Although the approach for correlating differential pressure or other operational changes to organic carbon in the RO feed

was limited, there was evidence that pretreatment chemicals and oxidation increased the biodegradable organic carbon in seawater. The addition of chloramines and SBS were indicative of increases in AOC but less often for changes to TOC and UV_{254} measurements (Table 2.5). Clean in place was performed on the RO membranes after increases in differential pressure were observed and reported by the plant's operations staff to be related to biofouling. Clean in place was performed on July 12 and December 6, 2012. Raw seawater results in June indicated more organic carbon compared to other sampling events (Table 2.5).

Bivariate correlations for organic carbon are reported in Table 2.6. In the full data set, differential pressure decreased over time as a result of cleaning and new membrane installations ($r = -0.778$, $p < 0.01$, $n = 58$), which was also reflected in a strong correlation with increasing specific flux ($r = 0.884$, $p < 0.01$, $n = 58$). TOC had a very strong positive relationship with differential pressure and a strong negative relationship with specific flux. AOC and UV_{254} in the RO feed did not have any remarkable relationship to differential pressure. Specific flux and AOC in the RO feed had the strongest negative correlation over the TOC and UV_{254} results. The team anticipated that differential pressure would be related to AOC, assuming that operating conditions and membrane types were the same in a modeled data set; however, this was not the case during the time in which the data were collected.

The membranes were changed in a set of 21 tests in November and December, which was part of another project being conducted at the plant. Although differential pressure could be higher with higher average feed/concentrate flow (for constant water temperature), the normalized specific flux should not vary unless the membranes were fouled. As seen in Figure 2.13, a flux decline occurred in the November and December data set. The decline in specific flux during the monitoring period correlated to each of the organic parameters that were measured, and AOC had the strongest and most significant relationship.

Table 2.6. Correlation and Significance of Predictor Variables from the WBMWD RO Feed for Differential Pressure and Specific Flux

	Differential Pressure		Specific Flux	
	Pearson Correlation	***p* (2-tailed)**	**Pearson Correlation**	***p* (2-tailed)**
AOC	-0.134	0.317	-0.705	<0.01
TOC	0.817	<0.01	-0.513	<0.01
UV_{254}	-0.176	0.185	-0.683	<0.01
Day	-0.778	<0.01	0.884	<0.01

Notes: June to December 2012; n=58; AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

2.4 Al Zawrah Desalination Plant

Al Zawrah is located in the Emirate of Ajman, United Arab Emirates, and the seawater intake uses surface water from the Arabian Gulf. Water quality in the gulf is poor, often with elevated temperatures and red tide occurrences; total dissolved solids (TDS) may be as high as 48,000 ppm, and there are numerous large-scale desalination plants (both thermal and RO) that discharge brine and waste in the area. Shock chlorination and posttreatment with SBS was historically conducted every 3 to 4 weeks. The desalination process consists of coagulation with ferric chloride, dual media filtration (DMF), cartridge filtration, and RO. Coagulant doses were 2.6 mg/L in May, 1.7 mg/L in July, and 2.5 mg/L in November. The media used in the DMF included a top layer of pumice (1.2–1.5 mm), which was 800 mm deep, and a bottom layer of silica sand (0.4–0.6 mm), which was 600 mm deep, at a filtration rate of 8 to 10 m/h. Cartridge filters were replaced approximately every 90 to 100 days. Adjustment of pH was done using sulfuric acid at the feed to the cartridge filters to achieve a level between 6.9 and 7.0.

2.4.1 Pretreatment and Organic Carbon Removal

Samples were collected within the treatment train from Al Zawrah on May 29, July 29, and November 4, 2012. Samples for water quality analysis included raw seawater from the intake without chemical addition, DMF feed and filtrate, and filtrate from the cartridge filters. In the May event, TOC ranged from 3 to 14 mg/L through the treatment steps, and AOC was 75 to 197 µg/L (Table 2.7). In the July sampling event, TOC averaged 1.1±0.1 mg/L, and AOC averaged 9±5 µg/L. Discussions with the plant manager indicated that during the May event an algal bloom in the area affected the intake pH of the seawater, which was typically 8.1 but had dropped to 7.5. Changes to organic carbon during pretreatment are graphically represented in Figure 2.14.

AOC and TOC concentrations were lower in July than in the May event, presumably because there were no impacts from red tide at the intake. TOC and UV_{254} measured in the November sampling were minimally impacted during pretreatment, but the AOC increased in the filtrate from the DMF. DMF filtrate removed between 21 and 43% of the AOC in the DMF feed in the previous sampling events. Organic carbon removal by DMF may occur through adsorption or biodegradation mechanisms (Naidu et al., 2013). Biologically active filters are dynamic in the sense that maturation of the filter affects organic removal potential; depending on the filter age, filtration rate, presence of disinfectant, or other factors, biodegradation in the filter could be reduced, and organic carbon breakthrough or microbial detachment may occur.

Table 2.7. Al Zawrah Organic Carbon and Water Quality Data

	Treatment Step	TOC (mg/L)	AOC (µg/L)	UV_{254} (cm^{-1})	pH
May (32° C)	Raw seawater	2.9	197	0.017	7.5
	DMF feed	13.7	143	0.033	7.5
	DMF filtrate	3.8	113	0.012	7.5
	CF filtrate	5.6	75	0.012	6.9
July (35° C)	Raw seawater	1.21	2	0.020	7.7
	DMF feed	1.17	14	0.052	7.7
	DMF filtrate	0.96	8	0.012	7.7
	CF filtrate	1.04	12	0.011	7.0
November	Raw seawater	1.26	4	0.013	7.7
(30° C)	DMF feed	1.24	2	0.012	7.7
	DMF filtrate	1.22	147	0.010	7.7
	CF filtrate	1.24	181	0.012	7.0

Notes: AOC=assimilable organic carbon; CF=cartridge filtration; DMF=dual media filtration; TOC=total organic carbon; UV=ultraviolet.

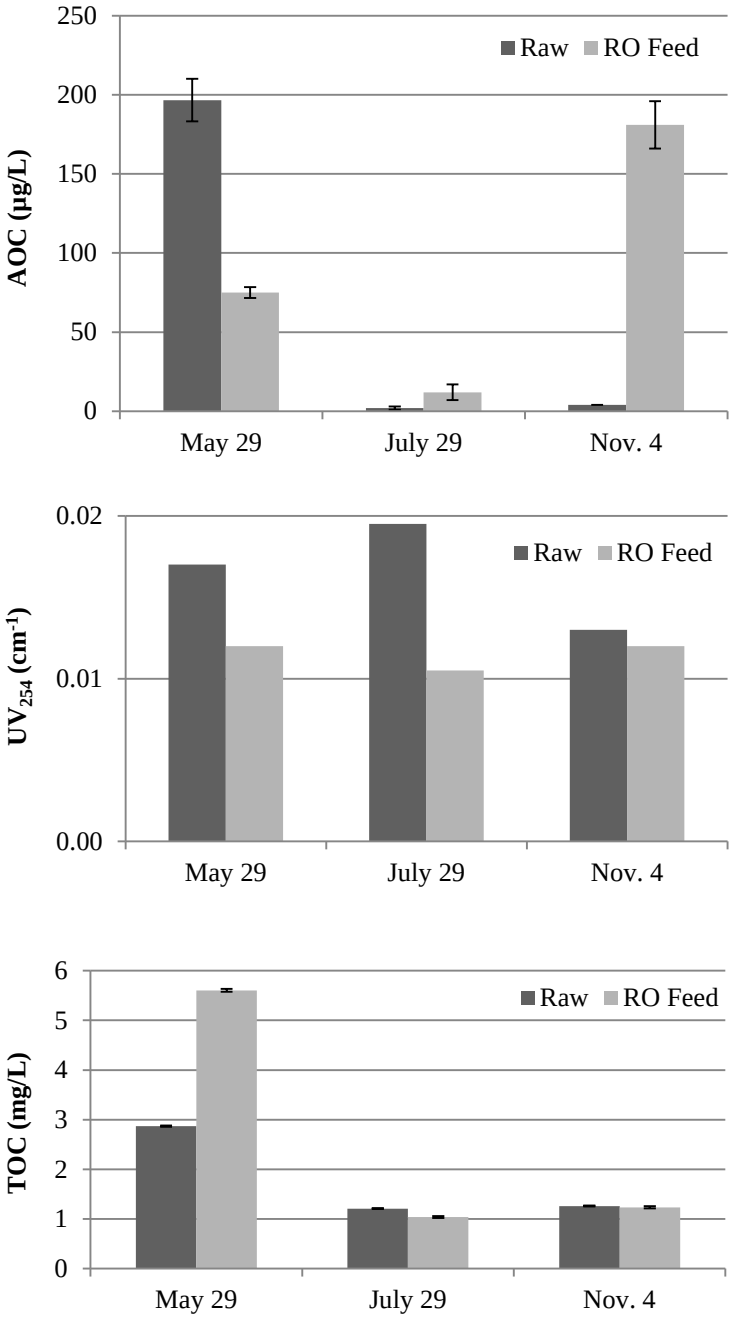

Figure 2.14. Al Zawrah: Organic carbon in raw seawater and RO feed.

2.4.2 Data Modeling Approach

Al Zawrah plant performance was evaluated using DMF and cartridge filter operational data. Manual log sheets were copied and submitted to the project team for analysis of the plant's condition. Records were submitted for the DMF (pressure, flow, temperature, online differential pressure transmitter, online filtrate turbidity, free chlorine in filter outlet), cartridge filter (online differential pressure transmitter, SDI, ORP), and pH of the RO feed. Operational data were collected in 4 hour increments for May, July, and October through November. During the collection times in 2012 the plant was not using normalization software for its record keeping. The absence of RO operating information limited the evaluation of water quality impacts on the RO system; however, the condition of the plant was evaluated with respect to differential pressure of the media and cartridge filters in conjunction with the organic carbon results from the same collection periods. Changes in differential pressure at the cartridge filter would provide evidence that biological growth may have occurred on the filters.

2.4.3 Operational Performance and Data Modeling Results

Organic measurements were extrapolated between May 28 and 30, July 28 and 30, and November 1 and 6. Differential pressure in the cartridge filter increased in July and November near the sampling events (Figure 2.15). ORP of the cartridge filtrate was greatest in November (Figure 2.16). The data showed strong positive correlation between differential pressure of the cartridge filters and AOC in the RO feed ($r = 0.984$, $p = <0.01$, $n = 48$). UV_{254} had strong positive relationships to the cartridge filter data (ORP and differential pressure; Table 2.8); however, the measurements in the data set were 0.011 and 0.012 cm^{-1} (average = 0.01 cm^{-1}±5%), which indicates no meaningful impact of UV_{254} on fouling.

The pressure differential for the DMF had strong relationships to the organic carbon data, but the meaning of that is not as clear because the function of the filters is not impacted only by organic carbon content of the water, but more so by flow rates, backwash frequency, source water quality, and turbidity. Of the plants investigated, only Al Zawrah had the potential for biological removal of AOC by a media filter (Tampa's sand filters contain chlorine residual); however, biological activity and subsequent removal of AOC was not consistent. TOC removal was not consistent either; maximum removal was 14%, but the other sampling events showed less.

Overall poor organic removal and inconsistent operations are widespread challenges in SWRO. The positive and strong relationships determined when AOC was investigated as a predictor variable for biological growth confirms the presence of biodegradable organic carbon and its impact on operations. Furthermore, AOC was not significantly correlated to TOC ($r = 0.38$, $p = 0.22$) or UV_{254} ($r = -0.11$, $p = 0.74$). No relationship was apparent for TOC and UV_{254} ($r = 0.29$, $p = 0.37$). Given the lack of relationships between these parameters, additional monitoring using AOC and operational changes to identify increases in the biofouling potential are recommended. Although RO data were not available, relationships between AOC and biological growth that lead to changes in differential pressure and other operational data exist. If AOC is monitored and pretreatment optimized for removal of organic carbon, biological fouling on both cartridge filters and ultimately on RO membranes would be reduced.

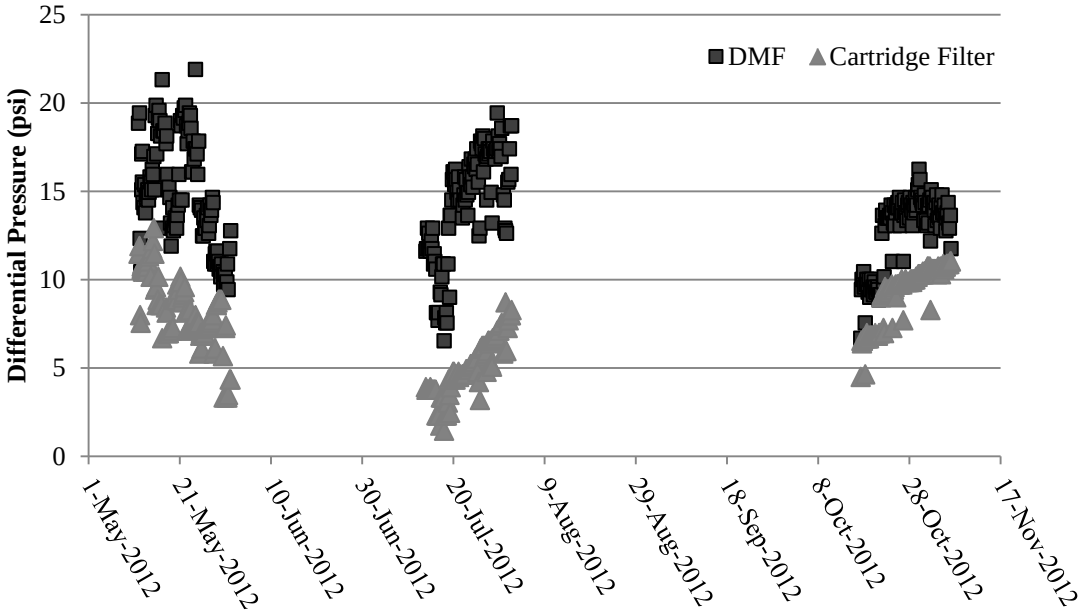

Figure 2.15. Al Zawrah: Differential pressures in RO pretreatment filters.

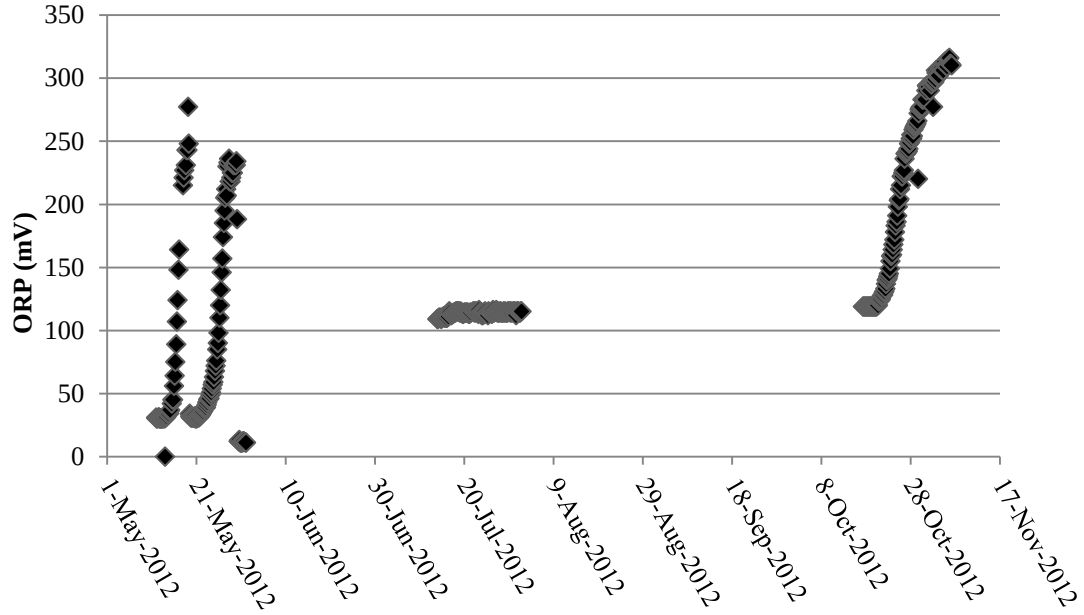

Figure 2.16. Al Zawrah: ORP of the RO feed.

Table 2.8. Correlation and Significance of Predictor Variables from the Al Zawrah RO Feed

	Dual Media Filter Differential Pressure		Cartridge Filter Differential Pressure		Cartridge Filter ORP	
	Pearson Correlation	***p* (2-tailed)**	**Pearson Correlation**	***p* (2-tailed)**	**Pearson Correlation**	***p* (2-tailed)**
AOC	-0.521	<0.01	0.980	<0.01	0.984	<0.01
TOC	-0.670	<0.01	-0.099	0.505	-0.034	0.816
UV_{254}	-0.852	<0.01	0.901	<0.01	0.930	<0.01

Notes: May to November; AOC=assimilable organic carbon; ORP=oxidation reduction potential; TOC=total organic carbon; UV=ultraviolet.

Chapter 3

Oxidation Testing

3.1 Introduction

In SWRO desalination plants, reactions between treatment chemicals and dissolved organic matter (DOM) have not been investigated for the purpose of evaluating the biodegradability of the treatment chemicals or the formation of byproducts. Measuring AOC will provide insight and quantifiable results about the biodegradability of seawater at different stages of pretreatment. The production of AOC would provide the nutrients for growth and proliferation of bacteria on the RO membranes, thereby leading to biofouling, associated flux decline, and other operational challenges. Monitoring AOC after pretreatment stages would provide the operator with the information needed to institute a control strategy for minimizing biofouling potential within the plant and before the RO membranes.

The presence of seawater DOM originates from various sources including terrestrial runoff, byproducts from micro- or macroorganisms, and anthropogenic sources such as wastewater, industrial, or agricultural discharges. A major component of terrestrially derived DOM is humic material. Humic matter has been reported to be an association of relatively small molecules bound together by intermolecular hydrophobic reactions (Conte and Piccolo, 1999) or high molecular weight macromolecules with aromatic structures and greater UV absorbance (on account of the molecular size) than other natural organic matter (NOM) and DOM fractions (Reckhow, 1990). In general, researchers agree that the humic structure is affected by pH, ionic strength, concentration, and divalent cations.

A significant amount of research has focused on the oxidation of humic matter in surface water, but there is very little information about its behavior and reactivity in water having high ionic strength, like seawater. A recent study by Schneider et al. (2013) reports that removal of DOM in testing humic acid in seawater is affected by ionic strength and divalent cations, which create calcium or magnesium complexes and steric stabilization. These mechanisms can inhibit the effectiveness of coagulation during seawater pretreatment.

Because coagulation is relied on for the removal of organic carbon, the chemistry of seawater has important implications for the presence of humic matter in desalination and ultimately the ability of a given desalination pretreatment process to remove humic matter. Humic matter is not readily biodegradable; however, if it persists after the coagulation step during pretreatment, then potential oxidation processes downstream could liberate AOC from the humic structures.

Although humic structures are generally considered refractory (i.e., not easily biodegraded or assimilated by microorganisms), photooxidation and biochemical transformations can liberate important nutrient reserves. Understanding the degree of transformation in seawater from refractory organic carbon into biodegradable organic carbon, including AOC, is of importance in seawater applications. Extensive literature has been published investigating the reactions of DOM with ozone, chlorine, or chloramine disinfectants typically used in drinking water treatment. Oxidation via ozonation or other advanced oxidation processes (AOP) transforms a complex organic structure into more biodegradable fractions and AOC used by bacteria for growth. Oxidation of specific components found in humic matter such as aromatic rings and carbon=carbon double bonds decreases UV_{254} and can increase the

proportion of biodegradable fractions, such as AOC or other disinfection byproducts, in freshwater (Hammes et al., 2006; Glaze and Weinberg, 1993). Such byproducts are often more biodegradable and would be amenable to removal through biological filtration. Filtration through biologically active media produces water that is more biologically stable and can effectively reduce disinfection byproduct formation potential. This project was conducted to quantify the impact of AOC as an important parameter for understanding the biological stability of treated water and the biofouling potential of seawater RO membrane processes.

3.2 Objectives

Chlorine, chlorine dioxide, and ozone were used in a series of bench-scale oxidation tests for the purpose of evaluating the biodegradability of DOM after reactions with typical disinfectants used in water treatment. The experiments are herein referred to as oxidation instead of disinfection because the testing was not conducted to evaluate biocidal effects, but rather to observe changes to a model organic structure and the naturally occurring organic matter in seawater.

3.3 Materials and Methods

3.3.1 Glassware Preparation

Reaction vessels were graduated 250 mL borosilicate bottles (KIMAX; Kimble Chase, Vineland, NJ) rendered carbon-free as previously described (Weinrich et al., 2009). Briefly, the bottles are washed, rinsed and baked at 550° C for 6 hours. The bottle closures were acid washed in 10% hydrochloric acid overnight, rinsed with laboratory grade water, dried, and autoclaved.

3.3.2 Model Seawater Matrix

Model seawater matrices (used for humic acid testing) were prepared from Milli-Q water and American Chemical Society (ACS) grade chemicals. Laboratory grade water was generated from a system using RO-purified, finished drinking water passed through ion exchange and activated carbon filtration and ultimately passed through a Milli-Q Academic System (Millipore Corporation, Billerica, MA). Prior to use, model waters were allowed to equilibrate at room temperature for at least 24 hours.

Milli-Q water (3 L) was amended with the following: 66 g sodium chloride (EMD Chemicals, Gibbstown, NJ), 1.65 g KCl, 0.024 g $NaHPO_4$, 0.006 g KNO_3, and 0.48 g $NaCO_3$. The solution is mixed, adjusted for pH, and autoclaved. Upon cooling, 3 mL each of 0.1 M calcium chloride and 1.0 M magnesium sulfate are added. This solution was used as the model seawater matrix into which humic acid was added.

3.3.3 Humic Acid Oxidation with Chlorine and Chlorine Dioxide

Three concentrations of humic acid from 1 to 5 mg/L were chosen to span the typical range found in seawater samples collected during field sampling (Chapter 2). A stock of humic acid was prepared in Milli-Q water at a concentration of 2.7 g/L of C (g/L as C) and dissolved by sonication overnight. Humic acid was used as the model DOM source in a laboratory-generated seawater matrix at pH 7.2.

Chlorine and chlorine dioxide tests were separately prepared at doses of 0.5 mg/L Cl_2 and reacted for 4 hours in laboratory generated seawater solutions containing humic acid. Sodium hypochlorite solution, 5%, Chemical Abstract Service (CAS) #7681-52-9 (J. T. Baker, Avantor, Center Valley, PA) was used to prepare a working solution of 100 mg/L Cl_2 for dosing the test solutions. Chlorine dioxide was purchased as a 3000 mg/L stock solution (0.3% chlorine dioxide; CDG Environmental, Bethlehem, PA) and used to prepare a 100 mg/L working solution. Stock and working solutions of chlorine dioxide were measured at absorbance at 445 nm using a spectrophotometer (DR 5000; Hach, Co., USA). The stock solution was stored in between experiments at 4° C. At the end of the reaction, sodium thiosulfate was used to quench the oxidant residual.

3.3.4 Seawater Oxidation with Chlorine and Chlorine Dioxide

A series of bench-scale chlorination tests were conducted to evaluate changes to organic carbon naturally occurring in seawater, with particular focus on AOC formation from geographically diverse locations. Bulk seawater samples were collected and shipped to Delran, NJ. Upon arrival, the water was stored at 4° C. Seawater from the intake at WBMWD in Redondo Beach, CA was collected on May 14, 2012 and shipped in a 10 gallon carboy. Staff from WBMWD reported the following water quality: pH = 8.1, ORP 352 mV, TDS 32.2 ppt (g/L), electrical conductance 50.3 mS. Weekly variability (June 13–July 5, 2012) was detected in control solutions retrieved from the container stored at 4° C. AOC ranged from 88 to 224 µg/L, TOC from 0.6 to 1.2 mg/L, and UV_{254} from 0.009 to 0.011cm^{-1}. Controls were analyzed with each experimental set to accommodate these differences.

Seawater from the Arabian Sea (35° C collection temperature, pH 7.7) from the Al Zawrah RO treatment plant in the Emirate of Ajman was collected on July 29, 2012 and pasteurized at 70° C for 30 min prior to shipment to inactivate any indigenous bacteria. The pasteurized samples were cooled and shipped in 0.5 L bottles.

Seawater from the intake of TBSDP at TECO was collected in a 5 gallon carboy and shipped to Delran, NJ for testing. Prior to testing, water was filtered through a 0.7 µm size glass fiber filter (GF/F).

Amber glass reactors were rendered chlorine demand–free by soaking in a 40 mg/L chlorine bath overnight. Sodium hypochlorite solution, 5%, CAS #7681-52-9 (J.T.Baker, Avantor, Center Valley, PA) was diluted in Milli-Q water to prepare a working solution of 430 mg/L Cl_2 for dosing test solutions. Chlorine dioxide was purchased as a 3000 mg/L stock solution (CDG Environmental, Bethlehem, PA) and used to prepare a 330 mg/L working solution for dosing. The raw seawater (250 mL volume) was treated with chlorine and chlorine dioxide for 4 hours at ambient temperature (22° C). At the end of the reaction time, sodium thiosulfate was used to quench the oxidant residual.

Chlorine and chlorine dioxide tests covered a range of oxidant doses from 0.5 to 15 mg/L as Cl_2. Chlorine dioxide was tested at doses from 0.5 to 4 mg/L as Cl_2 in WBMWD seawater and 1 to 10 mg/L in water from Tampa Bay and the Arabian Sea. Chlorine demand was measured at the end of the reaction time to quantify the amount of disinfectant that remained after reactions with various microbial and chemical components in the water.

3.3.5 Oxidation with Ozone

An ozone stock solution was prepared from Zero Grade oxygen (>99.8%; Airgas, Inc.; Malvern, PA) using an ozone generator (Pacific Ozone Technology, Benicia, CA) according to the batch method as outlined in Standard Methods 2350D (APHA, 2005) in Milli-Q water

chilled in an ice bath. Ozone concentrations in the stock were determined after dilution and preparation for measurement on the spectrophotometer at 600 nm using Indigo Method 8311 (DR 5000, Hach Co., USA).

Humic acid was prepared at concentrations ranging from 0.3 to 5 mg/L and tested at variable ozone:TOC dose ratios to identify maximum formation of AOC. Humic acid stock preparation is described in Section 3.3.3. Raw seawater collected from Tampa Bay and the Arabian Sea was tested at doses of 1:2 and 1:1 ozone:TOC.

3.3.6 Water Quality Analyses

Samples were analyzed for UV_{254}, TOC, and AOC (using methods described in Section 2.1). Free and total chlorine were measured using N,N-diethyl-p-phenylenediamine (DPD) reagents (Hach Co., USA) according to Standard Method 4500-Cl G (APHA, 2005).

3.4 Results and Discussion

3.4.1 Humic Acid Oxidation with Chlorine and Chlorine Dioxide

AOC concentrations in the humic acid control averaged 110 µg/L±19% before dosing with the oxidant (Table 3.1). The addition of more humic acid did not significantly increase the amount of AOC, but increasing concentrations were reflected in the UV_{254} and TOC measurements. In this case, a source of refractory carbon such as humic acid would be easily detected using nonspecific organic analyses, including UV_{254} and TOC. AOC was not expected to vary in the control solutions because humic acid is mostly refractory and not readily biodegradable.

Oxidation with chlorine (Cl_2) and chlorine dioxide (ClO_2) produced 155 and 103 µg/L AOC, respectively, at the lowest concentration of humic acid. Only in the chlorinated solution was AOC significantly increased (70%) compared to the control after reaction. There were no significant changes to UV_{254}, TOC, or AOC from the solutions with higher concentrations of humic acid using the same doses of chlorine or chlorine dioxide. Chlorine dioxide has a lower redox potential than hypochlorous acid (the active species during chlorination); therefore, the oxidation and chlorine substitution reactions may be further limited in high ionic strength seawater.

The structure of organic molecules, such as humic acid, is affected by high ionic strength; therefore, the increased concentrations of humic acid (5 vs. 1 mg/L) may not necessarily be more amenable to oxidation with just 0.5 mg/L of chlorine or chlorine dioxide (Table 3.1). Posttreatment oxidation with chlorine and chlorine dioxide effected nearly no change in UV_{254} absorbance (±2%) or TOC (-4%). Świetlik et al. (2004) reported that chlorine dioxide is capable of producing biodegradable byproducts, including aldehydes and carboxylic acids from humic acid in freshwater at doses of 1.2 mg ClO_2 mg^{-1} DOC reacted for 24 hours; however, under the doses and conditions in the seawater experiments reported here, biodegradable byproducts measured as AOC were not affected.

In this report, the experimental conditions consisted of a reaction time of just 4 hours, which was more consistent with preoxidation in a desalination plant. For instance, an oxidant is often added at the intake to inactivate organisms from the raw seawater, and the residual would be carried through the treatment until SBS is added before the RO membranes. Also, the dose ratio of chlorine dioxide to organic carbon ranged from 0.1 to 0.5 mg ClO_2 mg^{-1} DOC, which was a fraction of the dose tested by the Świetlik team. In practice, seawater desalination plants are often restricted by the potential formation of chlorite from chlorine

dioxide disinfection. The maximum contaminant level for chlorite is 1.0 mg/L, with a goal of 0.8 mg/L. The results from these preliminary experiments indicate that at low doses of 0.5 mg/L of chlorine and chlorine dioxide, the higher redox potential of chlorine is capable of breaking down the carbon bonds contained in humic acid and rendering the structure into BOM and therefore AOC as a reaction byproduct.

Table 3.1. AOC Formation in Humic Acid Solutions with Chlorine or Chlorine Dioxide

Humic Acid (mg/L)	Oxidant (0.5 mg/L)	UV_{254} (cm^{-1})	% Diff. Rel. to Control	TOC (mg/L)	% Diff. Rel. to Control	AOC (µg/L)	% Diff. Rel. to Control
1	Control	0.091		1.16		91	
1	Chlorine	0.093	2%	1.11	-4%	155	70%
1	Chlorine dioxide	0.089	-2%	1.04	-10%	103	13%
2	Control	0.182		2.48		109	
2	Chlorine	0.182	0%	2.39	-4%	121	11%
2	Chlorine dioxide	0.179	-2%	2.30	-7%	116	6%
5	Control	0.456		6.43		128	
5	Chlorine	0.456	0%	6.30	-2%	118	-8%
5	Chlorine dioxide	0.454	0%	6.48	1%	121	-5%

Notes: Applied dose of oxidant was 0.5 mg/L; AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

3.4.2 Seawater Oxidation with Chlorine and Chlorine Dioxide

In many locations, SWRO plant operators regularly apply chlorine during pretreatment at doses as high as 5 mg/L to reduce biological growth but may intermittently shock chlorinate using higher concentrations of chlorine to remove biofilm on intake structures, inactivate organisms in the feed, and overcome chlorine demand of the water. Operational evidence has suggested that this procedure can lead to biological fouling of the RO membranes Downstream of the initial application. The team hypothesized that chlorine and chlorine dioxide treatment would produce BOM, leading to reductions in UV_{254} and increases in AOC.

Organic constituents and byproduct precursors were expected to vary across the three seawaters tested on account of the geographical diversity of the sources and therefore would behave differently when dosed with an oxidant. The inherent variability between the types of water and constituents would explain the non-monotonic results in AOC formation or removal (Table 3.2), but trends among the water types became apparent. In most treatments TOC levels generally did not show any remarkable differences compared to the control. In Tampa Bay, TOC changes posttreatment varied from -7 to 2%, and Arabian Sea chlorination decreased TOC by 14% on average from 1.4 mg/L in the control to 1.2 mg/L after chlorination. TOC changes were more variable for chlorine dioxide treatment in Arabian Sea water; TOC decreased at 1 to 4 mg/L as Cl_2, but in the 10 mg/L chlorine dioxide dose TOC increased by 29%.

There is evidence that particulate matter may be rendered easier to oxidize in the TOC instrument (using high temperature combustion) after preoxidation (i.e., chlorine dioxide), which would be evident as an increase in TOC compared to the nonoxidized seawater control. In the same 10 mg/L chlorine dioxide treatment of Arabian Sea water, UV_{254} also increased by 44%, compared to the control when the lower dose treatments decreased UV_{254} by 22%. UV_{254} decreased in Tampa Bay water in both the chlorine and chlorine dioxide treatments at 10 mg/L; there was a 30% reduction from the starting absorbance in the control at 0.18 cm^{-1}. TOC also showed slight reductions to 8% in the same treatments. A study previously published reported that increasing doses of chlorine corresponded to decreasing UV absorbance at wavelengths greater than 250 nm, in which the chlorine treatment ranged from 0.2 to 1 mg/L (Weinrich et al., 2011).

The observations contained in this report indicate that UV_{254} decreased at all chlorine doses (1–10 mg/L) in TECO raw water from TBSDP and at 1 and 4 mg/L doses in Arabian Sea raw water. UV_{254} for Arabian Sea raw water was 0.02 cm^{-1} and was reduced with both chlorine and chlorine dioxide doses of 4 mg/L. When dosed with 10 mg/L, UV_{254} increased by 44% from the chlorine dioxide treatment and 51% from chlorine. These reported inconsistencies with organic carbon were not observed in West Basin seawater, where UV_{254} increased consistently for both oxidants. UV_{254} increased between 122 and 322% at 5 to 15 mg/L chlorine doses and from 9 to 136% in 0.5 to 4 mg/L chlorine dioxide treatments. Out of the three sources tested, West Basin seawater had the lowest organic carbon (UV_{254} and TOC) but had the highest AOC in the control.

Changes to aromaticity or carbon–carbon double bonds and other structures in humic acid would be exhibited as reductions in UV_{254}, but that change was not detected at the doses tested. Therefore, the data suggest that the organic carbon present in the West Basin water was not dominated by humic acid because consistent UV_{254} increases were observed. From the testing conducted in humic acid solutions treated with chlorine or chlorine dioxide, UV decreased or stayed the same. SUVA at 254 nm has been recently applied to evaluating the humic nature of seawater. Edzwald and Haarhoff (2011) adapt conventional drinking water guidelines to seawater in the following manner: (1) SUVA greater than 4 indicates that NOM

is mainly aquatic humic matter; (2) SUVA of 2 to 4 indicates that NOM is a mixture of AOM and aquatic humic matter; and (3) SUVA less than 2 indicates the NOM is composed primarily from AOM.

SUVA for West Basin was 0.9 L/mg/m, which suggests that the seawater did not contain much aquatic humic matter. The increases in West Basin suggest that liberation of organic matter during oxidation may have occurred. A study by Hammes et al. (2007) confirmed that the cytoplasm released from phytoplankton during ozonation increased AOC in both laboratory-generated water spiked with *Scenedesmus vacuolatus* and an environmental source from a lake. As an alternative to chemical treatment, physical disruption of algal cells would also liberate cytoplasm and increase AOC. During RO treatment, the shearing effect caused by physical treatment processes, specifically the high-pressure pumps used to deliver water to the membranes, can break algal cells apart. Rupturing algal cells through either physical processes or chemical oxidation could potentially increase AOC, thereby increasing the biofouling potential of the pretreated water.

Tampa Bay seawater had the most significant increases in AOC compared to the other water sources after chlorine and chlorine dioxide treatment. AOC increased as much as 114% with chlorine dioxide and 142% with chlorine treatment. Increases detected in treatments with both chlorine and chlorine dioxide suggest that normal and shock chlorination doses would react to produce or liberate biodegradable organic carbon. AOC formation was confirmed with these treatments, although changes to TOC concentrations were not detected.

The variability of organic carbon present in these geographically diverse waters indicates that AOC formation occurs when water is treated with disinfectants to control biological fouling. TBSDP experienced operational problems with organic fouling and biofouling of its RO membranes; it also had the highest organic concentrations of the seawaters tested. The type of organic matter present at the intake may also be predictive of the extent of reaction and type of transformations. It appears that, out of the sources tested, Tampa Bay contains the most humic material, which was highly reactive with oxidants and formed AOC as biodegradable oxidation byproducts. SUVA of TBSDP was 3.18 L/mg/m, indicating that it is in fact a mixture of humic and microbially derived (autochthonous) organic matter. The presence of humic material in TBSDP raw water was consistent with a previous study that evaluated coagulant removal (Schneider et al., 2011). In that report, raw TBSDP water was characterized using liquid chromatography–organic carbon detection, and humic substances were 50 to 70% of the organic carbon; SUVA was 3.24 to 5.5 L/mg/m.

AOC is consistently formed as a byproduct from oxidation of humic acid and the organic carbon present in TBSDP raw water. The formation of AOC as a byproduct would generate conditions amenable to bacterial proliferation and subsequent biological fouling of the RO membrane

Table 3.2. AOC Formation in Seawater with Chlorine or Chlorine Dioxide

		Dose ($mg/L\ Cl_2$)	Dose ($mg\ ClO_2/mg\ TOC$)	UV_{254} (cm^{-1})	% Diff. Rel. to Control	TOC (mg/L)	% Diff. Rel. to Control	AOC (µg/L)	% Diff. Rel. to Control
WBMWD		Control		0.009		1.00		110±21	
	Chlorine	0.5		0.012	33%	0.94	-6%	56±20	-49%
		2		0.015	67%	0.92	-8%	71± 6	-35%
		4		0.025	178%	0.95	-5%	29± 9	-74%
		10		0.031	211%	1.10	10%	2± 0	-98%
		15		0.038	256%	1.15	15%	92±11	-17%
		Control		0.011		0.6		88±19	
	Chlorine dioxide	0.5	0.8	0.012	9%	0.59	-2%	58±11	-34%
		2	3.3	0.021	91%	0.65	8%	34±8	-61%
		4	6.7	0.026	136%	0.65	8%	34±9	-61%
Tampa Bay		0		0.176		5.54		36±12	
	Chlorine	1		0.153	-13%	5.63	2%	78±4	117%
		4		0.127	-28%	5.60	1%	51±7	43%
		10		0.121	-33%	5.15	-7%	87±9	142%
	Chlorine dioxide	1	0.2	0.161	-9%	5.61	1%	49±8	37%
		4	0.7	0.131	-26%	5.41	-2%	77±18	114%
		10	1.8	0.121	-31%	5.16	-7%	65±0	81%
Arabian Sea	Chlorine	0		0.021		1.44		60±14	
		1		0.014	-32%	1.25	-13%	51±13	-15%
		4		0.019	-7%	1.24	-14%	41±13	-32%
		10		0.031	51%	1.22	-15%	58±12	-3%
	Chlorine dioxide	1	0.7	0.016	-22%	1.40	-3%	51±6	-16%
		4	2.8	0.016	-22%	1.26	-13%	10±2	-83%
		10	6.9	0.030	44%	1.86	29%	2±0	-97%

Notes: Applied dose of chlorine was 0.5 to 15 mg/L and chlorine dioxide was 0.5 to 10 mg/L; SUVA (L/mg/m): WBMWD=0.9, Tampa Bay=3.18, Arabian Sea=1.45; AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet; WBMWD=West Basin Municipal Water District.

Chlorine demand is typically used in drinking water to evaluate the dose needed to maintain a residual in the distribution system after the disinfectant reacts with DOM, bacteria, and other substances that can deplete the residual. It is not surprising that the untreated water from Tampa Bay is highly reactive with chlorine and chlorine dioxide. Chlorine demand of TBSDP intake water was 8 and 4 mg/L for chlorine dioxide. In comparison, Arabian Sea water had 80% less TOC and exhibited a demand less than 1.8 mg/L for both free chlorine and chlorine dioxide. WBMWD intake seawater had similar TOC levels to that from the Arabian Sea and exhibited a maximum chlorine demand of 2.5 mg/L when dosed with 15 mg/L chlorine. Arabian Sea chlorine demand was 1.8 mg/L. Demand from chlorine dioxide in WBMWD seawater was 3 mg/L; in Arabian Sea testing the demand was 1 mg/L.

3.4.3 Humic Acid Oxidation with Ozone

The results described in this section compare humic acid, a model organic compound, in a laboratory-generated seawater matrix of similar conductivity to other environmental seawater matrices near the same TOC concentration (Table 3.3). UV_{254} decreased by an average of 27% throughout all the samples (n=12) and by an average of 47% in the solutions reacted with the maximum ozone dose of 3:1 ozone:TOC. Ozone reacts with the carbon–carbon double bonds in the complex humic acid structure and also reduces aromaticity to create more biodegradable organic carbon structures. The reduction in absorbance suggests that bonds in the carbon structure were broken through ozone oxidation. TOC increased at all concentrations tested at the higher ozone doses, 3:1 and 2:1 ozone:TOC. TOC decreased at 0.7 dose ratio by an average of 21%, and at 0.3 dose ratio TOC decreased by 12%.

AOC was mostly removed in the 0.7 to 3 dose ratios. The removal of AOC would result from mineralization of the background AOC in the control and a lack of BOM produced by the batch test. AOC was consistently produced only at 0.3 dose ratio. AOC increased as much as 198% in the 1 mg/L humic acid solution. In freshwater, biodegradable organic carbon formation is maximized at ratios 1:1 and 0.5 mg ozone:TOC (von Gunten, 2003; van der Kooij, 1986). The ratios of AOC production were similar in our study at the 0.3 ozone:TOC ratio compared to the previously mentioned study; however, the complexity of humic substances in seawater makes a direct comparison difficult.

In fact, humic matter exhibits different properties in solutions of low ionic strength versus those of high ionic strength, such as seawater. For instance, humic matter is considered to be a conformation of molecules inherently hydrophobic, and at high ionic strength the molecules become more densely packed, thereby enhancing electrostatic repulsion and hydrophobicity in solutions with higher concentrations of humic matter (Conte and Piccolo, 1999; Yu et al., 2010). This behavior might offer some explanation as to the difference in AOC production that occurred in the 0.3 dose ratio, where the percent of AOC production decreased in increased humic acid concentrations. It is possible that the concentration of humic acid at 5 mg/L was not as amenable to oxidation as humic acid at a lower concentration of 1 mg/L if the hydrophobicity of the structure increased because of stronger intermolecular and hydrophobic arrangements of the available organic material.

Ozonation is widely used in surface water treatment for drinking water but has not been thoroughly investigated in desalination. Some information exists from treatment of ballast water and brackish waters with ozone. Ozonation has not been applied in desalination pretreatment for drinking water because of the formation of byproducts including bromate, a carcinogen. Other impacts from the presence of bromide would include the formation of hypobromous acid and the hypobromide ion, which could react with DOM to form bromoform and other brominated byproducts. Residual oxidants produced from ozonation may also damage RO membranes if not removed in the feed. This study aimed to quantify

whether AOC was formed at typical ozone:TOC dose ratios previously reported in freshwater literature. In the absence of adverse oxidation byproducts (such as bromate), breaking down high molecular weight and hydrophobic structures would be an option in seawater pretreatment. For instance, the hydrophobic nature and interactions between organic foulants and a hydrophobic membrane would exacerbate SWRO membrane fouling (Yuan, 1999; Yu et al., 2010).

Advanced oxidation for reducing these issues has been introduced in the past few years. For instance, applying AOP in seawater using UV and UV with hydrogen peroxide has been investigated in a seawater matrix (Penru et al., 2012) in order to reduce aromaticity of humic matter and increase biodegradability. If treatment applications could be developed for seawater in which humic hydrophobicity is reduced and removed through biodegradation in a biological filter, minimizing bromate and other unwanted byproducts during pretreatment, AOPs could target both organic and biological fouling by removing the structures that lead to these issues.

Table 3.3. AOC Formation in Humic Acid Solutions with Variable Ozone Doses

Dose Ratio (mg:mg)	Humic Acid (mg/L)	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
3 O_3:TOC	0.3	-39%	8%	-98%
	0.5	-41%	35%	-97%
	1.3	-61%	35%	-98%
2 O_3:TOC	0.3	-29%	69%	-59%
	0.5	-27%	62%	-21%
	1.3	-42%	72%	6%
0.7 O_3:TOC	1.0	3%	-20%	-15%
	2.0	-8%	-19%	3%
	5.0	-20%	-24%	-42%
0.3 O_3:TOC	1.0	-12%	-8%	198%
	2.0	-17%	-12%	84%
	5.0	-33%	-15%	49%

Notes: AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

For the humic acid solutions containing 1 mg/L, the full range of ozone doses from 0 to 3 mg:mg/1 was compared (Figures 3.1–3.3). UV_{254} and TOC were generally stable in all of the ozone tests with humic acid. AOC increased when ozone:TOC was 0.3; otherwise, AOC was nearly the same in reactors at 0.7 and 2 ozone:TOC (Figure 3.3).

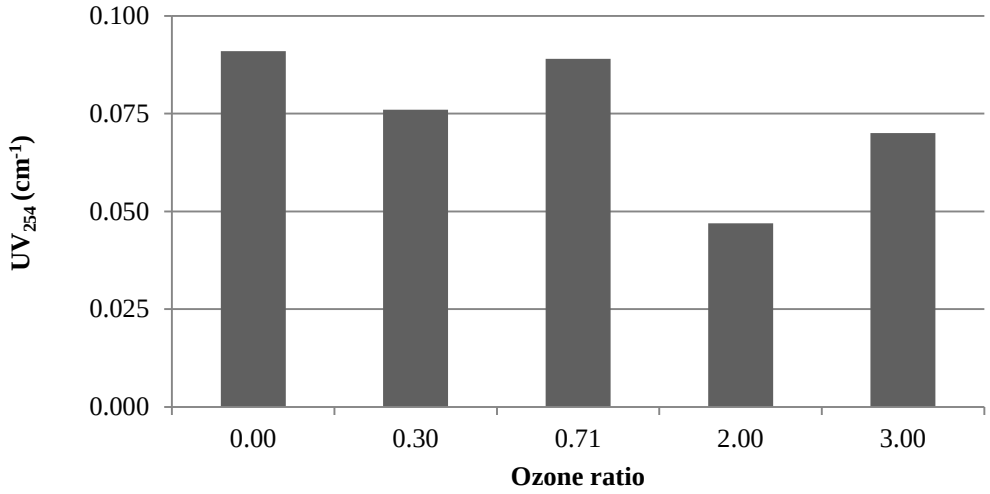

Figure 3.1. UV_{254} results from ozone: TOC dose ratios in 1 mg/L humic acid solutions.

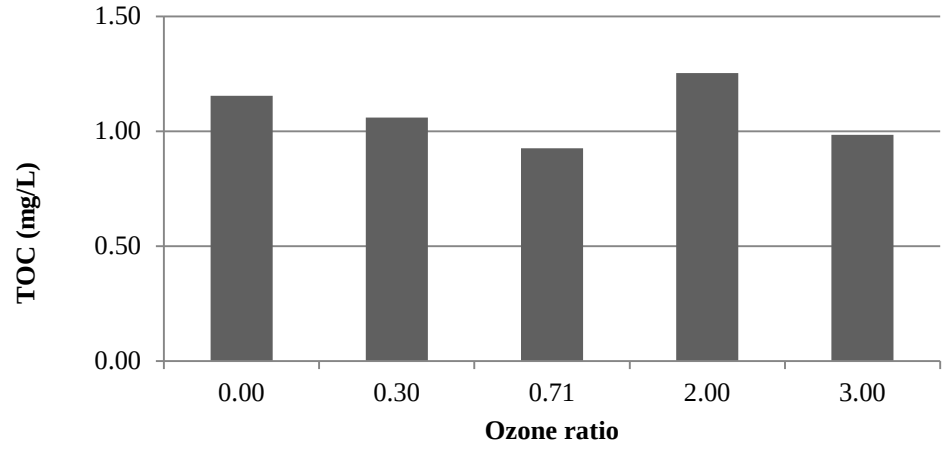

Figure 3.2. TOC results from ozone: TOC dose ratios in 1 mg/L humic acid solutions.

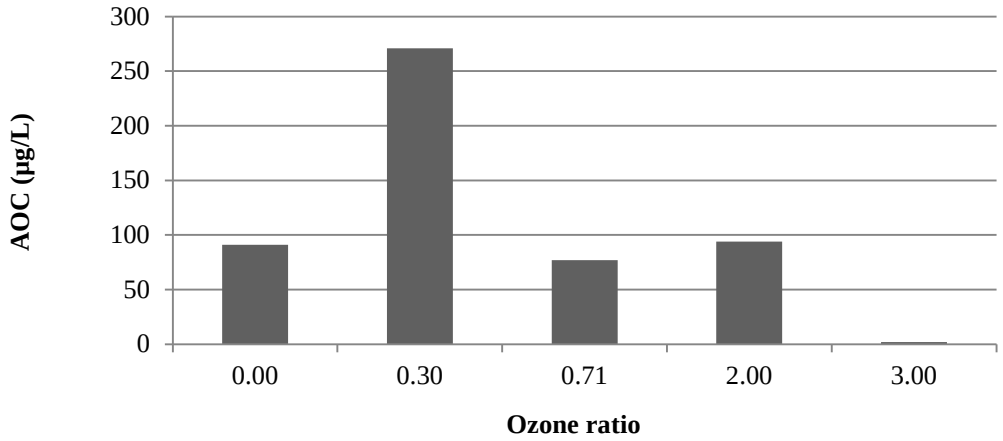

Figure 3.3. AOC results from ozone: TOC dose ratios in 1 mg/L humic acid solutions.

3.4.4 Seawater Oxidation with Ozone

Bulk seawater from Tampa Bay and the Arabian Sea was treated with 1:2 and 1:1 ozone: TOC to evaluate the impact of ozonation on environmental samples having a complex mixture of organic carbons (Table 3.4). Ozonated Arabian Sea water had nearly no change to UV_{254} or TOC (1.32 mg/L). UV_{254} was low at 0.01 cm^{-1}, suggesting that the inherent organic carbon was not high in aquatic humic matter (SUVA 1.0 L/mg/m). It is interesting to note that, although the content of the seawater had low organic carbon, ozonation increased AOC levels three-fold at 1:1 O_3:TOC dose ratio and nearly six-fold at 1:2 O_3:TOC.These results are similar to the previous test with humic acid (Figure 3.4). The comparison reveals that increased ozone doses do not increase AOC by the same magnitude and also suggests that the organic matter in the seawater is a more complex mixture than the model organic humic acid. Ozonated Tampa Bay seawater, which contained more TOC (5.95 mg/L), had nearly no change in AOC at a 1:2 dose ratio, but decreases were apparent for both UV_{254} and TOC.

Table 3.4. AOC Formation in Seawater with Variable Ozone Doses

	Ozone Dose (mg O_3: mg TOC)	UV_{254} (cm^{-1})	% Diff. Rel. to Control	TOC (mg/L)	% Diff. Rel. to Control	AOC (µg/L)	% Diff. Rel. to Control
Tampa Bay	Control	0.171		5.95		57±14	
	1:2	0.108	-37%	5.17	-13%	66±25	16%
	1:1	0.079	-54%	4.19	-30%	19±0	-67%
Arabian Sea	Control	0.014		1.32		13±3	
	1:2	0.012	-29%	1.33	1%	69±19	431%
	1:1	0.010	-14%	1.32	-1%	36±2	177%

Notes: AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

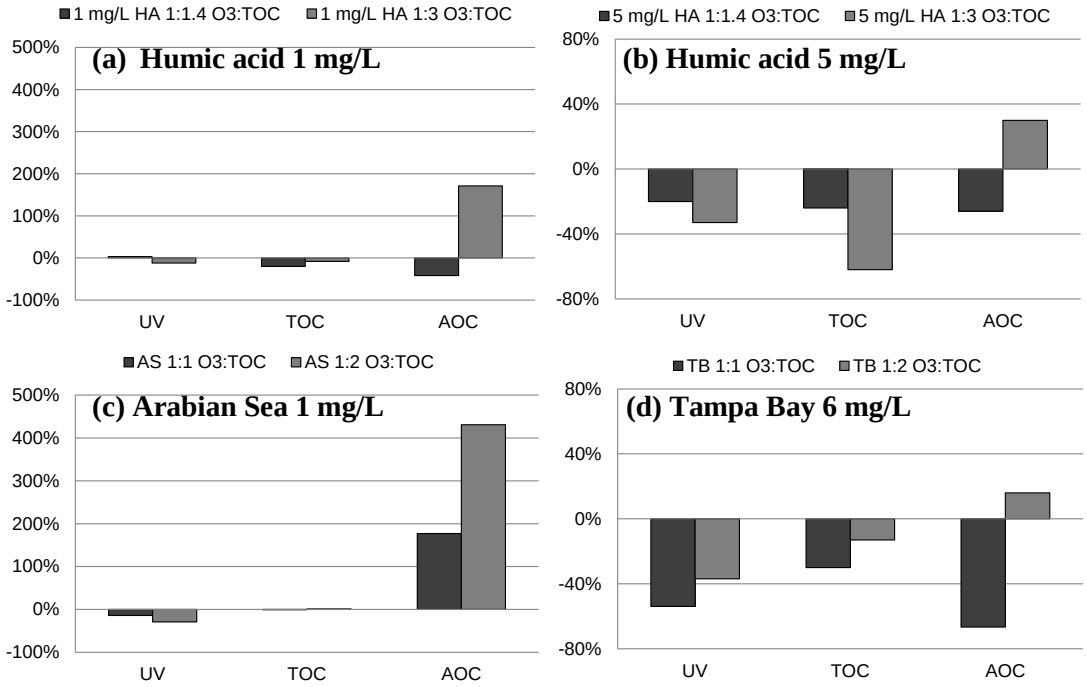

Figure 3.4. Comparison between organic carbon after ozonation of humic acid (a) 1 mg/L, (b) 5 mg/L, and raw seawater from (c) Arabian Sea (1 mg/L), and (d) Tampa Bay (6 mg/L).

Chapter 4

RO Pretreatment Chemicals

4.1 Introduction

Polyphosphates, polyphosphonates, polyacrylates, and polycarboxylates are the most frequent types of antiscalants manufactured and used during SWRO pretreatment to inhibit inorganic fouling (i.e., scaling) that occurs when the concentration exceeds solubility in the brine and the salts precipitate. Although antiscalant application is effective for preventative maintenance of salt precipitation onto the RO membrane, unwanted side effects such as biofouling have been reported. Various reports in freshwater and seawater have indicated that these chemicals provide nutrients and promote conditions that lead to proliferation of bacteria and formation of biofilms. Recent studies using *Vibrio fischeri* have shown that bacterial deposition and biofilm formation increased in solutions containing 20 to 100 mg/L polyphosphonate- and polyacrylate-based antiscalants (Sweity et al., 2013).

Predicting the biofouling potential as a side effect of chemical dosing is further complicated by the proprietary nature of the chemical industry. Manufacturers provide dosing guidelines and often list the percent of the active component in the product, but the specific ingredients are trade secrets and rarely listed. Researching the chemical makeup was nearly impossible; manufacturer websites, distributors, and material safety data sheets (MSDS) lacked clarification. Available information does indicate that carbon and phosphate are often inherent components of antiscalant solutions, which are also essential nutrient supplies for the growth and proliferation of bacteria. Although antiscalants are complex molecules and not easily assimilated, they may contain impurities including phosphoric acid and phosphorous acid that may be present between 0.5 and 2.0%. Even if phosphate is specifically measured, an increased biofouling potential in the RO feed water from these impurities would be better evaluated by measuring the biodegradable nature of the substance through the AOC test.

Often the pretreatment strategy in SWRO plants is to manage ORP as a last step during pretreatment and immediately before the RO feed. Operators aim to control biological growth using chlorine throughout the treatment process and control inorganic fouling by dosing antiscalants. In this scenario, the chlorine residual is often not removed until after the antiscalant is added, providing the opportunity for the treatment chemicals to react. Antiscalants applied in SWRO processes were investigated to understand the biodegradable nature of these chemicals, the inherent chemical impurities, and the byproducts, namely AOC, formed from reaction with chlorine.

4.2 Objectives

Pretreatment chemicals commonly used in SWRO for membrane cleaning and protection were analyzed for their biodegradability and potential to increase AOC in seawater matrices. Antiscalants, citric acid (cleaning agent), and SBS (for ORP control) were tested alone and in combination. Typical strategies in SWRO pretreatment were targeted to evaluate the production of BOM and AOC formation when sequential addition of antiscalants, oxidants, or SBS occurs.

4.3 Methods and Materials

Antiscalants and other chemicals (Table 4.1) were tested in a laboratory-generated seawater matrix (Section 3.3.2) and in seawater (Section 3.3.4) from the Arabian Sea, Redondo Beach, CA, and Tampa Bay, FL. The matrix enabled the project team to evaluate the results for inherent organic carbon content from the antiscalant without any influence or contributing background organic levels found in environmental seawater. The seawater matrix was prepared with necessary nutrients, including nitrogen, phosphorus, and sulfate, but without bromide to minimize formation of hypobromous acid. By preparing the matrix in the laboratory, the project team was able to evaluate reaction and degradation of the antiscalants in the presence of free chlorine residual.

Water quality analyses were conducted for AOC, TOC, and UV_{254} (Section 3.3.6). Phosphate was measured as orthophosphate through the ascorbic acid method (Standard Method 4500-P-E; Hach 8048) at 880 nm; results are reported as mg/L PO_4^{3-}.

Batch experiments targeted low and high range dosing scenarios for each antiscalant. Chemical manufacturers were contacted to discover the most widely used antiscalants in SWRO and for guidance on treatment conditions and dosing. Antiscalants were prepared at two concentrations in the laboratory generated seawater matrix and dosed with 10 mg/L Cl_2 from a 5% sodium hypochlorite solution (J.T.Baker, Avantor Performance Chemicals, Inc., Center Valley, PA). Sodium hypochlorite was employed as the oxidant for testing because of its widespread use in the SWRO industry. The concentrations of the chlorine stock and its dosing solutions were measured by ferrous ammonium sulfate titration with DPD indicator in accordance with Standard Method 4500-Cl F (APHA, 2005).

After the chlorine dosing solution was added to the individual antiscalant solutions and mixed in volumetric flasks, the solution was transferred headspace-free into 250 mL chlorine demand–free amber bottles and placed in the dark at 25° C, where the reaction took place for 18 hours. At the end of the reaction time, chlorine residual measurements indicated that the initial high dosage of chlorine was not depleted, and the samples were therefore appropriately quenched of the free chlorine residual before analysis. A control was also subjected to the same chlorine dosing, reaction, and storage conditions. An aliquot of the initial antiscalant solution was reserved for the same suite of analyses, and results are reported relative to the control. The control had the following levels: 20 µg/L AOC, 0.04 mg/L TOC, UV_{254} 0.003 cm^{-1}, and phosphate 5.5 mg/L PO_4^{3-}.

Table 4.1. Common SWRO Pretreatment Chemicals

Type	Name	CAS#	Manufacturer and Description	Dose (mg/L)
Phosphate	Hypersperse™ MDC 704*	7722-88-5	Contains 1–5% (w/w) of sodium pyrophosphate (diphosphoric acid, sodium salt). GE Betz, Inc. (Trevose, PA)	2–10
	sodium hexametaphosphate; molecular formula $(NaPO_3)_6$	68916-31-1	A. Pfaltz & Bauer (Waterbury, CT)	variable
		10124-56-8	B. tech grade, Alfa Aesar (Ward Hill, MA)	
		68916-31-1	C. glassy, approx. $(NaPO_3)_n$; Spectrum Chemical Mfg. Group (Gardena, CA)	
		68916-31-1	D. Macron Fine Chemical, Avantor Performance Materials, Inc. (Center Valley, PA)	
Polyphosphonate (carbon–phosphorus bond)	A-102 Plus*	composition proprietary	American Water Chemicals (Plant City, FL). TOC 26 mg/g	1–10
	1-hydroxyethylidene-1,1-diphosphonic acid	2809-21-4	minimum 95%. StremChemicals (Newbury, MA)	1–5
	Hypersperse™ MDC 150*	22042-96-2	Contains diethylenetriamine pentamethylene phosphonic acid, sodium salt. GE Betz (Trevose, PA). TOC 40 mg/g	3–6

Table 4.1. Common SWRO Pretreatment Chemicals

	Vitec® 3000	composition proprietary	Avista Technologies, Inc. (San Marcos, CA). Contains a bacteriostat to inhibit bacterial growth during storage.	2–5
Polymer/polycarboxylate	Acumer-DOW™ 1035*	composition proprietary	polyacrylic acid, sodium salt (34.0–36.0%). Average MW=2000. Rohm and Haas/The Dow Chemical Company	1–10
	Acumer-DOW™ 2000*	composition proprietary	sulfonate, carboxylate; acrylic polymers (42.0–44.0 %). Residual monomers <500 ppm. Average MW=4500. Rohm and Haas/The Dow Chemical Company	1–11
	Acumer-DOW™ 2100*	composition proprietary	sulfonate, carboxylate; acrylic polymers (36.0–38.0 %). Average MW=11,000. (Rohm and Haas/The Dow Chemical Company)	1–7
	AWC A-104*	not available	American Water Chemicals (Plant City, FL). Information provided only for similar product on MSDS.	1–10
	citric acid	77-92-9	anhydrous; EMD (Gibbstown, NJ)	1–5
	FloCon + N	not available	20% active ingredient. A neutralized aqueous solution of organic acids. BWA™ Water Additives (Tucker, GA)	10% w/w

Table 4.1. Common SWRO Pretreatment Chemicals

	SpectraGuard™ Super Concentrate (SC) 11X	not available	Professional Water Technologies. Phosphate and phosphate-derivative free, macromolecule “dendrimer” antiscalant	2–6
Other	sodium bisulfite	120002-56-4	ACS grade; Fisher Scientific (Fair Lawn, NJ). Dechlorination agent/ORP control	1–5

Notes: *=Antiscalant Material Safety Data Sheet available; ACS=American Chemical Society; CAS=Chemical Abstracts Service; MW=molecular weight; ORP=oxidation reduction potential.

4.4 Results and Discussion

Chemicals added during seawater RO desalination pretreatment may include a pH adjustor, antiscalant, and oxidant residual either alone or in combination. Chemicals such as citric acid, which may be used as part of a membrane cleaning or for pH adjustment, provide a readily biodegradable source of organic carbon and therefore an opportunity for unwanted bacterial proliferation on the RO membrane. In addition, comparisons between various chemical sources (e.g., sodium hexametaphosphate [SHMP]) indicated that impurities from different chemical grades and manufacturers may be an additional source of biodegradable carbon.

4.4.1 Chemical Grades and Impurities

Four different manufactured sources of SHMP (SHMP A–D) were obtained to evaluate concentrations of organic carbon variability in solutions at two doses, 1 and 5 mg/L (Table 4.2). SHMP was used as a reliable chemical in RO pretreatment because of its ability to sequester and prevent calcium from precipitating as a scale; however, biofouling of RO membranes at plants using SHMP became a detrimental consequence (Alawadhi, 1997; Voutchkov, 2010). SHMP was selected for testing in this study to establish a baseline of biodegradable organic carbon from dosing a chemical known to cause biofouling. Chemical impurities have also been reported to cause biological fouling on RO membranes (Vrouwenvelder et al., 2001), and that potential side effect would not necessarily be detected in TOC (or even UV_{254}) measurements, which are not specific to the biodegradability of the organic carbon. Three sources (SHMP B–D) provided an average of 100 µg/L AOC. The source with the lowest AOC (<30 µg/L) was SHMP A, but that had the greatest TOC concentration. AOC levels for SHMP D were similar for both solutions tested at 1 and 5 mg/L, 130±10 and 100±20 µg/L AOC, respectively. In all the samples UV_{254} was less than 0.01 cm^{-1}, which suggests that the impurities were not aromatic or carbon–carbon double bonds detected at that wavelength.

Only SHMP B showed a significant difference in AOC between the two doses; a 1 mg/L dose had 67 µg/L AOC, and 5 mg/L had 141 µg/L AOC. SHMP B is technical grade and therefore may have more impurities than the other chemicals, which were more expensive and of a higher grade. SHMP C and SHMP D concentrations also showed evidence of elevated organic carbon in higher dilutions, in spite of the fact that they were the same CAS number as SHMP A. SHMP B was also dosed at 1 mg/L into WBMWD intake seawater, with expected results: 164 µg/L AOC (control was 101 µg/L, SHMP 67 µg/L); however, neither UV_{254} nor TOC increased significantly. These results provide evidence that impurities in treatment chemicals may be sources of nutrients or a substrate for bacterial growth that may lead to biofouling. Furthermore, UV_{254}, and TOC are not effective methods for predicting the potential for bacterial growth, unlike the AOC test.

Polyphosphonates contain two or more phosphonate groups and may also be referred to as organophosphorous compounds because the structure contains at least one carbon. The simplest structure that has been widely used in industry as an antiscalant and corrosion inhibitor is 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP). HEDP was tested at doses of 1 and 5 mg/L in a laboratory-generated seawater matrix and in seawater from the intake at WBMWD (Table 4.3). The chemical was purchased neat and had variable AOC levels as high as 100 µg/L in seawater but less than 30 µg/L when tested in the buffer alone. A similar effect was seen in seawater for SHMP in that the AOC in the seawater test was increased by the amount of AOC in the laboratory-generated matrix. Results reported are the average (and standard deviation) from two separate experiments in the WBMWD seawater.

Table 4.2. Organic Carbon in Solutions Containing Two Doses of SHMP from Various Manufacturers

	Dose (mg/L)	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
SHMP A	1	0.004	1.0	27
	5	0.004	1.2	27
SHMP B	1	0.004	0.6	67
	5	0.003	0.6	141
SHMP C	1	0.003	0.7	101
	5	0.005	0.7	104
SHMP D	1	0.001	<0.25	130
	5	0.004	<0.25	100
SHMP B in seawater	Control	0.009	0.99	110
	1	0.010	1.06	164

Notes: AOC=assimilable organic carbon; SHMP=sodium hexametaphosphate; TOC=total organic carbon; UV=ultraviolet.

Table 4.3. Organic Carbon in Solutions Containing Polyphosphonate HEDP

	Dose (mg/L)	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
HEDP	1	0.003	0.90	29
	5	0.003	1.80	20
HEDP in seawater	Control	0.009	0.99	110
	1	0.01	1.1	138±47
	5	0.01	1.6	120±7

Notes: AOC=assimilable organic carbon; HEDP=1-hydroxy ethylidene-1,1-diphosphonic acid; TOC=total organic carbon; UV=ultraviolet.

The concentration of organic carbon was evaluated for linearity at increasing doses of antiscalants (Table 4.4). Active chemicals used for antiscalant applications in seawater RO are rarely identified specifically by the manufacturer and are a fraction of the concentration in the neat product sold. According to the MSDS assembled for this project, active concentration is generally 10 to 60% of the solution, averaging 35%. For dosing purposes, this is not taken into account, and the manufacturers recommend calculating the dose based on 100% product concentration (or even super concentrates to facilitate easier shipping and storage with smaller volumes). Testing at the elevated doses was planned to target only the active concentrate and thereby ascertain the potential for biodegradation of the neat chemical; however, testing using this approach to determine elevated ranges prevented AOC measurement because of the inhibition of the biocide, and chemical makeup of the concentrated antiscalant prevented growth of the AOC test organism. TOC and UV_{254} were measured, and correlations were made at normal dosing ranges (<10 mg/L) to the elevated range (40,000 mg/L).

The coefficient of determination indicated that the dose and resulting TOC showed a very strong correlation ($r^2 > 0.9$), partially because the range of concentrations spanned up to four magnitudes. For the antiscalant AWC A-104, there is a 1:1 relationship for dose versus TOC as indicated by the slope1.02. AWC A-104 is a polycarboxylate (inherently composed of

organic carbon) with proprietary active ingredients, whereas the other chemicals are polyphosphonates without organic carbon as part of the proprietary formulation. At the lowest doses tested as recommended for the individual antiscalants, TOC increased 16 to 38% for phosphonates and 19 to 60% for the polymer/polycarboxylates. Based on this information, organic carbon loading would occur from the addition of these chemicals. The potential for TOC to be broken Down by oxidants into biodegradable carbon fractions could be significant depending on the treatment process, application, and dosing location. Furthermore, membrane fouling caused by elevated organic matter is a possibility if a treatment plant incorrectly doses antiscalant during pretreatment.

Table 4.4. Correlations between Organic Carbon and Antiscalant Doses in Typical and Elevated Ranges

		Typical Range		Elevated Range			
Polyphosphate	**MDC 704 (mg/L)**	3	10	3800	40,000	slope	R^2
	TOC (mg/L)	0.59	0.79	40	144	0.003	0.966
	UV_{254} (cm^{-1})	0.01	0.01	0.01	0.01	9.6E-8	0.422
Polyphosphonate	**AWC 102+ (mg/L)**	1	10	100	500	slope	R^2
	TOC (mg/L)	0.16	1.45	33	146	0.29	0.999
	UV_{254} (cm^{-1})	0.004	0.006	0.020	0.068	1.3E-04	0.997
	MDC 150 (mg/L)	3	10	3000	8500	slope	R^2
	TOC (mg/L)	0.61	2.54	96	343	0.04	0.994
	UV_{254} (cm^{-1})	0.007	0.011	0.15	0.34	3.9E-05	0.994
	Vitec 3000 (mg/L)	2	7	3800	40,000	slope	R^2
	TOC (mg/L)	0.75	1.37	172	833	0.02	0.987
	UV_{254} (cm^{-1})	0.01	0.008	0.05	0.32	7.7E-06	0.999
Polycarboxylate/ polymer	**AWC A-104 (mg/L)**	1	10	100	500	slope	R^2
	TOC (mg/L)	0.60	4.86	107	508	1.02	0.9997
	UV_{254} (cm^{-1})	0.008	0.007	0.008	0.019	2.38E-05	0.971
	FloCon + N (mg/L)	3	10	3000	9000	slope	R^2
	TOC (mg/L)	1.16	3.64	232	816	0.091	0.997
	UV_{254} (cm^{-1})	0.005	0.011	0.37	1.19	1.3E-04	0.999
	SpectraGuard™ SC	2	6	143,000	275,000	slope	R^2
	TOC (mg/L)	0.37	0.37	1342	1860	0.007	0.962
	UV_{254} (cm^{-1})	0.001	0.001	0.285	0.511	1.9E-06	0.999

Notes: Antiscalants were dosed with proprietary active ingredients into a laboratory-generated seawater matrix; AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

The polymer AWC A-104 had the greatest composition as TOC; the chemical is phosphorus-free, with an active concentration of a proprietary chemical. Depending on the dose (Table 4.5), TOC ranged from 50 to 100% of the composition of the antiscalant. AWC 102+, a polyphosphonate that contains phosphorus, not in phosphate form, produced by the same manufacturer, was tested similarly. By comparison, the TOC composition of AWC 102+ was dose-dependent but ranged from 15 to 29%. A typical dosing rate for both chemicals is 1 mg/L for SWRO plants operating at 45 to 50% recovery.

AWC A-102+ and A-104 were dosed into seawater collected from the intake at WBMWD to evaluate the organic carbon levels in a seawater matrix. Targeted concentrations were 1 and 5 mg/L as outlined by the manufacturer. Two different tests were conducted (Table 4.5), and the results reported are the average (and standard deviation) from two separate experiments using the WBMWD seawater. In Test 1 the 5 mg/L dose seemed to be slightly lower than in Test 2, according to TOC concentrations. Inhibition by the bacteriostat in the 5 mg/L doses would explain the lower amount of AOC. By comparison with the 1 mg/L antiscalant doses in seawater, AOC levels are between 73 and 100 µg/L for the polymer A-104 and 109 to 163 µg/L for the polyphosphonate A-102 +. UV_{254} was generally within 20% of the seawater control.

Table 4.5. Organic Carbon in Seawater from WBMWD Intake Dosed with Polyphosphonate and Polymer Antiscalants

	Dose (mg/L)	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
Seawater	control	0.009	1.00	110±21
AWC A-104	1	0.011±0.001	1.47±0.3	87±19
	5	0.011±0.003	3.86±2.0	27±16
AWC A-102 +	1	0.011±0.002	1.12±0.1	136±38
	5	0.012±0.001	1.76±0.8	62±65

Notes: AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

Table 4.6. Organic Carbon in Solutions Dosed with Polycarboxylate Citric Acid

	Dose (mg/L)	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
Citric acid	1	0.003	1.50	310
	5	0.003	3.90	543
Citric acid in seawater	control	0.009	0.99	110
	1	0.010±0.001	1.38±0.10	779±510
	5	0.014±0.004	3.45±0.06	1020±180

Notes: AOC=assimilable organic carbon; TOC=total organic carbon; UV=ultraviolet.

Citric acid has been used for pretreatment in seawater RO and has already been shown to be an assimilable food source for *V. harveyi* used in the AOC test (Weinrich et al., 2011). Understanding the chemical composition is an important part of predicting biological fouling potential. In some cases, such as citric acid, the actual chemical used for treatment can provide a food source for microbial growth. There were two different tests conducted, and the results reported are the average (and standard deviation) from two separate experiments in the WBMWD seawater (Table 4.6). Citric acid is used for membrane cleaning but also provides a nutrient source and increases the potential for biological growth in membranes. Tests of citric acid at concentrations of 1 and 5 mg/L in a laboratory-generated seawater matrix resulted in AOC levels of 310 and 543 µg/L, respectively. In seawater, doses of 5 mg/L resulted in an average of 1020 µg/L. Citric acid is a known chemical food source for the marine AOC test organism; therefore, even if a high purity grade chemical is used, the inherent chemical component is easily assimilated. After cleaning, any residual citric acid that was not flushed or otherwise removed may cause increased AOC in the RO feed and additional nutrients for bacterial growth.

SBS was tested at doses of 1 and 5 mg/L (Table 4.7). SBS (alone or as a mixture of sodium metabisulfite) is applied during treatment to remove oxidant residual (e.g., chlorine) and protect membranes from oxidant damage. Many RO membrane warranties are contingent on keeping the ORP below a set point. Although UV_{254} and TOC levels were the same at both doses (UV_{254}=0.003 cm^{-1} and TOC=0.7 mg/L), AOC increased with increasing doses, from 58 µg/L in the 1 mg/L test solution to 116 µg/L for 5 mg/L SBS. SBS did not increase TOC or UV_{254} levels at the two doses tested, but the amount of BOM measured by AOC increased.

Table 4.7. Organic Carbon in Seawater from WBMWD Intake Dosed with Sodium Bisulfite

	Dose (mg/L)	UV_{254} (cm^{-1})	TOC (mg/L)	AOC (µg/L)
SBS	1	0.003	0.7	58
	5	0.004	0.6	116
SBS in seawater	control	0.011	0.99	88
	5	0.012	0.97	102

Notes: AOC=assimilable organic carbon; SBS=sodium bisulfite; TOC=total organic carbon; UV=ultraviolet.

4.4.2 Byproducts of Antiscalant and Chlorine Reactions

SBS is often the last chemical added before the RO membrane feed (i.e., after the cartridge filters), applied to reduce ORP, quench the disinfectant residual, and protect the membranes from the damaging effects of oxidants and disinfectants. Current pretreatment strategies often entail antiscalant dosing prior to the addition of SBS; manufacturers recommend dosing antiscalant prior to the cartridge filters. In this scenario, the disinfectant residual (e.g., chlorine) would not have been quenched by SBS and would remain in the water during antiscalant addition. Because chlorine is a nonselective oxidant, the disinfectant would not only inactivate bacteria but also react with other components in the water, including NOM and an antiscalant (if present). Byproducts from those reactions should be carefully considered. The following section discusses the potential for increased nutrient levels, for example, AOC and phosphate that would occur following reactions between chlorine and frequently used antiscalants.

Antiscalant chemicals were tested from various manufacturers for each class: polyphosphates, polyphosphonates, and polycarboxylates. A total of 11 chemicals were tested at two doses each, and the following results examine the changes to organic carbon and phosphate composition after reacting with free chlorine for 18 hours at 25° C. Polyphosphate had the greatest AOC level of all the chemicals (Table 4.8; 90 µg/L AOC at the 10 mg/L dose). Polyphosphonates and polycarboxylates generally had low AOC background levels (concentration before chlorination); AOC was only 10 µg/L higher than the control.

After reaction with chlorine, AOC increased by greater than 10 µg/L in seven of the solutions from five chemicals. Increases in AOC were not specific to a certain class of antiscalant; the results show that at least one chemical in each class had an increase in AOC after chlorination. The greatest increase was seen in the polyphosphonate chemical AWC A-102+ in the 10 mg/L solution, which increased AOC from 10 to 372 µg/L AOC, followed by an increase of 175 µg/L AOC in the 10 mg/L dose of polymer Acumer-Dow™ 2000 and an increase of 71 µg/L AOC in the 3 mg/L dose of polyphosphate Hypersperse™ MDC704. These and the other increases of biodegradable organic carbon are important considering that even a minor increase in AOC contributes to conditions where sufficient nutrients exist for bacteria to grow and proliferate. For a few of the chemicals, chlorination did not have an impact on AOC (i.e., ΔAOC was 0): HEDP, Acumer-DOW™ 2100, and AWC A-104.

Phosphate averaged 0.4±0.6 mg/L, median 0.2 mg/L (n=22). Phosphate increased in all polyphosphate and polyphosphonate antiscalants after reaction with chlorine. This latter observation may be explained by an oxidation mechanism that breaks Down one or two of the phosphonate groups from the carbon (Figure 4.1) to form orthophosphate. Although phosphate impurities in the polycarboxylate/polymer antiscalants averaged 0.4 mg/L, no increase was measured in the chlorinated solutions. No increase in phosphate was anticipated; the inherent makeup of polycarboxylate/polymers is not phosphate or phosphate derivative–based, although the composition is proprietary.

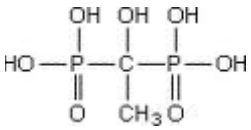

Figure 4.1. 1-Hydroxy ethylidene-1,1-diphosphonic acid (HEDP).

In the previous section, results were presented for the increase of TOC after addition of the antiscalant. Even at the minimum recommended doses, TOC increased by 0.5 and 2 mg/L in the minimum and maximum recommended doses, respectively. The range of changes in TOC was -0.3 to 0.3 mg/L. Although dosing the chemical increased TOC, changes to TOC were not detected after chlorination. For UV_{254} all levels were less than 0.01 cm^{-1}; these levels would be too low practically to identify impacts from treatment changes in an environmental seawater source. In fact, measurements for organic carbon, including TOC and UV_{254}, that are nonselective to BOM do not provide meaningful information regarding nutrients for bacterial growth and cannot be used as a BOM indicator measurement like AOC or even a direct phosphate nutrient measurement.

Chlorine demand was also monitored to evaluate the reactivity of the antiscalant; chlorine was measured after the 18 hour reaction time and subtracted from the residual in the matrix control. Chlorine demand was greatest in both Hypersperse™ MDC150 and Vitec® 3000 at 5.5 mg/L Cl_2. These chemicals are both polyphosphates; as such, the major byproduct did not appear to be AOC, but rather phosphate. Phosphate increased by 3.3 and 3.4 mg/L in the postchlorination solutions for Hypersperse™ MDC150 and Vitec® 3000, respectively.

Many of these antiscalants would react with chlorine to increase the amount of biodegradable carbon or other nutrients in the RO feed, which would create optimum conditions for biological growth on the membranes. Therefore, the treatment strategies could be amended to minimize additional AOC formation and phosphate liberation by removing the oxidant residual before the antiscalant is added. AOC and phosphate measurements both indicate the presence of necessary nutrients for bacterial growth and proliferation. A strategy to minimize nutrients would best be suited for the ultimate control of RO membrane biofouling.

Table 4.8. Nutrient and Organic Carbon Data for 11 Antiscalants before and after Reaction with Chlorine in a Laboratory-Generated Seawater Matrix

			Baseline Levels				Post-Reaction with Chlorine											
Trade Name	**Dose** mg/L	**pH**	**AOC (µg/L)**	**PO_4^{3-} (mg/L)**	**TOC (mg/L)**	**UV_{254} (cm^{-1})**	**Cl_2 demand (mg/L)**	**AOC (µg/L)**	**PO_4 (mg/L)**	**TOC (mg/L)**	**UV_{254} (cm^{-1})**	**Δ AOC**	**Δ PO_4**	**Δ TOC**	**Δ UV_{254}**	**% ΔAOC**	**% ΔPO_4**	**% Δ TOC**	**% Δ UV_{254}**
Polyphosphate																			
Hypersperse MDC 704	3	8.8	76	1.2	0.55	0.001	2.9	147	1.5	0.39	0.001	71	0.4	-0.2	0.000	93%	32%	-29%	0%
	10	8.9	90	0.9	0.84	0.001	4.8	118	4.7	0.91	0.001	28	3.9	0.1	0.000	31%	446%	9%	0%
Polyphosphonate																			
AWC A-102+	1	8.8	0	0.0	0.12	0.001	4.2	10	0.4	0.25	0.003	10	0.4	0.1	0.002	0%	0%	105%	200%
	10	8.8	10	0.0	1.41	0.001	4.5	372	5.0	1.51	0.005	362	5.0	0.1	0.004	3620%	0%	7%	400%
HEDP	1	8.8	9	0.5	0.80	0.001	1.1	10	0.5	0.90	0.002	1	0.1	0.1	0.001	10%	18%	0%	100%
	5	8.6	10	0.1	1.70	0.001	1.6	10	1.2	1.80	0.009	0	1.1	0.1	0.008	0%	1892%	0%	800%
Hypersperse MDC 150	3	8.7	10	0.3	0.57	0.001	4.2	58	2.8	0.61	0.007	48	2.6	0.0	0.006	480%	952%	8%	600%
	10	8.7	2	0.3	2.50	0.005	5.5	10	3.7	2.21	0.005	8	3.4	-0.3	0.000	342%	1107%	-12%	0%
Vitec 3000	2	8.9	5	0.0	0.71	0.004	4.2	50	2.5	0.44	0.004	45	2.5	-0.3	0.000	900%	0%	-38%	0%
	7	8.9	10	0.0	1.33	0.002	5.5	10	3.3	1.25	0.002	0	3.3	-0.1	0.000	0%	0%	-6%	0%
Polycarboxylate/ polymer																			
Acumer-DOW 1035	1	8.7	7	2.8	0.15	0.001	0.5	10	0.0	0.22	0.005	3	-2.8	0.1	0.004	42%	-100%	43%	400%
	10	8.5	1	0.1	1.73	0.001	0.0	10	0.0	1.55	0.000	9	-0.1	-0.2	-0.001	688%	-100%	-10%	-100%
Acumer-DOW 2000	1	8.6	10	0.4	0.28	0.001	0.5	12	0.0	0.50	0.003	2	-0.4	0.2	0.002	22%	-100%	81%	200%
	10	8.6	0	0.5	2.03	0.003	0.5	176	0.1	2.03	0.000	175	-0.4	0.0	-0.003	55340%	-85%	0%	-100%
Acumer-DOW 2100	1	8.7	3	0.0	0.19	0.003	1.1	10	0.0	0.23	0.003	7	0.0	0.0	0.000	195%	0%	21%	0%
	10	8.7	10	0.0	1.66	0.003	0.8	10	0.0	1.74	0.003	0	0.0	0.1	0.000	0%	0%	5%	0%
AWC A-104	1	8.8	1	0.0	0.56	0.002	0.7	10	0.0	0.68	0.005	9	0.0	0.1	0.003	890%	-100%	21%	150%
	10	8.8	10	0.3	4.82	0.001	0.0	10	0.0	4.79	0.008	0	-0.3	0.0	0.007	0%	-100%	-1%	700%
FloCon + N	3	8.6	10	0.1	1.12	0.001	0.2	10	0.0	1.26	0.004	0	-0.1	0.1	0.003	0%	-100%	12%	300%
	10	8.4	4	0.3	3.60	0.005	0.3	10	0.0	3.89	0.009	6	-0.3	0.3	0.004	150%	-100%	8%	80%
SpectraGuard SC	2	8.4	10	0.2	0.10	0.001	0.0	18	0.0	0.06	0.000	8	-0.2	0.0	-0.001	80%	-100%	-42%	-100%
	6	8.7	0	0.1	0.10	0.001	0.2	10	0.0	0.22	0.009	10	-0.1	0.1	0.008	6049%	-100%	108%	800%

Notes: AOC=assimilable organic carbon; HEDP=1-hydroxy ethylidene-1,1-diphosphonic acid; TOC=total organic carbon; UV=ultraviolet.

Chapter 5

Focused Investigation of Biological Fouling on RO Membranes

5.1 Introduction

Monitoring data at full-scale treatment plants showed significant correlations with AOC. RO membrane differential pressure increases and specific flux decreases were correlated with AOC. Conducting experiments at the bench- and pilot-scale were required to further investigate the effects of AOC on biological fouling. Using a single membrane provided testing conditions that were easily monitored and controlled, and therefore a focused investigation of the RO feed water quality, specifically AOC, was effective for evaluating biological fouling and the resulting impact on differential pressure and specific flux. Two approaches examined these operational conditions; the first used a 500 gpd RO pilot that housed one 29 ft^2 membrane, and the second was a bench-scale test unit that housed one 0.0452 ft^2 membrane coupon. In the latter testing, the coupon was used so that multiple tests could be conducted using baseline and elevated AOC–containing RO feed water.

5.2 Objectives

AOC was evaluated as a useful and significant predictor of biological fouling potential. To achieve this, operational changes (e.g., permeate flux, driving pressure) using a flat sheet membrane test cell and a pilot-scale RO unit were compared to the water quality and AOC in the RO feed.

5.3 Methods and Materials

5.3.1 Pilot Unit Operation

Water quality and operational data were collected from a 500 gpd pilot unit deployed at TBSDP. A new thin film composite RO membrane was installed into the system and operated under constant permeate flux for the purpose of further evaluating AOC as a tool for monitoring fouling.

5.3.1.1 Pilot Unit Configuration with TBSDP Feed

The pilot unit (Figure 5.1; Tomar TV-500SW, Tomar Water Systems, Inc., San Marcos, CA) contains a multimedia (sand) prefilter, chemical injection system, and UV sterilizer integrated on a stainless steel skid frame powered by a single-point AC power connection. SBS was used in the chemical injection system. The unit was operated at 13% recovery; permeate flow rate was set at 0.317 gpm (457 gpd). By maintaining constant product water settings (e.g., flux), operational changes were monitored daily. Feed water from TBSDP was pumped from the rapid mix basins prior to the sand filters. A sump pump lifted water from the treatment basin over the basin wall and Down through piping into a 32 gallon reservoir in the pilot unit shed. An automatic feed of SBS was dosed into the reservoir to quench the residual. A lift pump moved the water from the reservoir to the sand filter, followed by a cartridge filter prior

to the RO membrane vessel. Pressure gauges were installed before and after the cartridge filter and after the RO feed pump to the RO vessel and brine flow. A digital readout monitored temperature and conductivity of RO permeate. A new RO membrane was installed at the beginning of the test, a Dow Filmtec™ seawater element SW30-2540. This unit can withstand 800 psi applied pressure at a 700 gpd flow rate with average 99.4% salt rejection. The element is 40 in. long and 2.4 in. wide. The active area of the membrane is 29 ft^2 and made of polyamide film wrapped in fiberglass.

5.3.1.2 Water Quality

Seawater was pretreated at the plant with approximately 0.5 to 1.1 mg/L chlorine dioxide. Chlorine dioxide residual ranged from 0.01 to 0.39 mg/L. After the junction box, seawater was dosed with sulfuric acid (~20–22 mg/L), hypochlorite (4–6 mg/L), and ferric chloride (~4–5 mg/L). Daily water quality data were collected from TBSDP, including temperature and conductivity at the intake; turbidity, pH, alkalinity, and chlorine dioxide residual at the junction box; chlorine residual in the rapid mix basin; and SDI_{15} of the RO feed (Table 5.1). Grab samples were collected at the pilot unit and analyzed for TOC, AOC, UV_{254}, and phosphate. Phosphate levels were 0.3 mg/L, and nitrate was 0.09 mg/L.

Figure 5.1. Mobile RO skid deployed at TBSDP.

Table 5.1. Seawater Pretreatment Records from TBSDP

	Day	Intake Temp. (° C)	pH	Alkalinity (mg/L)	Chlorine Dioxide (mg/L)	Cl_2 (mg/L)	SDI_{15} Cart. Filter
3/26/2013	1	27.1	7.90	127	0.161	0.84	3.76
3/27/2013	2	22.8	8.03	123	0.010	0.77	3.62
3/28/2013	3	16.7	7.96	127	0.173	0.87	3.73
3/28/2013	3.5	25.9					
3/29/2013	4	21.4	7.96	127	0.010	1.09	3.77
3/29/2013	4.5	23.9					
3/30/2013	5	23.9	7.82	123	0.199	0.74	3.74
3/30/2013	5.5	27.0					
3/31/2013	6	26.5	7.91	114	0.010	0.94	3.52
4/1/2013	7	26.0	7.82	124	0.392	1.10	3.66
4/1/2013	7.5	28.6					
4/2/2013	8	27.1	7.76	127	0.010	1.22	3.39
4/2/2013	8.5	30.4					
4/3/2013	9	29.3	7.89	124	0.010	0.69	3.43
4/3/2013	9.5	28.7					
4/6/2013	12	28.5	8.00	119	0.039	0.65	3.39

Note: SDI=silt density index.

5.3.2 Membrane Test Cell

5.3.2.1 Water Quality

Experiments to monitor the biological fouling effect on permeate flux decline were conducted onsite at TBSDP with a bench-scale membrane test cell using the pretreated RO feed because it was the most representative water source for conducting fouling tests. Pretreated seawater from TBSDP was diverted from the sampling station prior to the high-pressure RO pump to the test cell's feed tank. The RO feed water had undergone complete pretreatment conditions at TBSDP, and SBS was added to remove remaining chlorine residual after the cartridge filtration step. Inherent water quality and organic solute concentration were maintained by configuring the feed in once-through mode to most effectively capture the water quality of the RO feed to TBSDP. The effects from recirculation and bacterial consumption may have varied the concentration of solute (AOC). Operational data from TBSDP were collected for the RO feed and included turbidity, SDI, pH, and ORP at 4 hour intervals. At the end of the experiments, the membrane was retrieved from the test cell and prepared for imaging using scanning electron microscopy (SEM).

Samples were collected from the RO feed and analyzed immediately onsite at TBSDP for nitrogen and phosphorus with a portable spectrophotometer (DR2400, Hach, USA). Phosphate was measured as orthophosphate through the ascorbic acid method (Standard Method 4500-P-E; Hach 8048) at 880 nm; results are reported as mg/L PO_4^{3-}. Ammonia was measured as ammonia nitrogen using the salicylate method (Hach 8155) at 655 nm; results are reported as mg/L NH_3–N. Nitrate was measured as nitrate nitrogen using the cadmium reduction method (Hach 8171) at 400 nm; a standard curve was prepared according to the seawater calibration as outlined in the method, and the results are reported as NO_3^-–N. Nitrite was measured as nitrite nitrogen using the diazotization method (Hach 8507) at 507 nm; results are reported as NO_3^-–N. Additional samples were shipped overnight on ice to Delran, NJ, where they were processed and analyzed for AOC, UV_{254}, TOC, and SUVA (methods in Section 2.1).

5.3.2.2 Experimental Setup

The experimental setup was composed of a cross flow test cell, pump, motor, pressure gauges, valves for flow and pressure control, and flow meters. The CF042 membrane cell (Sterlitech, Kent, WA) holds a flat sheet RO membrane with an active area of 42 cm^2. The permeate carrier was a 20 µ sintered 316L stainless steel plate. Dow Filmtec SW30HR membranes were used for the experiments and came precut. The SW30HR is a smooth, hydrophilic commercial flat sheet, thin film composite RO membrane. A high-pressure, positive displacement, diaphragm pump with a maximum flow rate of 1.8 gpm (6.8 Lpm) was used. Pressure was manually adjusted to remain constant over the experiment. Feed to the cell was pumped from a 5 gallon stainless steel conical feed tank onto the test cell at a flow rate of 5.5 Lpm.

There was no recirculation of the concentrate or permeate to preserve the representative organic loading directly from the RO feed at TBSDP. Prior to testing, TBSDP second-pass RO permeate was used to compress the membrane at the operating pressure for 1 hour before testing. Permeate was also used to flush the system at the end of the experiment. Temperature, feed pressure, flow, pH, and conductivity were measured at 20 minute intervals. After the initial compression period, the unit was operated for each test for 2 days. Specific flux was calculated from the driving pressure and normalized for temperature and the initial flux of the SWRO30 membrane. Operational parameters between the two membrane tests were nearly the same, as seen in Table 5.2.

Table 5.2. Membrane Test Cell Feed Water Quality and Operating Parameters

	AOC Baseline	AOC (1000 µg/L)
AOC (µg/L)	30	997
TOC (mg/L)	4.3	5.4
SUVA (L/mg/m)	1.4	1.3
UV_{254} (cm^{-1})	0.06	0.07
Total nitrogen (mg/L as N)	0.4	0.8
Phosphate (mg/L)	0.16	0.13
Operating pressure (psig)	820	820
Temperature (°C)	28.2	28.0
pH	6.88	6.89
Feed conductivity (mS/cm)	40	40
SDI (15 min)	3.2	2.9
Feed turbidity (NTU)	0.12	0.09
Permeate conductivity (mS/cm)	0.3	0.3
Salt rejection	99.2%	99.2%
Membrane flux J_0 (Lmh)	20	20
Flux decline	3%	24%

Notes: AOC=assimilable organic carbon; NTU=nephelometric turbidity units; SDI=silt density index; SUVA=specific ultraviolet absorbance; TOC=total organic carbon; UV=ultraviolet.

5.3.3 Analyses of Membrane Sections

5.3.3.1 Adenosine Triphosphate on the Membrane Surface

Adenosine triphosphate (ATP) analysis was conducted on the membrane surface from the pilot unit to evaluate microbial activity. ATP occurs in all living organisms and is a useful-assay because it measures metabolically active biomass irrespective of whether such biomass is culturable. Small sections of about 1 cm^2 were portioned for triplicate ATP analysis. The sections were placed in 1.5 mL microcentrifuge tubes containing 100 µL of phosphate buffer and incubated in a 30° C water bath. At the same time, a tube containing 300 µL of BacTiter-Glo™ Reagent is placed in the water bath, and both tubes are incubated for 3 minutes. Then the reagent is transferred to the tube for 1.5 minutes in the water bath and mixed every 30 seconds. The tube containing the membrane portion and the reagent are then removed, and 200 µL is transferred to a clean tube. Luminescence is measured 30 seconds later on a GloMax™ 20/20 luminometer. Triplicates for each sample were established. Luminescence is measured and then converted to ATP concentration using a calibration curve constructed using rATP (Promega Cat# E6011). Final results are reported on an ATP per area basis by dividing the concentration of the 200 µL sample by the area of the RO portion; units are reported as ng ATP/m^2 RO membrane.

5.3.3.2 Scanning Electron Microscopy

Membrane surfaces were imaged using a FEI XL30 environmental scanning electron microscope (ESEM; FEI Hillsboro, OR) operating under high vacuum between 10 and 20 kV to observe the extent of biological fouling deposited on the RO membrane surface removed from the membrane testing cell and pilot unit. Membrane sections were processed to stabilize biofilm and other fouling deposits prior to being mounted on aluminum SEM stubs and sputter coated with a thin layer of gold and palladium. The procedure was modified from the US Environmental Protection Agency for SEM imaging of biomass on granular activated carbon (GAC) used in filters for drinking water treatment. Other modifications include drying in a desiccator and sputter coating with platinum and palladium instead of gold and palladium.

Sections from the RO membranes were cut using a sterile razor blade, gently rinsed with deionized water for 30 seconds to remove extra debris, and then fixed with 2.5% gluteraldehyde with 4% paraformaldehyde in 0.1 M cacodylate buffer adjusted to pH 7.3. Samples were fixed overnight and washed with cacodylate buffer twice, for 15 minutes each. They were then washed again in deionized water for an additional 15 minutes. After washing, the samples were post-fixed for an additional hour in 1% osmium tetroxide in deionized water, then washed three times for 15 minutes each. After osmium fixation, the samples were dried using a dilution series of ethanol (25, 50, 75, 95, and 100% x2) for 30 minutes each. RO membrane portions were air dried in a chemical fume hood for 1 hour on filter paper, then transferred to a desiccation jar. Prior to imaging, the membrane was mounted on aluminum SEM stubs and sputter coated with platinum and palladium for 30 seconds. Multiple sets were examined to ensure continuity of imaging for the samples.

5.4 Results and Discussion

5.4.1 Pilot Unit Results

The system was set at 13% recovery, and under this constant permeate flow setting, the changes to driving pressure were monitored and further evaluated. Feed pressure ranged from 660 to 720 psig during operation, and pressure of the concentrate (or brine) ranged from 590 to 620 psig. Initial pressure conditions were 660 psig at the feed line and 610 psig at the brine outlet. Differential pressure was monitored from March 26 through April 3, 2013 and increased from 50 to 90 psig during the 9 day operating period (Table 5.3, Figure 5.2). Even though the permeate flow rate was set at 0.317 gpm (457 gpd), specific flux decreased during operation. Permeate flow was normalized for temperature and pressure at each of the data points and then divided by the net driving pressure to determine specific flux. Specific flux decreased from 0.32 to 0.25 gpm, a 22% decrease (Figure 5.2). Salt rejection remained consistent and ranged from 99.6 to 99.8% (data not shown).

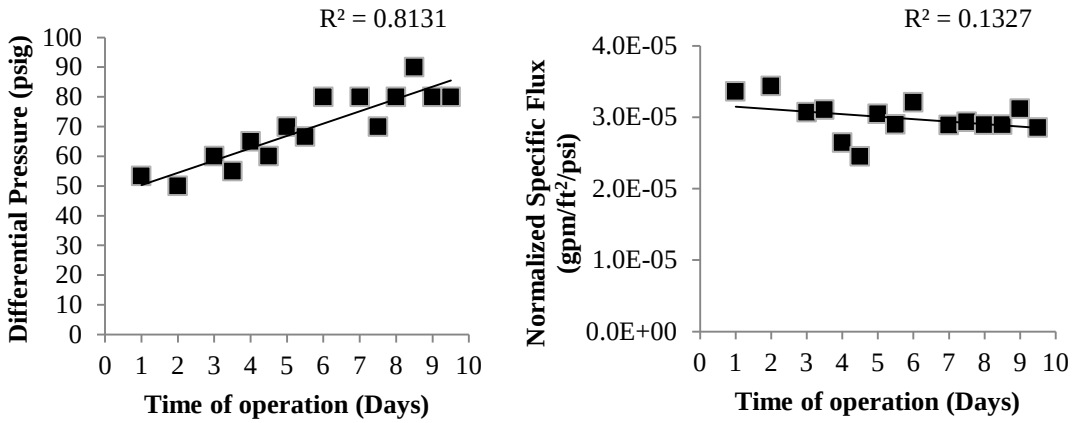

Figure 5.2. Pilot unit RO differential pressure and specific flux over time.

Organic carbon was present in the RO feed throughout the duration of the experiment (Table 5.3). TOC ranged from 3.6 to 4.3 mg/L, and UV_{254} ranged from 0.09 to 0.12 cm^{-1}. SUVA ranged between 2 and 3 L/mg/m, which suggests that the organic matter may be a mixture of algae-derived organic carbon with less humic matter present; the water had already been coagulated, so the low ratio of humic matter was consistent. AOC fluctuated during the first 5 days of operation between 22 and 161 µg/L and decreased throughout the duration of the testing, following a trend exhibited by TOC data. Average AOC was 60 µg/L, and the median was 50 µg/L AOC.

Increases in differential pressure detected between the feed and concentrate suggest that fouling material deposited on the membrane inhibited the flow through the RO membrane. The nature of the fouling that caused the increase was further investigated during the membrane autopsy (Section 5.4.1.2). AOC present in the feed provided a source of nutrients for bacterial growth and proliferation on the membrane. Biological fouling was evident on the membrane surface; it inhibited flow and led to the observed increase in differential pressure. To further evaluate the impact of the different organic carbon measurements, the data were modeled. Statistical significance of the constituents is discussed in the following section.

Table 5.3. Pilot Unit Operational and Organic Carbon Data

Day	Differential Pressure (psi)	Specific Flux ($gpm/ft^2/psi$)	AOC (µg/L)	AOC μ_{max} (hr^{-1})	TOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg/m)
1	53	0.000034	63	0.01	4.29	0.09	2.07
2	50	0.000034	161	0.02	4.09	0.09	2.11
3	60	0.000031	60	0.02	4.01	0.10	2.37
3.5	55	0.000031	68	0.02	3.75	0.08	2.19
4	65	0.000026	57	0.02	3.73	0.09	2.34
4.5	60	0.000025	113	0.01	3.46	0.09	2.66
5	70	0.000030	22	0.03	3.71	0.10	2.72
5.5	67	0.000029	71	0.01	3.79	0.09	2.29
6	80	0.000032	48	0.01	3.67	0.09	2.45
7	80	0.000029	36	0.01	3.50	0.09	2.54
7.5	70	0.000029	43	0.01	3.77	0.12	3.26
8	80	0.000029	45	0.02	3.80	0.10	2.55
8.5	90	0.000029	20	0.01	3.65	ND	ND
9	80	0.000031	50	0.01	3.62	0.09	2.54
9.5	80	0.000029	50	0.01	3.50	0.09	2.63

Notes: AOC=assimilable organic carbon; ND=not detected at method limits; SUVA=specific ultraviolet absorbance; TOC=total organic carbon; UV=ultraviolet.

5.4.1.1 Pilot Unit Data Modeling

Using SPSS analytical software, regression analyses and bivariate correlations were investigated for differential pressure and normalized specific flux. These dependent variables were selected for evaluation of the organic carbon constituents of the RO feed that were correlated to biological fouling. Although recovery was held constant throughout operation, a 22% decline in normalized specific flux occurred (Figure 5.2). Predictor variables were AOC, TOC, SUVA, and UV_{254}, listed by significance in Table 5.4. The dependent variables (differential pressure and normalized specific flux) were also analyzed for correlation and significance to the day of operation.

The correlation between differential pressure and operating day was 0.90 ($p < 0.01$), which is consistent with the trends observed. In other words, differential pressure showed a positive increase over the duration of the testing. For normalized specific flux, the correlation indicated that a decrease occurred during operation (r = - 0.41), which was also determined by the calculations, which showed a 22% decrease. Bivariate correlations indicated that AOC was more significant ($p < 0.01$) than TOC ($p < 0.05$) for predicting differential pressure changes. Correlations between differential pressure with AOC and TOC were negative; AOC and TOC decreased over the duration of the test (Table 5.3). Plots of the predictor variables showing linear regression trends and coefficients of correlation (R^2) are presented in Figure 5.3.

Conclusions drawn from this data set would suggest that AOC measured in the RO membrane feed has a statistically significant impact on changes to differential pressure of the RO. Similar to the previous results reported in Section 2.2.3 for TBSDP water quality monitoring, AOC showed no significant relationship with UV_{254} (r = -0.36, p = 0.20) or TOC (r = 0.32, p = 0.24). Although TOC and UV_{254} were correlated at TBSDP during the previous monitoring, there was no relationship between these parameters in the pilot testing reported here (r = -0.06, p = 0.84).

Given that TOC and AOC both had a significant relationship with differential pressure, a regression model was determined for these parameters. By incorporating TOC and AOC into a model, both AOC and TOC were significant predictor variables for differential pressure (p = 0.001, $F(2,12)$ = 12.83, adjusted R^2 = 0.628). UV_{254} was not a significant predictor in the regression model. Given the consistent evidence for AOC as a significant predictor of operational impacts from biological fouling, it is important that utilities incorporate this evaluation into their monitoring plan. In some cases TOC, in addition to AOC, would be useful for understanding organic impacts on fouling.

Table 5.4. Pilot Unit Correlation and Significance of Predictor Variables

	Differential Pressure		Normalized Specific Flux	
	Pearson Correlation	***p* (2-tailed)**	**Pearson Correlation**	***p* (2-tailed)**
AOC	-0.71	<0.01	0.19	0.488
TOC	-0.63	0.012	0.73	<0.01
SUVA	0.52	0.059	- 0.51	0.065
UV_{254}	0.26	0.380	- 0.19	0.514
Op. Day	0.90	<0.01	- 0.41	0.133

Notes: n=15; AOC=assimilable organic carbon; Op. Day=day of operation; SUVA=specific ultraviolet absorbance; TOC=total organic carbon; UV=ultraviolet.

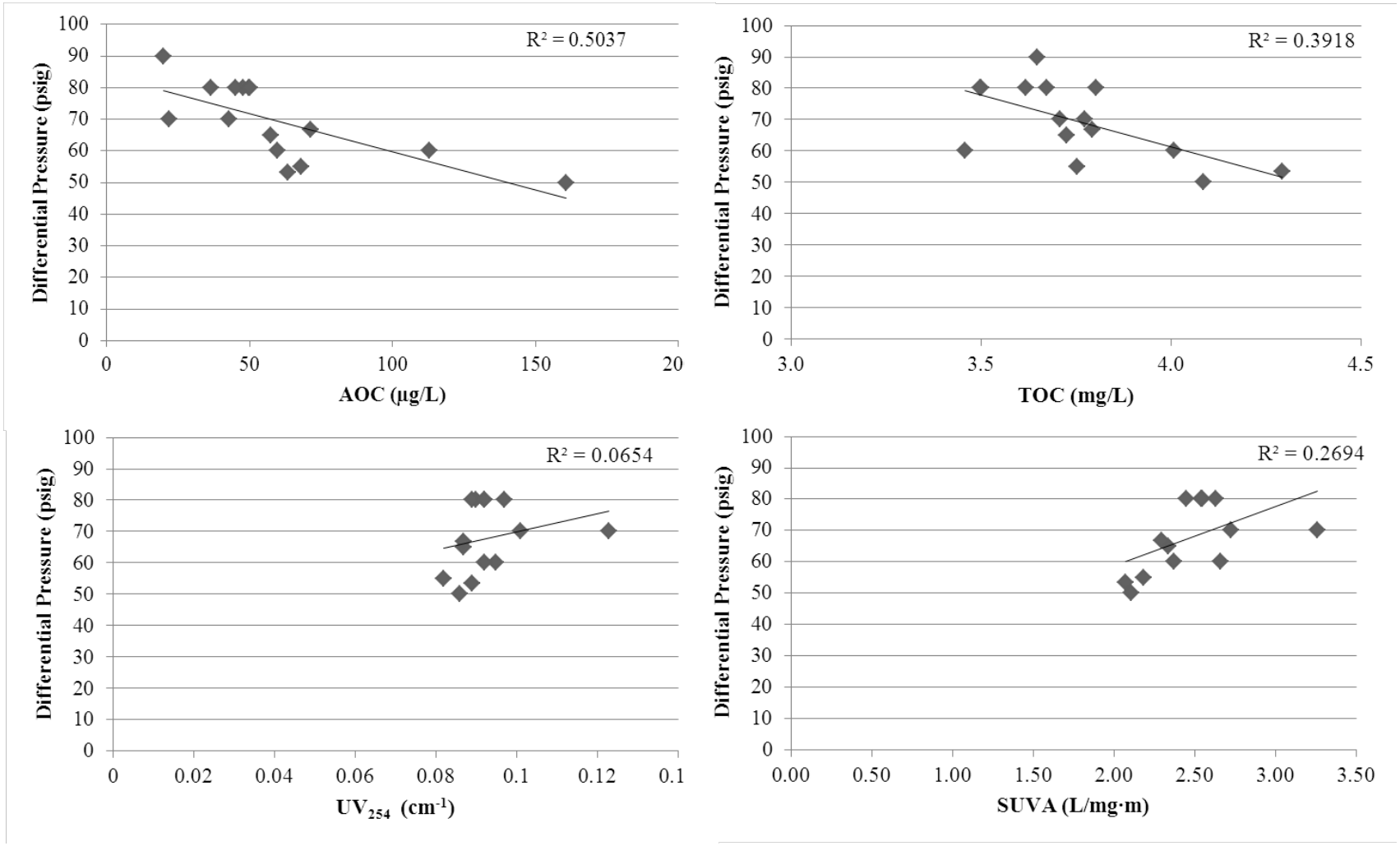

Figure 5.3. Pilot unit differential pressure and organic carbon data regression plots.

5.4.1.2 Membrane Examination: Visual Inspection, ATP, and SEM

The membrane was removed on April 6, 2013 and sent to Delran, NJ for an autopsy. Photos were taken of the membrane prior to dissection (Figure 5.4). A circular saw was used to remove the end caps and split the fiberglass housing. The cross flow direction was noted to track the feed, middle, and brine regions of the element. It was carefully unrolled, and membrane swatches were removed from the three regions using a sterilized razor and portioned for ATP analyses and SEM.

Visual inspection indicated brownish deposits on the membrane and the feed spacer. The deposited material was slimy in texture and did not appear to be hard scale buildup. The deposition appeared to be organic or biological. The product collector did not show any discoloration or buildup. When the feed spacer was separated from the membrane, the pattern was evident in the deposited material (Figure 5.4).

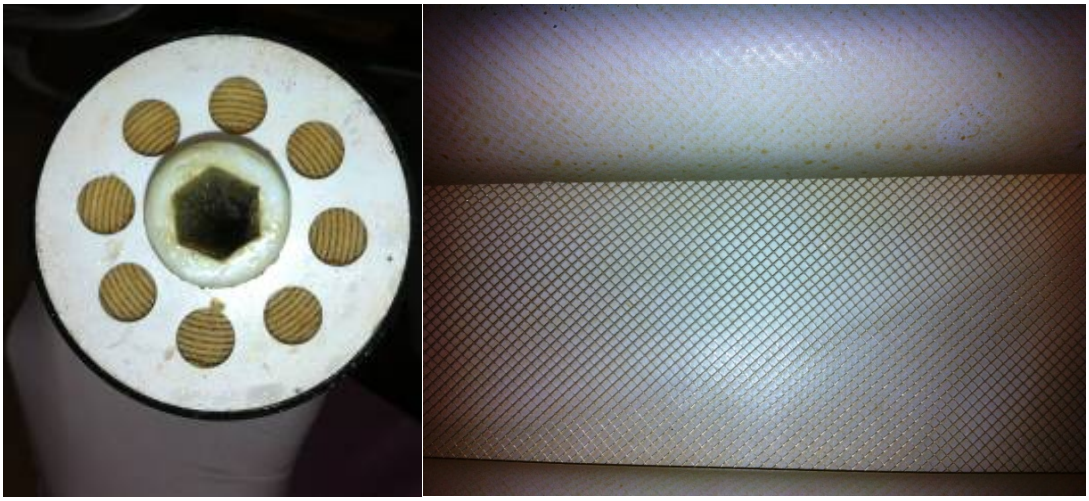

Figure 5.4. Pilot RO membrane after operation.

Note: The spiral-wound membrane element opened during autopsy had evidence of biological fouling**.**

Table 5.5. Pilot RO Membrane ATP Results

Location	Replicate	Area (cm^2)	Area (m^2)	Luminescence	ng ATP/m^2 RO
Feed	1	1.40	0.000140	720161	1.9E+03
	2	1.40	0.000140	763553	2.1E+03
	3	1.08	0.000108	864099	3.1E+03
	mean			782604	2.4E+03
	SD			73835	6.4E+02
Middle	1	1.56	0.000156	1848179	5.3E+03
	2	0.80	0.000080	962957	4.8E+03
	3	0.60	0.000060	941638	6.2E+03
	mean			1250924	5.4E+03
	SD			517347	7.3E+02
Brine	1	0.36	0.000036	493725	4.8E+03
	2	0.91	0.000091	881294	3.8E+03
	3	0.84	0.000084	799109	3.7E+03
	mean			724709	4.1E+03
	SD			204215	6.5E+02

Notes: ATP=; RO=reverse osmosis; SD=standard deviation of three replicates.

ATP analysis of the membrane surface was conducted for three replicates from each location at the feed, middle, and brine areas on the membrane. ATP ranged from 1900 to 6200 ng ATP/m^2 on the RO membrane surfaces. The lowest ATP was measured from the feed sections (Table 5.5).

There was a slimy fouling layer on the membrane and spacer observed during the visual inspection. Chemical fixation was conducted on the membranes to prepare the sections for imaging using SEM. By fixing and dehydrating the sample, evidence of biological fouling and bacterial deposition was preserved on the membrane. Fouling was examined on the membrane and feed spacers in SEM images. Bacteria approximately 1 µm in length were evident on both the feed spacer and the membrane (Figures 5.5 and 5.6). The biofilms did not cover the entire imaged areas but were evident in patchworks in all samples.

Images from the membrane spacer on the brine side and the RO membrane had fouling layers and diatom fragments as well (Figure 5.7). The fouling layers had an accumulation of bacterial growth byproducts surrounding the bacteria, known as extracellular polymeric substances (EPS). Bacteria (as well as other cellular organisms) and EPS form the biofilm on the surface of the membrane. Based on the inspection and imaging of the membrane and ATP analysis, the results suggest that biological growth occurred on the membrane. The relatively short operation of the pilot system still provided sufficient biological growth substrate for proliferation as well as an observed decline in permeate flow and increase in differential pressure. By the fifth day of operation, sufficient fouling had occurred to maximize the differential pressure to a constant 80 psi for the duration of the testing.

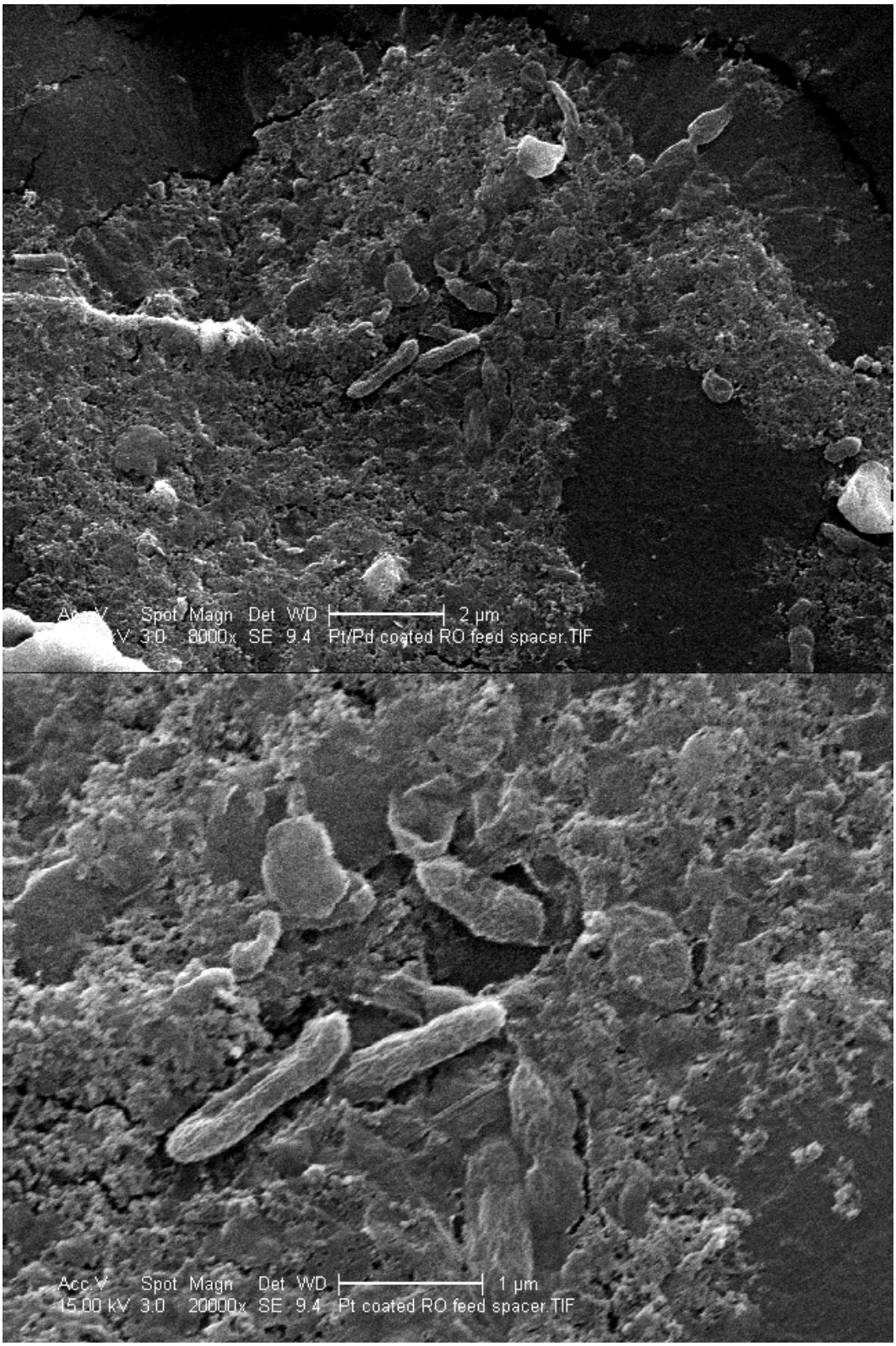

Figure 5.5. SEM image of pilot RO membrane feed spacer at 8000 and 20,000X magnification.

Notes: Bacterial rods approximately 1 µm were detected within a biofilm matrix.

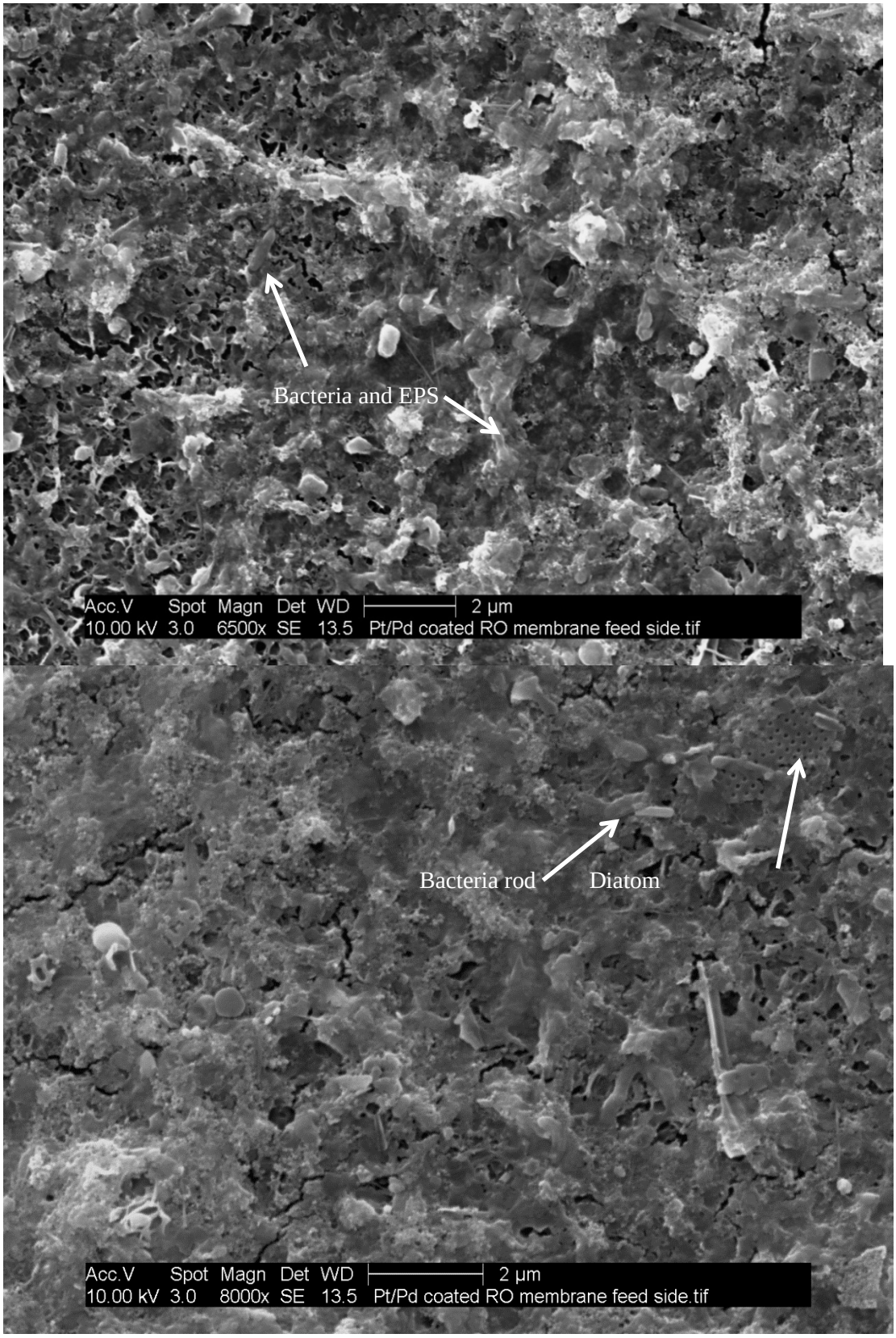

Figure 5.6. SEM image of pilot RO membrane from two different locations on the feed side.

Notes: Biofilm contains bacteria, EPS, and diatoms.

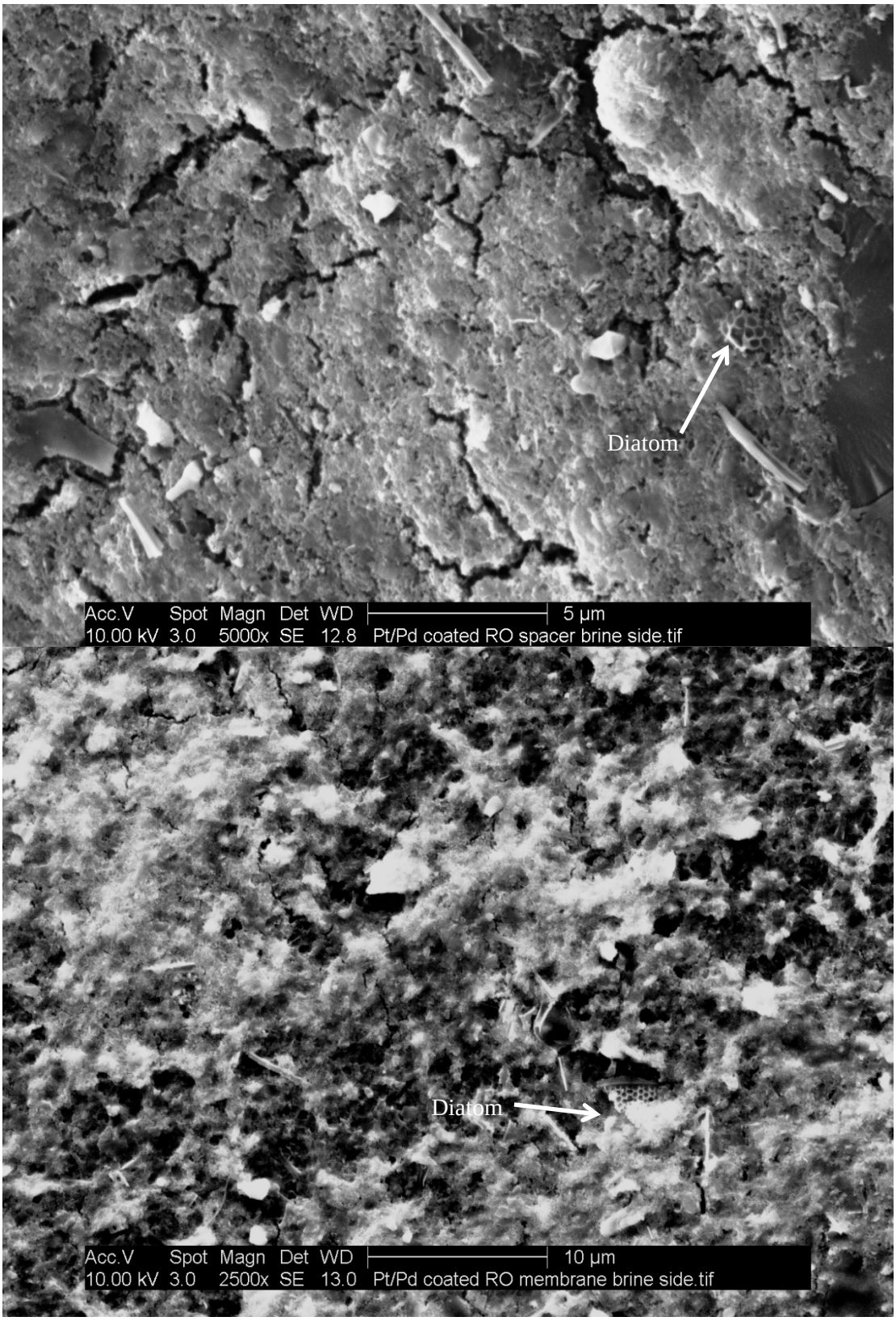

Figure 5.7. SEM image of pilot RO membrane feed spacer (top) and brine side RO membrane (bottom) with fouling layer and diatoms.

5.4.2 Membrane Test Cell Results

Experiments were conducted using a once-through mode without recirculation to most closely mimic RO feed conditions and determine whether elevated AOC would be indicative of increased fouling potential. To achieve this objective, changes to permeate flux were compared in two experiments under similar operational conditions and constant pressure. RO feed water from TBSDP was used for the first baseline test. In a second test, acetate was injected to amend the RO feed with 1000 µg/L acetate carbon as an additional AOC nutrient source. Comparisons of permeate flux and autopsied membrane sections were evaluated to determine the extent of fouling from two different AOC feeds.

5.4.2.1 Permeate Flux Results from the Membrane Test Cell

The permeate flux (J) from the baseline test was compared to the test from the elevated AOC experiment (Figure 5.8). Flux was calculated by dividing permeate flow (Lpm) by the membrane surface area (0.0042 m^2). The initial flux (J_0) of the membrane was 20 $L/m^2/h$; average normalized flux was 97±5% during the baseline experiment and 76±7% during the experiment in which seawater contained 1000 µg/L AOC (as acetate carbon). With comparable nutrient levels and operational conditions in the two experiments, AOC was the targeted variable to evaluate its impact on flux. Biofilm growth and deposition occurred during these experiments and resulted in 24% flux decline in the AOC amended test compared to just 3% decline in the baseline test. SEM images confirmed that the membrane from the AOC amended test having greater flux decline showed evidence of bacterial, algal, and biofilm deposits throughout the membrane sections (Figures 5.13–5.16).

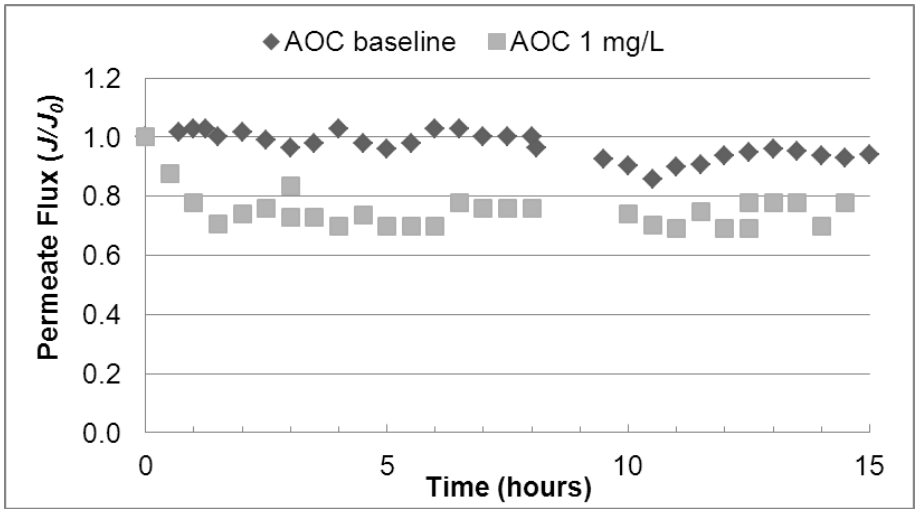

Figure 5.8. Normalized permeate flux from the membrane test cell using TBSDP RO feed.

Notes: Pretreated TBSDP RO feed contained 30 µg/L AOC (baseline). Separate test used RO feed that was amended with 1000 µg/L acetate.

Figure 5.9. RO membrane from the membrane test cell (left: baseline feed test; right: acetate amended feed).

5.4.2.2 Membrane Autopsy: Visual Inspection and SEM

Visual inspection of the membranes revealed the compression marking from the permeate carrier plate in the center of the element (Figure 5.9). Sparse brownish particulate was visible across the active areas of the membrane. In the membrane from the test with the acetate amended feed (Figure 5.9, right) membrane wrinkling occurred that appeared to follow the flow direction of the feed across the membrane (horizontally from right to left).

Images of the membrane were taken of the feed, middle, and brine sides according to the orientation in the test cell. SEM was useful for evaluating the morphology of the membrane surface after operation. Compared to the virgin membrane cut from a section beyond the active area in the test cell (Figure 5.10), the images of membrane from the baseline tests (Figures 5.11–5.13) were similar, and nearly no occurrence of fouling material was detected on the feed and middle sections. On the sections taken from the brine side of the membrane (Figure 5.13), there were areas of compression on the membrane and singular 2 μm rods that were either bacteria or inorganic deposit.

In the SEM images taken of the membrane with acetate amendment, there was evidence of organic or biological fouling. The feed side had numerous areas of biofilm and bacterial rods within a biofilm and inorganic deposits (Figure 5.14). Images from the middle of the membrane mostly depicted slight coverage of fouling material; the membrane structure was still visible underneath (Figure 5.15), and some locations had more extensive deposits and areas of fouling and singular organisms (not shown). Images from the brine side of the membrane had less fouling, but there was some inorganic scaling and even a singular diatom with biofilm deposited near the upper left of the structure (Figure 5.16). Overall, the membrane from the AOC amended feed had more areas of fouling material covering the membrane compared to the membrane with the unamended baseline RO feed.

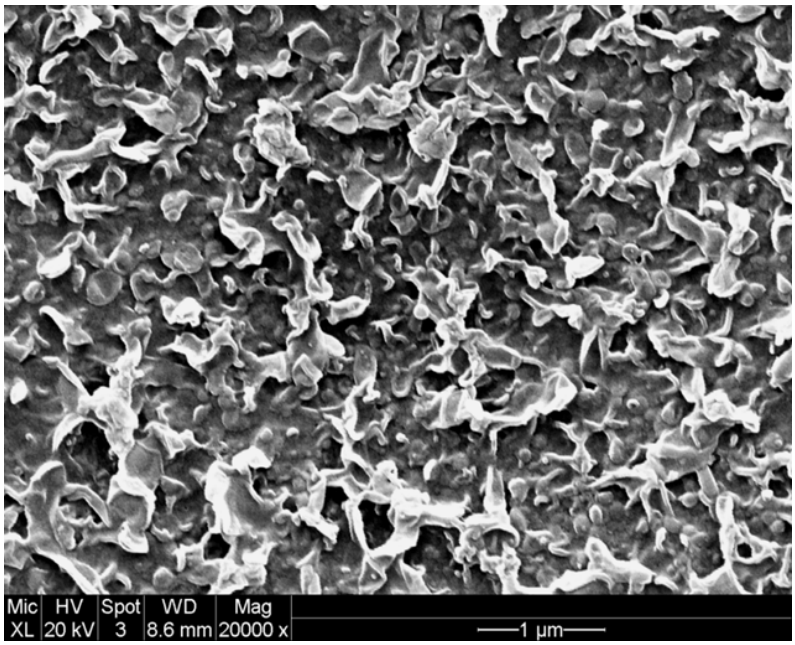

Figure 5.10. SEM image of virgin membrane at 20,000X magnification.

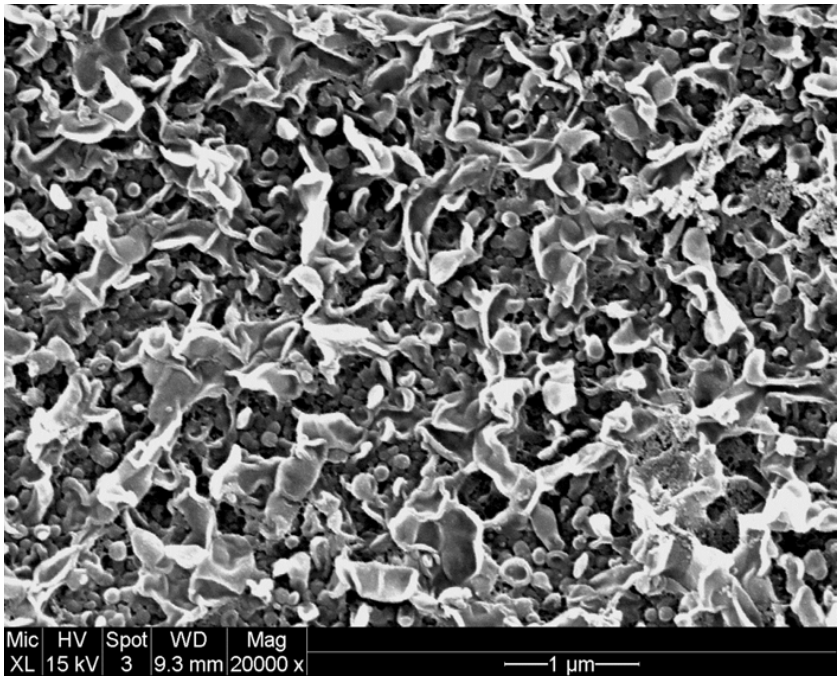

Figure 5.11. SEM image of baseline test at 20,000X magnification: Feed section.

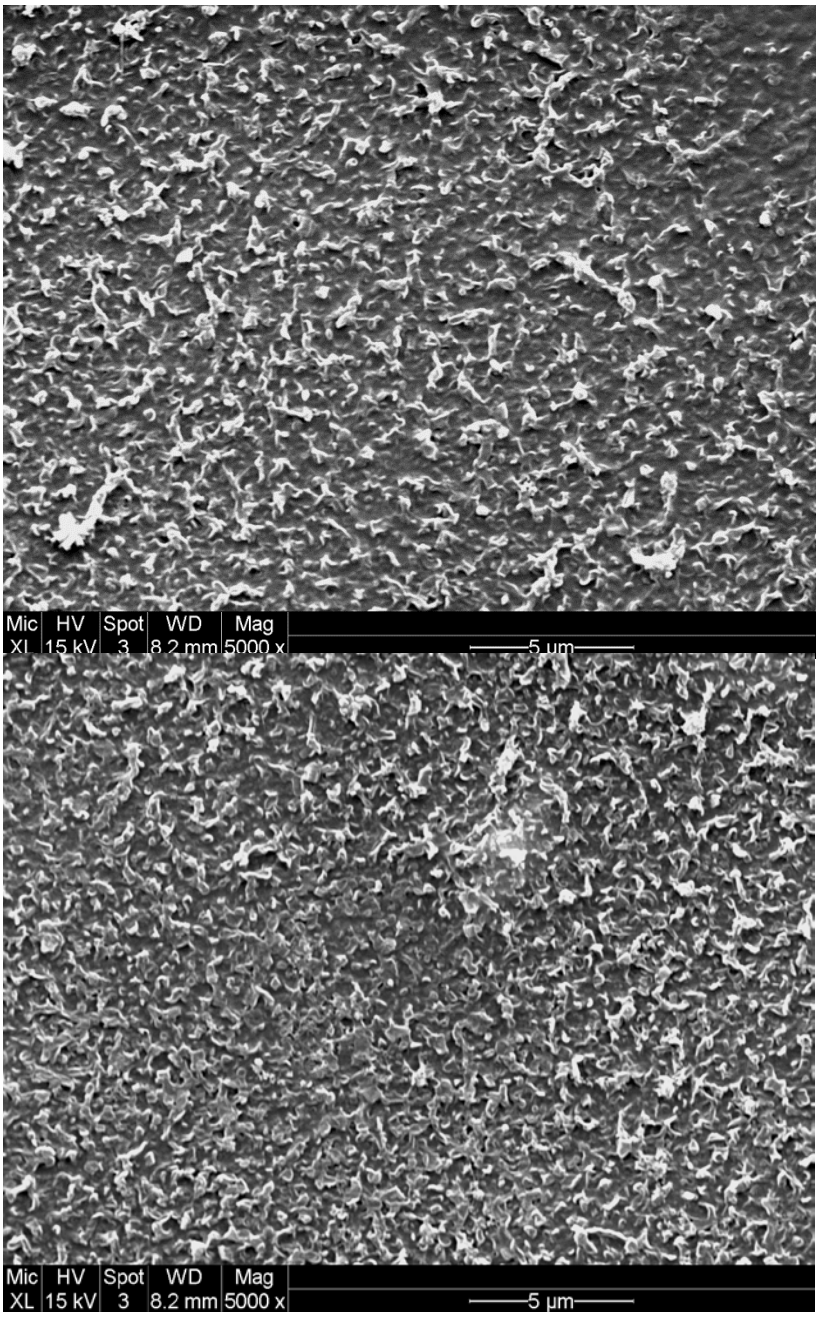

Figure 5.12. SEM images from baseline test at 5000X magnification: Middle section of the RO membrane that is mostly intact without major occurrence of deposited fouling material.

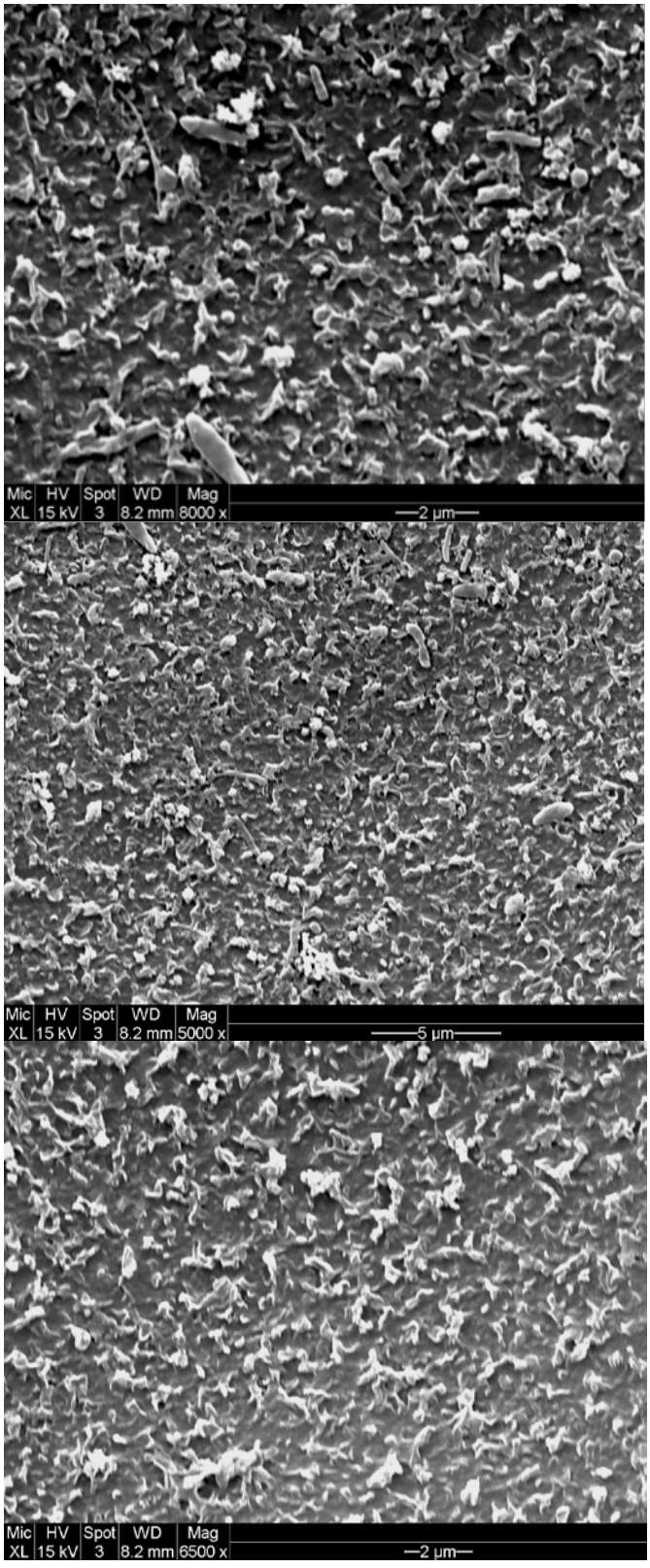

Figure 5.13. SEM images from baseline test: Brine sections of RO membrane are visible.

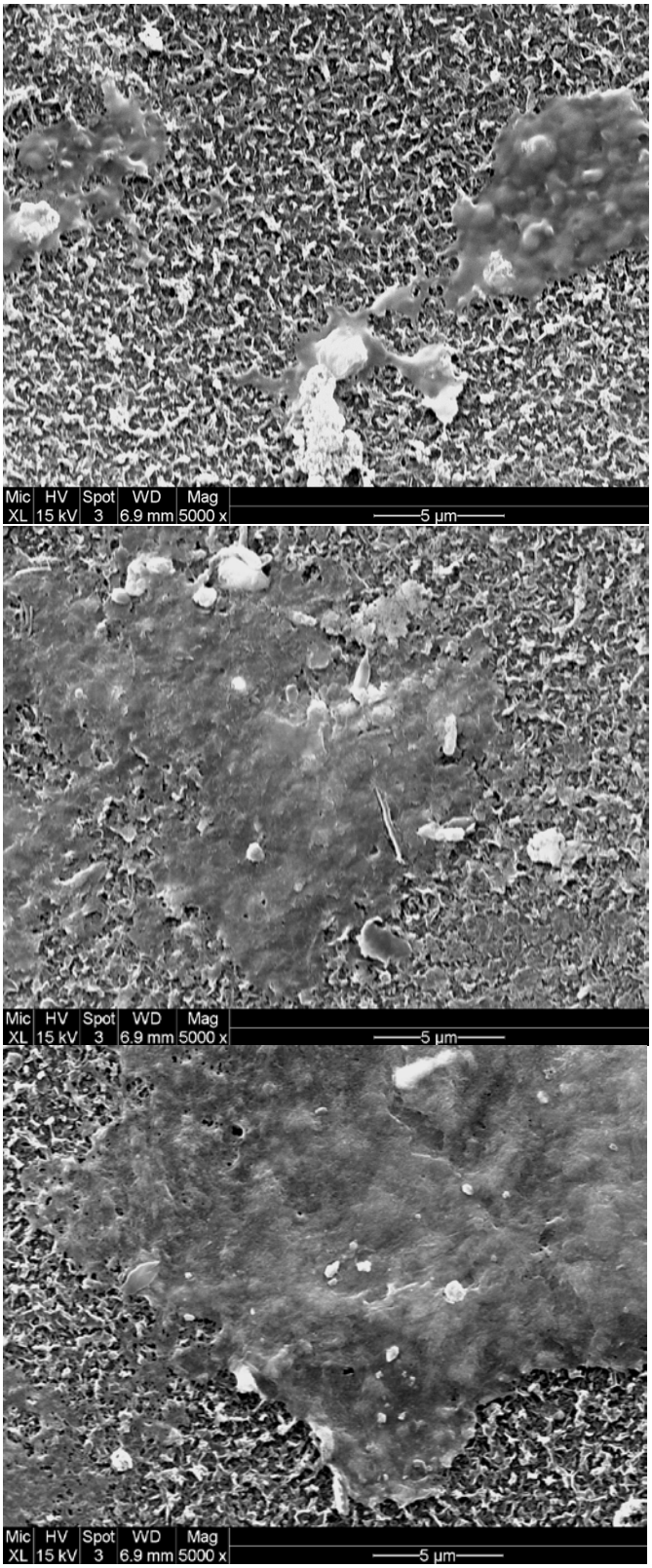

Figure 5.14. SEM images from AOC amended test at 5000X magnification: Feed sections of the RO membrane are largely covered with biofilm.

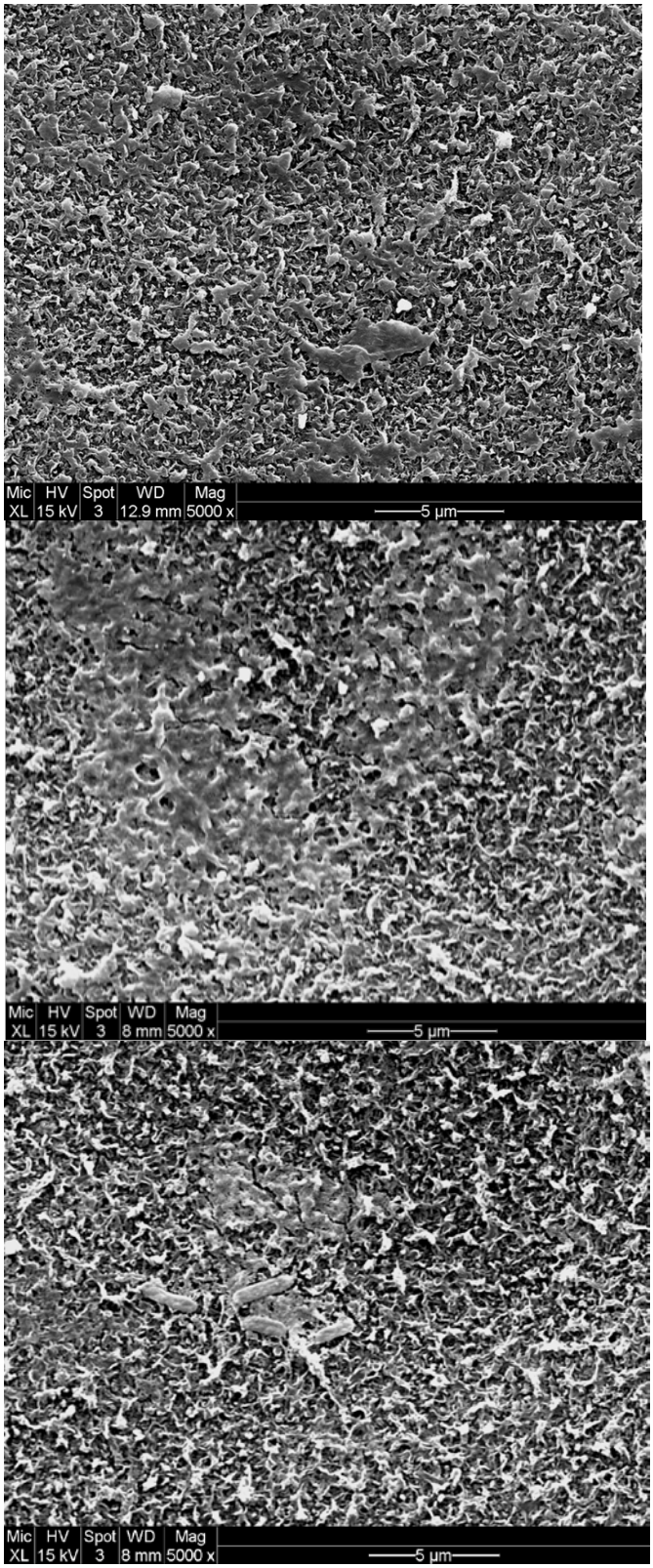

Figure 5.15. SEM images from AOC amended test at 5000X magnification: Middle sections of the RO membrane are intermittently covered with biofilm, and bacterial rods are present.

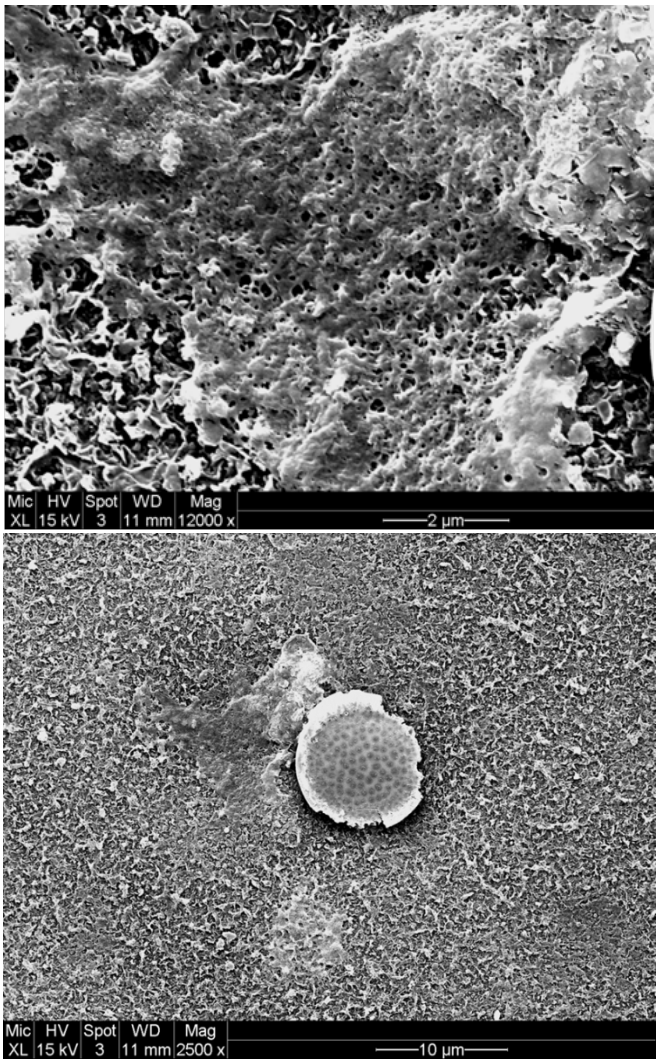

Figure 5.16. SEM images from AOC amended test at 12,000X and 2500X magnification: Brine sections of the RO membrane are intermittently covered with fouling; diatom and surrounding fouling.

5.4.2.3 Nutrient Composition in the RO Feed

TOC concentrations differed by 1.1 mg/L in the two experiments on account of the amendment of acetate carbon (1000 µg/L was delivered through injection of a concentrated feed). The baseline RO feed had 30 µg/L AOC versus 997 µg/L AOC in the amended feed. SUVA was near 1.4 L/mg/m, which is lower than the reported values in the previous sections because of pretreatment coagulation that removed humic material. Phosphate and nitrogen were present in sufficient supply and varied slightly between the two experiments. Phosphate was 0.16 and 0.13 mg/L in the baseline and amended AOC tests, respectively. Nitrogen was reported as the sum of nitrite, nitrate, and ammonia. In both tests, nitrite was 0.001 mg/L NO_2-N, and nitrate was 0.3 mg/L NO_3-N. Ammonia was 0.07 mg/L NH_3-N in the baseline feed and 0.4 mg/L as N in the amended feed. The limiting nutrient in the baseline test was carbon, as determined by the molar carbon:nitrogen:phosphate (C:N:P) nutrient ratio of 69:5:1. In the AOC amended feed, nutrients were present in sufficient supply and had a C:N:P ratio of 107:11:1.

Nutrient balancing has been investigated as a way to control membrane fouling caused by biological growth and the production of EPS, which is generated when bacteria are present in a nutrient-limited environment specifically with reference to phosphate. The bacteria excrete a nutrient reserve to protect continued proliferation and adhesion to the surface. In conditions where the nutrients are balanced, bacteria are able to proliferate freely and do not produce EPS in the same amounts. The lower carbon ratio in the baseline test in conjunction with evidence from the SEM images of minimal bacterial attachment suggest that biofilm development did not occur to the same extent as in the amended feed, and therefore the difference in carbon (i.e., AOC) between the baseline and amended feed was critical to changes in substrate loading available for bacterial growth on the membrane.

When the test cell was operated under constant pressure, the membrane permeate flux decreased when the RO feed contained 1000 µg/L of AOC and a nutrient ratio of 107:11:1 C:N:P. In that experiment, SEM imaging showed a higher distribution and occurrence of fouling and bacterial growth compared to the membrane without acetate amendment. Elevated AOC affected operation by reducing flux as a result of deposition and proliferation of bacteria into a biofilm, as seen on feed and middle sections of the membrane. SWRO flux decrease typically is affected by poor water quality and deposits on the membrane or in the membrane pores (fouling). Compared to a water source fully pretreated both with a minimum and maximum AOC content under similar operating conditions, the permeate flux decreased by more than 20% as a result of fouling of the membrane.

There are numerous opportunities in which AOC could increase in RO feed water. AOC increases occur from oxidation of organic matter, increased chemical dosing, and water quality fluctuations such as algal blooms. In full-scale applications, RO permeate flux decline would be exacerbated during those water quality conditions in which AOC is elevated. Additional testing would be needed to identify the minimum AOC level and appropriate nutrient ratio for the control of biofilm growth and bacterial proliferation. From these results, a ratio of 72:6:1 and AOC 30 µg/L were effective for reducing bacterial adhesion and biofilm proliferation. Determining the critical level of AOC in which bacterial proliferation is minimized under normal operating conditions would be an appropriate step for RO treatment plants. Alternative treatment or maintenance strategies could be addressed to avoid flux decline and other operational issues that occur as a result of biological growth.

Chapter 6

Summary

The AOC test proved to be a useful tool to monitor the impact of BOM on biological fouling. The desalination industry previously lacked a method for seawater monitoring, and the development of the *V. harveyi* bioluminescence-based AOC test supplied a necessary demand. *V. harveyi* is a naturally occurring, bioluminescent marine organism that is nutritionally versatile. Building upon an established approach for determining the amount of AOC and biofouling potential, the *V. harveyi* test expands application of measuring AOC in high salinity water, such as seawater. The bioluminescent properties of the organism provide an additional advantage for measuring growth on sample BOM by using a sensitive, automated luminometer, which has a 96-well microtiter plate format. The instrumentation enables high throughput and low cost replicate analyses. Compared to traditional biofouling potential tests, the *V. harveyi* AOC test has a very short turnaround time of 2 to 3 days for most samples. The AOC test was developed to minimize labor and consumable costs and increase sample turnaround and is an important parameter for predicting water quality changes and biofouling impacts from RO pretreatment approaches in pilot- and full-scale seawater applications.

Water quality and operational parameters in full-scale SWRO plants and at the bench and pilot scales were monitored along with chemical dosing records and other common water quality parameters including TOC and UV_{254}. Full-scale SWRO treatment plants generally had poor or inconsistent TOC removal. AOC was present in the RO feed at all locations between 10 and 180 µg/L. In most cases, neither TOC nor UV_{254} had a statistically significant relationship to AOC. Increases in RO membrane differential pressure and decreases in specific flux were two operational changes most consistent with the effects of fouling on the RO membranes. These operational changes were further investigated at the bench scale using constant driving pressure to monitor changes to specific flux and also at the pilot scale under constant flux to monitor changes to differential pressure. In both instances, AOC was a statistically significant variable for increased differential pressure and decreased specific flux to the RO membrane. Membranes in those tests were autopsied, and biological fouling was evident. AOC remained as the primary statistically significant parameter for predicting biological fouling.

Changes to organic carbon in laboratory-generated humic acid seawater matrices and environmental samples changed with the application of pretreatment chemicals. Oxidants (chlorine, chlorine dioxide, and ozone) were tested for their impact on AOC formation in the water. Citric acid used for cleaning carbonate scales, SBS used for reducing the ORP of seawater, and numerous antiscalants used for inhibiting inorganic fouling from precipitating salts were investigated to identify sources of BOM and AOC that could exacerbate biological fouling in seawater RO plants. These chemicals all increased AOC and therefore should be carefully considered in SWRO operations for their biofouling potential.

6.1 Plant Performance

A complete data set was evaluated for each of the seven trains at TBSDP, and Train 4 had the greatest percent decrease in specific flux for the investigated period (53% from startup in

August until a cleaning in November 2012). Differential pressure increased during this period as well. Predictor variables were modeled to determine the impact of water quality on differential pressure and specific flux; SDI was not a significant predictor despite routine monitoring at the plant. The addition of SBS increased AOC and established conditions indicative of biological fouling. SBS dosing increases AOC, which was correlated to changes in differential pressure and specific flux.

The pretreatment processes examined were typically not effective for removal of organic carbon. The removal of TOC by the pretreatment process at TBSDP ranged between 3 and 6%, and UV_{254} was not reduced by more than 16% to a minimum of 0.11 cm^{-1}. TOC was greater than 5 mg/L in the RO feed (around 5–6 mg/L at the intake). AOC within the TBSDP pretreatment steps was generally low in the diatomaceous earth filtrate but increased in the postcartridge filter sampling point (i.e., RO feed). Chemical addition of SBS accounted for the increase in AOC. AOC in the RO feed led to biological growth and subsequent RO membrane fouling; at TBSDP, fouling was observed as elevated differential pressure in November 2012 and a decrease in specific flux over the time period investigated.

During the collection periods at the WBMWD desalination demonstration plant, membrane changes and hybrid configurations were being evaluated. The changing operations challenged meaningful interpretations of the impact on differential pressure. The plant had reported challenges in the past with biological fouling of the RO membranes. From the data modeling, decreased specific flux had the strongest correlation to AOC levels at the plant. Other observations from plant operations indicated that chemical dosing accounted for higher AOC levels upstream of the RO membranes, even when the seawater at the intake had the lowest organic carbon content compared to the other sampling events. The trends were comparable by observing increased AOC effected from cleaning agent residuals and the addition of SBS; the increased biodegradable organic carbon was not observed in the TOC measurement alone.

Operational data from the Al Zawrah plant were limited because the staff was not using normalization software for record keeping. The absence of RO operating information limited the evaluation of water quality impacts on the RO system, but changes in differential pressure at the cartridge filter provided information about their condition and evidence that biological growth may have occurred. The data showed a very strong positive correlation for differential pressure of the cartridge filters and AOC in the RO feed ($r=0.984$, $p<0.01$; $n=48$). UV_{254} also had a strong relationship to the data cartridge filter data. This plant was the only facility of the three in this project that had potential for AOC removal through DMF; however, AOC removal across the filters was not consistent. If AOC is monitored and pretreatment is optimized for the removal of organic carbon, biological fouling on both cartridge filters and ultimately on RO membranes could be minimized.

Poor organic carbon removal and inconsistent operations are widespread challenges in SWRO. The positive and strong relationships determined from investigating AOC as a predictor variable for biological growth confirms the presence of biodegradable organic carbon and the resulting adverse impact on operations. Based on the results from TBSDP, a threshold between 30 and 60 µg/L AOC would increase the potential for biofouling. Other SWRO plants should evaluate their systems to identify impacts of chemical addition on the presence of AOC and determine the thresholds at which the system would experience increased biofouling potential and operational changes.

6.2 Role of Oxidants and Chemical Addition

Laboratory-generated seawater solutions containing humic acid and environmental seawater were tested in a series of bench-scale oxidation tests using chlorine, chlorine dioxide, and ozone to observe the impacts of these oxidants on BOM formation. AOC was formed as a byproduct of reactions with these disinfectants commonly used in water treatment. In many of the treatments, the biodegradability of the water increased; in full-scale applications, these effects would generate conditions amenable to bacterial proliferation and subsequent biological fouling. AOC was increased by 70% in seawater with 1 mg/L humic acid and a chlorine dose of 0.5 mg/L Cl_2; changes to UV_{254} and TOC were minimal (2 and -4%, respectively). Higher concentrations of humic acid did not produce additional AOC, most likely because of the high ionic strength of the seawater matrix and internal hydrophobic molecular interactions of humic acid that have been reported to inhibit expansion of the molecule.

Implications from these results suggest that even plants with low TOC (1 mg/L) would be vulnerable to reaction with the oxidant and subsequent increased RO feed biodegradability. Chlorine dioxide reacts slowly with humic acid and did not significantly change UV_{254}, TOC, or AOC in testing with a 4 hour contact time. Longer contact times or greater chlorine dioxide doses may have a different effect. The reactivity between oxidants and environmental seawater sources varied. Except for the intake seawater from WBMWD, UV_{254} decreased or remained unchanged in all the water tested. Decreases in UV_{254} are usually from the breakdown of aromatic and double carbon bonds in humic structures. UV_{254} increased in the seawater collected from West Basin when chlorine or chlorine dioxide was applied.

Increases are not as clearly understood but may have resulted from the breakdown or lysis of microbial components (e.g., algae) that released intracellular organic material. When the AOC and therefore inherent biodegradability of the seawater increased after treatment, TOC did not follow the same trend. In test solutions with either chlorine or chlorine dioxide that exhibited increases in UV_{254} (West Basin) and AOC (Tampa Bay), TOC changes averaged 3 and -2%, respectively. TOC does not provide insight into the changes to the biodegradability of the water. Unfortunately, TOC is often the only organic carbon parameter used in SWRO water quality monitoring, although it is not an informative tool for the plant operators to predict biofouling potential.

Chemical impurities in treatment chemicals were shown to increase AOC concentrations (e.g., SBS increased AOC at a baseline level of 58 µg/L for 1 mg/L of SBS) that were otherwise undetected by UV_{254} and TOC measurements. Antiscalants increase organic carbon concentration linearly by dosing the neat chemical. Antiscalants often contain a bacteriostat to inhibit bacterial growth during storage. If the solution is underdosed, the biocide will be diluted, and inherent nutrients or chemical impurities have been shown to increase AOC during bench-scale testing. Phosphate and AOC are byproducts of reactions between antiscalants and chlorine. The byproducts could lead to biological fouling on the RO membrane because of the increased assimilable nutrient loading and potentially decrease effectiveness of the antiscalant. Better operational practices that include removing the chlorine residual prior to dosing the antiscalant would alleviate the adverse effect of AOC byproducts.

6.3 Modeling AOC in Bench and Pilot Studies

Changes to differential pressure were monitored in pretreated TBSDP water under constant flux conditions in a pilot unit. Increased differential pressure was associated with RO membrane biological fouling when the median AOC concentration naturally present in TBSDP was 50 µg/L and permeate flux was constant. Even with a constant setting, flux decline occurred from biological fouling, and membrane pores were blocked by biofilm growth. AOC was more significant for predicting changes to differential pressure than TOC. A regression model with AOC and TOC combined was significant for predicting differential pressure; however, UV_{254} was not a significant predictor variable.

Using a cross flow RO membrane test cell, RO feed that contained 1000 µg/L acetate carbon was used to evaluate whether increased AOC loading would affect RO membrane fouling as compared to the 30 µg/L AOC baseline. The extreme difference in AOC concentrations was used to increase the fouling occurrence and monitor the effect in a shorter time period. Permeate flux decline was associated with RO membrane biological fouling when AOC was elevated and other conditions were constant, including operating pressure and water quality. Flux decline under the same operational conditions was greater in the test where the RO feed contained more AOC from additional biofilm formation and organic fouling. Biofilm and bacterial deposits were apparent from the SEM imaging. Fouling was detected on more portions of the RO membrane when AOC was higher.

6.4 Conclusions and Recommendations

SWRO plant manager would benefit from investigating more efficient techniques for the removal of organic carbon during treatment. TOC removal efficiency is typically very poor, and the pretreatment impacts on AOC levels should be understood and controlled in SWRO plants that have biological fouling problems. Certain pretreatment chemicals were shown to increase AOC if present along with a disinfectant residual. In addition to effective organic carbon removal, minor pretreatment configurations may help control AOC levels in the RO feed. SWRO plants should investigate the sources of AOC during pretreatment. In some cases, water quality at the intake may affect the AOC level if there is a red tide or an algal bloom event; however, this report has shown that antiscalant, membrane cleaning, and dechlorinating agents could be wholly responsible for increasing AOC at the RO feed. Monitoring chemical supplies for impurities is one option for AOC control. Changing the configuration to reduce ORP before addition of antiscalant would reduce the contact time between the disinfectant and the antiscalant, which may break Down the parent compound and produce AOC as a byproduct.

Pretreatment applications have largely been focused on physical separation. Membrane pretreatment, for example, using MF or UF membranes can be effective for particulate removal and even some removal of TOC, but low molecular weight organic molecules can readily pass through those membranes. These molecules typically compose the AOC fraction of water. Therefore, membrane pretreatment systems would still be vulnerable to biological fouling on the RO membranes unless the AOC fraction was controlled. Further development of biological treatment to reduce nutrients in RO feed water would be valuable.

Evaluating pretreatment impacts using new methods such as the bioluminescent AOC test will facilitate control measures to optimize chemical addition and achieve reduced biodegradable nutrient loading and fouling rates. Additional focus on information collection for data modeling applications and real-time monitoring is recommended. Other quantitative

and qualitative techniques for monitoring water quality and microbiology of seawater intakes and during pretreatment will aid current and future SWRO applications. Additional SWRO research and development are crucial for the efficiency of this growing industry.

Biological filtration and other pretreatment management options should be investigated for removal of biodegradable byproducts to minimize AOC and subsequent biological fouling. AOC was shown to be a significant predictor variable for biological fouling impacts on increased differential pressure or permeate flux decline in bench-, pilot-, and full-scale research from this SWRO study. SWRO treatment plant personnel interested in minimizing these adverse operational effects should, at a minimum, consider the following scenarios for understanding and mitigating biofouling occurrence on the RO membranes:

- Measuring the water quality at the intake and the RO feed would be a first step in determining the effectiveness of pretreatment on AOC removal.
- Systems that use oxidants (e.g., hypochlorite, chlorine dioxide) should monitor AOC after typical and extreme dosing scenarios.
- Systems that use antiscalants should reduce ORP first (e.g., with SBS/sodium metabisulfite) before it is added to minimize antiscalant loss and formation of AOC. SBS solutions may also contain impurities that increase AOC, so dosing should be carefully considered.
- Chemical dosing should be evaluated through bench-scale tests to minimize AOC, maximize desired outcome, and optimize the treatment process for better operational control.
- Fluctuating water quality at the intake should be tracked to correlate sources of AOC increases (algae, increased organic loading, rain events) so that operations may be adjusted to account for changes in AOC and minimize biofouling potential.

Future studies should be conducted at individual treatment plants to evaluate the maximum AOC threshold for controlling biological fouling given their water quality and process train. Plant managers may thereby institute measures to control the nutrients entering the RO feed; pretreatment adjustment by maximizing organic carbon removal or minimizing chemicals that may exacerbate the biodegradability of the RO feed would be efficient preliminary approaches. Identifying the locations during pretreatment in a specific system where AOC is formed or increased would be the first step to control biofouling occurrence and minimize its potential and the associated adverse effects on SWRO plant operations.

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Appendix

Seawater AOC Test

The seawater assimilable organic carbon (AOC) test was published in *Applied and Environmental Microbiology*, 2011, pp. 1148–1150 (doi:10.1128/AEM.01829-10). The following summary of the materials and procedures is provided for an overview with particular focus on preparation of the standard curve solutions for operations and laboratory staff interested in using the application for monitoring AOC in their facilities.

A.1 Principle

The biological fouling potential of seawater was evaluated through the application of a predictive tool, the seawater AOC test, in which the maximum biomass density of an inoculum is measured in a pasteurized water sample. Pasteurization inactivates native microflora so nutrients are not depleted by other organisms. The test organism is a heterotrophic, nutritionally diverse, bioluminescent marine organism, *Vibrio harveyi*. *V. harveyi* exhibits constitutive luminescence, an attribute that facilitates a proportional relationship between light produced and biomass, where biomass results in assimilation of available substrate (i.e., AOC in water). The growth of *V. harveyi* follows Monod bacterial growth kinetics, and maximum growth (N_{max}) occurs during the stationary phase when maximum biomass is produced following depletion of available substrate. Standard curves are used to convert N_{max} luminescence units into µg acetate carbon equivalents per L (µg C/L). A series of standard curves are prepared to confirm reproducibility in the laboratory. Once established, blank, yield, and growth controls may be used for quality control per set of analyses. Minimizing carbon carryover or bacterial contamination should be carefully controlled. Laboratories equipped with clean preparation areas and a laminar flow hood would facilitate appropriate contamination control. If not available, additional procedural controls to reduce and monitor contamination will be necessary.

A.2 Apparatus

1. *Luminometer*: programmable, photon-counting microplate reader such as SpectraMax L (Molecular Devices, LLC, Sunnyvale, CA) operated using SoftMax® Pro software v5.4. Readings were reported in relative light units, defined as the integral of the photon count versus the time–reaction curve. Units were considered to be relative because the formula can be modified manually, which added to the ease of data monitoring and reporting. The software was programmed for automated reading of the samples in the microplate wells with a chamber temperature of 30° C. Settings were adjusted for fast kinetic integration (1 second) over 30 second intervals. Data analysis and automated calculations were adjusted by the user from SoftMax® Pro exports in spreadsheet processing software. The average luminescence values for replicates were monitored until maximum growth was reached (further description under the standard curve section).

2. *96-Well plates*: Microlite™ 1+ Flat bottom (Thermo Milford, MA, part number 7571) or similar 96-well opaque, white, polystyrene microplates with very low cross talk. Plates were covered using an adhesive sealing film during analysis.

3. *Sampling vessels*: Organic carbon–free borosilicate glass vials (45 mL capacity) with tetrafluoroethylene-lined silicone septa. Vials were rendered free of organic carbon through washes with 2% Citrajet® (Alconox, White Plains, NY), drying, and muffling at 550° C in a furnace for 6 hours. Closures were detergent washed, then soaked overnight in 10% hydrochloric acid (American Chemical Society Grade, EMD Chemicals, Gibbstown, NJ) and rinsed three times with Milli-Q water, dried, then autoclaved. Optional: AOC-free, precleaned subsample vials (Scientific Specialties Inc., 2000 class, part number 276720).

4. *Stock preparation vessel*: Screw thread, graduated, borosilicate glass bottles (250 mL capacity) were used for the preparation of the reagents and the *V. harveyi* culture. Caps were black polypropylene welded to a polytetrafluoroethylene (PTFE)/silicone liner (Kimble Chase Supplier No. 61110P-250). The PTFE/silicone liner eliminates the possibility of glue contamination to bottle contents.

5. *Hot water bath* capable of achieving and holding 70° C.

6. *Micropipettes*: adjustable volume, capable of delivering volumes between 10 and 100 µL and 100 and 1000 µL.

A.3 *V. harveyi* Stock and Reagent Solutions

1. *V. harveyi*: ATCC® 700106™; American Type Culture Collection, Manassas, VA. Stock was propagated according to product sheet directions. A reference stock was stored at -80° C in marine broth and 10% glycerol. From the reference stock, a refrigerated inoculum stock was prepared for each analysis set and enumerated before sample testing. Enumeration was conducted by spreading 0.1 mL of the refrigerated stock onto marine agar plates. Dilutions were necessary to achieve plate counts in the 30 to 300 cfu range. Typical stock solutions were 1x10^7 cfu/mL.

    a. *Refrigerated inoculum stock* was prepared by streaking the frozen stock onto a marine agar plate incubated at 30° C (overnight, ~18 hours). A single colony was then inoculated into a sterile saline buffer containing acetate carbon (1X M9 salts [BD and Co., Sparks, MD] in 1000 ml laboratory grade water with 2% sodium chloride, 0.1 mM CaCl2, and 1.0 mM $MgSO_4$ and adjusted to pH 7.2, fortified with 2 mg of acetate carbon/L) and incubated at 30° C. The stock was then enumerated and stored in the refrigerator for the inoculation of water samples. Stocks were stable up to 1 month.

    b. *Marine agar plates* (for enumerating *V. harveyi* stock*)* prepared by dissolving the following in laboratory grade water (/L): 10 g peptone, 5 g yeast extract, 15 g agar (BD and Co., Sparks, MD), and 20 g sodium chloride (EMD Chemicals, Gibbstown, NJ). The agar was heated with frequent agitation, boiled for 1 minute to completely dissolve the additives, and then autoclaved at 121° C for 15 minutes, cooled to 50° C, and poured into petri dishes; as an alternative, premade plates may be used.

2. *Standard Curve*:

    a. *Approach*: Using 40 mL, carbon-free sampling vessels, 20 mL of the saline buffer was fortified with acetate carbon working solution (20 mg/L) and then

inoculated with 10^3 cfu/mL of *V. harveyi* stock inoculum. Solutions were mixed to distribute cells, and 300 µL was then immediately transferred into replicate wells in the microplate. The microplate was covered with adhesive film and put into the luminometer. Luminescence is measured immediately and then at predetermined intervals until maximum growth during the stationary growth phase is reached (Figure A.1). The regression line produced for acetate carbon concentration versus maximum luminescence was used for converting environmental sample luminescence into acetate carbon equivalents (Figure A.2). Depending on the frequency of readings, an average of the stationary growth phase readings may be used for construction of the standard curve. As an alternative, the Monod model may be applied to determine substrate maximum and growth rates.

b. A 2000 mg/L stock solution of acetate carbon was prepared by adding 113 mg of sodium acetate (ACS grade; Mallinckrodt, Paris, KY) to 100 mL of Milli-Q water. The acetate carbon stock was then sterile filtered into an autoclaved borosilicate bottle by using an Acrodisc syringe filter 0.2 m HT Tuffryn membrane (PALL, East Hills, NY) and a 10 mL Luer-Lock-tip syringe (BD, Franklin Lakes, NJ). This stock was stored up to 6 months at 4° C and used for preparing standard curves and positive controls.

c. Standard curve test solutions were prepared by adding the requisite volume of acetate stock to sterile saline buffer (1X M9 salts in 1000 mL laboratory grade water with 2% sodium chloride, 0.1 mM CaCl2, and 1.0 mM $MgSO_4$ and adjusted to pH 7.2) at concentrations ranging from 10 to 1000 µg acetate carbon/L. Instead of this saline buffer, alternative solutions such as a seawater or marine mix for aquarium applications may be used, although these sources may have impurities that should be considered.

A.4 Sample Analysis

1. Samples were collected in 40 mL vials and pasteurized for 30 minutes once the temperature of the proxy reached 70° C. After pasteurization, the cooled samples were analyzed as soon as possible; in some cases, samples were stored at 4° C for no longer than 1 week. Half of the aliquot from the collection vessel was reserved (20 mL) and inoculated with 10^3 cfu/mL *V. harveyi* from the refrigerated inoculum stock. Solutions were mixed to distribute cells, and 300 µL was then immediately transferred into replicate wells in the microplate. Once all were transferred, the microplate was covered with adhesive film, and luminescence was measured immediately and then at predetermined and programmed intervals (e.g., 4 hours) until maximum growth during the stationary growth phase is reached.

2. *Quality control*: Because the method produces a bacterial growth curve, sample toxicity is readily apparent from very low or decreasing luminescence over time in the inoculated samples. For confirmation of bacterial activity per set of analyses, controls are to be analyzed in the same manner described in the procedure section. Negative controls should show little or no luminescence increase over time. Positive controls containing 100 µg acetate/L will have the appropriate luminescence response.

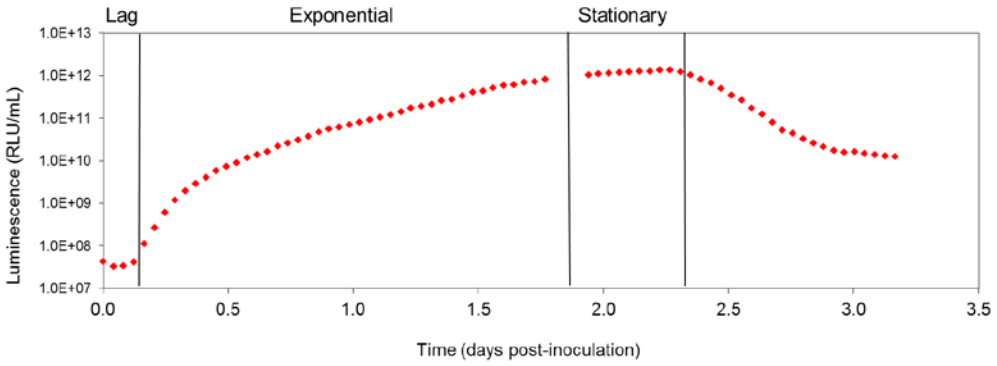

Figure A.1. Luminescence during *V. harveyi* growth phases measured on SpectraMax L.

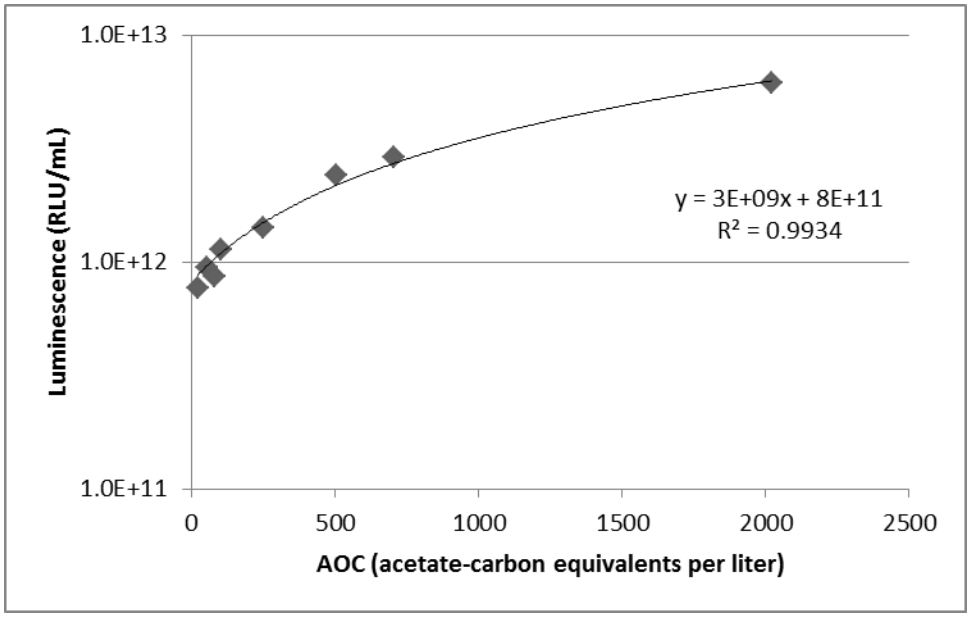

Figure A.2. Standard curve of maximum stationary phase luminescence for *V. harveyi* for acetate carbon concentrations.




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