Effect of solution chemistry on assimilable organic carbon removal by nanofiltration: full and bench scale evaluation

I. C. Escobar, A. A. Randall, S. K. Hong and J. S. Taylor

ABSTRACT

The effectiveness of nanofiltration (NF) to control assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC), the main indicators of biological stability of finished potable water, was systematically investigated at the 30,000 m^3/day NF membrane plant located in Southern Florida. One year of full-scale operation showed that nanofiltration effectively reduced BDOC, but was not able to reject AOC. The insignificant AOC rejection observed was probably due to the low pH, high hardness, and high ionic strength (TDS) of the processing water. In order to verify this hypothesis, a series of well-controlled bench-scale experiments were conducted at simulated solution chemistries. The bench-scale study clearly demonstrated that AOC removal by NF membranes decreased markedly with decreasing pH (a 25% decrease in pH led to a 20% decrease in AOC removal), and increasing hardness (10-fold increase led to a 90% decrease in AOC removal) and ionic strength (a 25-fold increase led to a 50% decrease in AOC removal). These solution environments repress the electrostatic repulsion between charged AOC compounds and membranes, resulting in low AOC rejection. Lastly, an empirical model was statistically developed based on bench-scale data and utilized to estimate full-scale performance. AOC removal predicted by the model showed good agreement with values observed in full-scale operation (R^2=0.98).

Key words | assimilable organic carbon (AOC), biostability, nanofiltration, solution chemistry, zeta potential

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INTRODUCTION

Membrane filtration is a newly applied technology for potable water treatment that is capable of removing wide ranges of the contaminants regulated by current and future drinking water rules, such as Stage 2 of the Disinfection/Disinfection By-Product Rule (Taylor & Hong 2000). In particular, nanofiltration (NF) has been found to remove 90% of the organic matter, and hence significantly reduce the formation of disinfection by-products (Taylor *et al.* 1987). However, little is known about the effectiveness of the NF process with respect to reducing assimilable organic carbon (AOC) and/or biodegradable dissolved organic carbon (BDOC). Since these are the parameters normally used to quantify the microbial regrowth potential (i.e. biostability) of the finished water

entering the distribution system, AOC and BDOC removal by the NF process needs further quantitative assessment.

AOC refers to a fraction of the total organic carbon (TOC), which can be utilized by specific strains or defined mixtures of bacteria, resulting in an increase in biomass concentration that is quantified. AOC typically comprises just a small fraction (0.1 to 9.0%) of the TOC (Van der Kooij 1992). AOC represents the most readily degradable fraction of BOM (biodegradable organic matter), and a significant correlation exists between the AOC concentration and the density of heterotrophic bacteria in distribution water supplies (LeChevallier *et al.* 1987; Van der Kooij 1992). Van der Kooij (1992) showed that heterotrophic bacteria in a non-chlorinated system did not

increase when the AOC was lower than 10 µg/l while LeChevallier *et al.* (1987) suggested that coliform regrowth may be limited by AOC levels less than 50–100 µg/l in systems maintaining a 3–6 mg/l chlorine residual.

The BDOC test measures the gross amount of organic matter that is biodegraded by an inoculum of suspended or fixed (on sand or glass beads) bacteria over a predetermined period of time. The BDOC concentration represents the fraction of dissolved organic carbon (DOC) that is both mineralized and assimilated by heterotrophic flora (Joret & Levi 1986; Servais *et al.* 1987; Frias *et al.* 1992; Volk *et al.* 1994; Kaplan *et al.* 1995). Joret *et al.* (1991) suggested that BDOC accounts for 10 to 30% of the total dissolved organic carbon content of drinking water. Kaplan *et al.* (1994) concluded that while AOC addresses concerns about bacterial regrowth, BDOC addresses reduction in chlorine demand or disinfection by-product formation.

Many researchers observed that, even though membrane filtration considerably reduces the DOC of the permeate water, it might let through a significant portion of the raw water AOC. The few existing studies (Clair *et al.* 1991; Agbekodo *et al.* 1996; Noble *et al.* 1996; Sibille *et al.* 1997) showed that reverse osmosis (RO) and NF were effective in rejecting higher molecular weight compounds typically quantified as DOC and BDOC. However, lower molecular weight compounds, typically quantified as AOC (*e.g.* acetic acid and amino acids), were rejected to varying degrees depending on the membrane characteristics, organic properties, and solution chemistry. From the limited experiments performed, it is obvious that more profound studies on the effects of membrane filtration on AOC removal are needed at both full- and bench-scales.

This research project was directed to determining the capability of full-scale nanofiltration, as a drinking water treatment alternative, for the removal of AOC. The project was divided into two separate phases: (i) one-year monitoring of a full-scale membrane water treatment plant located in West Palm Beach, Florida and operated by Palm Beach County Water Utilities District (PBCWUD); and (ii) bench-scale flat-sheet membrane filtration experiments performed at various feed solution chemistries to elucidate the fundamental mechanisms of AOC removal by NF membranes. Commercial thin-film

Table 1 | Average water quality in the Biscayne Aquifer (source: Escobar *et al.* 1999)

Parameter	Range (average) values
Dissolved oxygen	< 1–2 mg/l
pH	6.5–7.5 (7.0)
Alkalinity	200–250 (219) mg/l as $CaCO_3$
Total hardness	225–278 (249) mg/l as $CaCO_3$
Color	30–45 (32) PCU
Ammonia-nitrogen	1.08–1.32 (1.20) mg/l
Sulfate (SO_4)	16–24 (20) mg/l
Total dissolved solids (TDS)	150–300 (200) mg/l
Dissolved organic carbon (DOC)[1]	11.3 ± 2.8 mg/l

[1]DOC concentration is average of 12 sampling campaigns ±1 standard deviation.

composite softening membranes (TFCS, Fluid Systems, San Diego, CA) were used for all tests. Lastly, the bench-scale test results were utilized to develop a statistical empirical model that could be used to predict full-scale performance.

METHODS AND MATERIALS

Full-scale membrane water treatment plant

The NF membrane plant treats raw water from the Biscayne Aquifer in Southern Florida which is a shallow, surficial aquifer, with significant surface influence and some salt-water intrusion. The raw water characteristics shown in Table 1, with the exception of DOC which is the average of 12 monthly sampling campaigns, are based on historical values obtained from PBCWUD. No information on the phosphate (PO_4) concentration is available. This plant utilizes a 32:16 NF membrane array, made of TFCS spiral-wound elements designed to reject 95% of hardness and 85% of chlorides under normal operating conditions (Table 2). The NF plant was operated with an average of 3×10^4 m³/day (7.8 mgd) during the study.

Table 2 | Characteristics of Fluid Systems TFCS spiral-wound elements (8929)

Parameter	Characteristic
Molecular weight cut-off	200 daltons
Nominal diameter	0.2032 m
Nominal length	1.016 m
Thin film composite	Cross-linked aromatic polyamide rejecting surface
Active membrane surface area	37.16 square metres
Water transport coefficient	22×10^{-5} g/cm^2-sec-atm
Salt transport coefficient	18×10^{-5} cm/sec
Performance[1]	34.83 m^3/day, 85% chloride rejection, 95% hardness rejection

[1]Under test conditions: 0.552 MPa, 25°C, 500 mg/l NaCl, 10% recovery.

Before the static cartridge filters, 140 mg/l of sulfuric acid were added to lower the pH to 5.5, and 2 mg/l of anti-scalant (proprietary) were added to reduce scaling. The membrane-filtered water was disinfected by adding 4 mg/l of chlorine and 1.3 mg/l of ammonia. The water was then aerated and 45 mg/l of sodium hydroxide was added for pH adjustment.

The sampling point was located immediately after the membranes. Sample collection and storage were performed as outlined in *Standard Methods* (AWWA 1995). The procedure requires the addition of 20 mg/l sodium thiosulfate ($Na_2S_2O_3$) solution to neutralize the chlorine residual in the samples. Kaplan & Bott (1989) found that the addition of thiosulfate did not significantly stimulate the growth of *Pseudomonas fluorescens* strain P17 or *Spirillum volutans* strain NOX, thus having no effect on AOC concentrations. On the other hand, Maclean *et al.* (1996) determined that the addition of thiosulfate leads to some interference with the BDOC measurements that could be minimized if less than 20 mg/l of thiosulfate were added.

Raw water quality for bench-scale experiments

The laboratory tap water at the University of Central Florida was utilized to prepare the raw water matrix because of the inability to continuously acquire raw source water from the plant. It should be noted that using two different sources of water may weaken some of the predictive power of the bench-scale work, and thus the results were mainly used to provide qualitative interpretation of observations. The raw water samples were carefully withdrawn after a 5-minute flushing period. The raw water contained 2.0 mg/l DOC, 120 mg/l as $CaCO_3$ of alkalinity, 190 mg/l as $CaCO_3$ of hardness, total dissolved solids of 160 mg/l, pH of 7.50–8.00, and turbidity of 0.25 NTU. The background AOC and BDOC were 55.6 µg acetate-C/l and 220 µg C/l, respectively.

The raw water was spiked with 200 µg/l carbon as sodium acetate, to determine the retention of AOC. Therefore, the total raw water AOC and BDOC after the spike addition were 256 µg acetate-C/l and 420 µg C/l, respectively. No experiments were performed without the acetate spike because the level of tap water AOC (55.6 µg acetate-C/l) was considered low as compared with the full-scale raw water (AOC = 141 µg as acetate-C/l). The AOC spiked also accounted for the full-scale second-stage membrane units treating the concentrate from the first-stage. Ionic strength and divalent cation concentrations were varied by adding NaCl and $CaCl_2$, respectively, to the raw water in order to simulate various solution chemistries experienced during actual full-scale

membrane operation, especially the concentrates from the first stage of a membrane treatment plant. More specifically, at pH values of 7.5 and 5.5, the hardness and ionic strength were changed from 1.90×10^{-3} M to 2.5×10^{-2} M (190–2500 mg/l as $CaCO_3$) and from 4.0×10^{-3} to 1.0×10^{-1} (TDS = 160–4160 mg/l), respectively.

Bench-scale membrane test unit and protocol

Bench-scale membrane filtration experiments were conducted using a flat sheet cell unit consisting of two circular cells, each with 81.3 cm² (12.6 in²) active membrane area. Feed flow of approximately 1.14 l/min (0.3 gpm) per cell was supplied by a single 0.25 Kw (1/3-hp) pump. New membranes were used for every experiment, and the membranes were rinsed with distilled water prior to the experiment. The performance of flat sheet membranes was evaluated at operating conditions of approximately 17–34 l/m²-hr (10–20 gsfd) flux and 1–5% recovery, which were equivalent to 0.5–3.5 ml/min permeate and 345 ml/min concentrate for the given membrane surface area. Temperature was controlled to ambient conditions ($\cong 22°C$) by closed loop recirculation of a side stream of the feed water in a continuously-fed bath for heat exchange. One litre of permeate was collected for AOC analysis.

Zeta potential measurements

The zeta potentials of the membrane surface were determined using a streaming potential analyzer (BI-EKA, Brookhaven Ins., Holtsville, NY) to assess changes in membrane surface charge at various solution chemistries. A new membrane, rinsed with distilled water and soaked overnight, was used for each experiment prior to measurements. The divalent cation (Ca^{2+}) concentration in testing solutions ranged from 10^{-4} to 0.05 M with a background electrolyte concentration of 10^{-2} M NaCl.

AOC bioassay

AOC was measured using the rapid method of LeChevallier *et al.* (1993), except that plate counts were used to enumerate bacteria rather than ATP fluorescence,

in conjunction with *Standard Methods* procedure # 9217 (AWWA 1995) and the method of van der Kooij (1992). Details of the procedure used are outlined in Escobar & Randall (1999). Quality control for the AOC bioassay was performed using blank controls, and 100 µg C/l sodium acetate standards. The 100 µg C/l sodium acetate standards inoculated with P17 produced an average AOC of 93.80 ± 20.00 µg/l as acetate-C, while for NOX, they produced an average AOC of 77.20 ± 12.53 µg/l as acetate-C. No controls were made to assess the effect of thiosulfate since it has been determined not to affect AOC concentrations (Kaplan & Bott 1989).

Biodegradable dissolved organic carbon

The procedure for BDOC determination followed the technique using sand fixed bacteria (Joret & Levi 1986; Escobar & Randall 1999), with an MDL (method detection limit) of 0.15 mg/l.

RESULTS AND DISCUSSION

Full-scale AOC and BDOC removal

The AOC and BDOC concentrations of the NF membrane plant were collected over approximately 12 months starting from September 1997 (Figures 1 & 2). The quality of the water obtained from the Biscayne Aquifer showed a high variation, which is attributed to the rainfall occurring on the surface in February, March, and particularly in July 1998. All of the maximum source water values for AOC and BDOC occurred during the month of July, coinciding with a period of heavy rainfall, 116.84 mm (4.60 inches), following a drought, when only 0.51 mm (0.02 inches) of rain fell. High AOC and BDOC values during the period of heavy rainfall resulted from a higher than normal DOC concentration of 17.0 mg/l. The significant effect of precipitation on AOC and BDOC was not surprising since the source water was obtained from a surficial aquifer.

The year-average raw water and nanofiltration effluent AOC concentrations were 141 and 147 µg/l as acetate-C, respectively. There was no significant difference
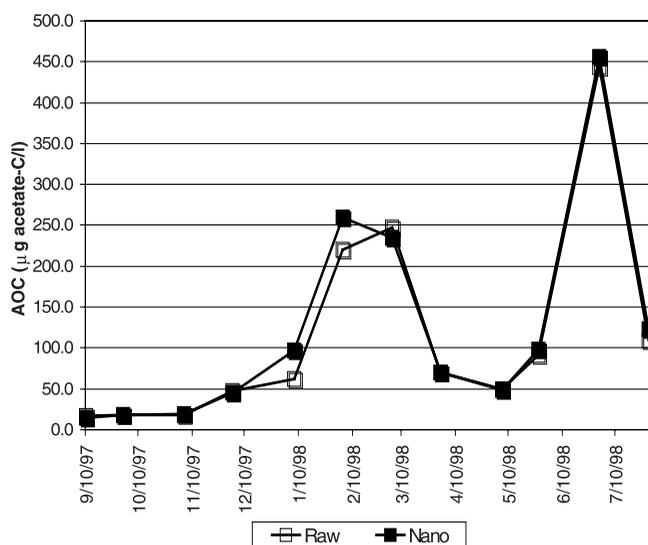
Figure 1 | Monthly AOC concentrations for raw water and nanofiltrate. (Reprinted from *Journal of Membrane Science*, **175**(1), 2000, pp. 1–17, 'Removal of assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) by reverse osmosis and nanofiltration membranes,' by I. C. Escobar, S. Hong and A. A. Randall, with permission from Elsevier Science.)
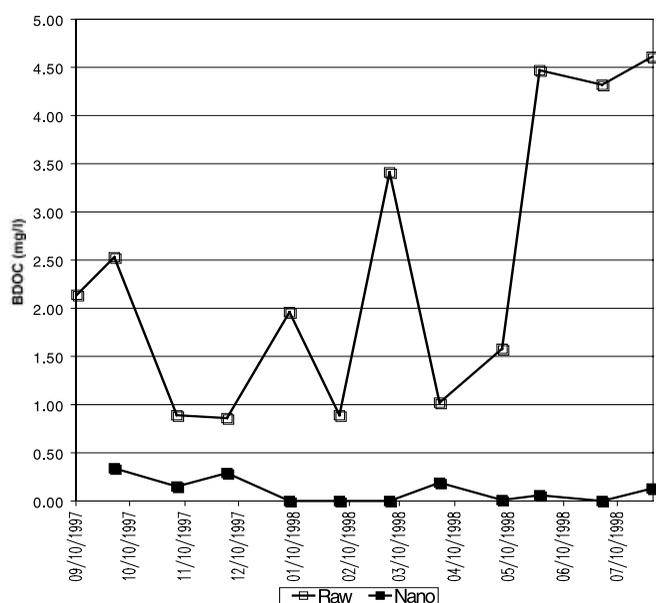

Figure 2 | Monthly BDOC concentrations for raw water and nanofiltrate. (Reprinted from *Journal of Membrane Science*, **175**(1), 2000, pp. 1–17, 'Removal of assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) by reverse osmosis and nanofiltration membranes,' by I. C. Escobar, S. Hong and A. A. Randall, with permission from Elsevier Science.)

(t-critical = 2.07, p-value = 0.89) between the raw water and the nanofiltrate, suggesting that nanofiltration did not remove AOC from the raw water. In fact, the average effluent AOC concentrations increased slightly compared to the raw water AOC. This may have been due to the addition of antiscalant and low purity acid, which may have contained carbon-compound impurities, but this was not verified in this study. AOC contribution from chemical feeds has been seen and documented previously (Hiemstra *et al.* 1999; Van der Kooij *et al.* 1999).

In contrast to the AOC observations, monthly BDOC data showed that nanofiltration removed approximately 97% of the raw water BDOC. Average raw water and nanofiltration effluent BDOC concentrations were 2.80 and 0.10 mg/l, respectively. There seemed to have been several instances where BDOC concentrations appeared to be lower than AOC concentrations (Figures 1 & 2); however, the majority of AOC concentrations were indistinguishable from their BDOC counterparts since the BDOC test is not able to distinguish values less than approximately 150 μg C/l, which is the BDOC detection

limit. Moreover, the fraction of DOC in the form of BDOC (i.e. BDOC/DOC) in the raw water was 0.27, and in the form of AOC (i.e. AOC/DOC) it was 0.01, while for the permeate, BDOC/DOC was 0.21 and AOC/DOC was 0.18. In addition, unlike AOC, the BDOC of the nanofiltrate did not change as the raw water BDOC varied, suggesting that the main mechanism of BDOC removal by NF membranes was size exclusion. When size exclusion is the governing rejection mechanism, the concentration of the permeate will remain constant regardless of changes in the membrane feed water (AWWA 1996). Volk *et al.* (2000) determined that, on average, BDOC-forming compounds consist of 75% humic substances, 30% carbohydrates, and 4% amino acids, with 39% of the molecules >100,000 daltons. Thus, it is expected that the BDOC was significantly removed by the TFCS NF membrane which has a molecular cut-off (MWCO) of 200 daltons.

The poor AOC rejection observed in the full-scale system, on the other hand, suggested that diffusion and charge repulsion might play a significant role in AOC removal by NF membranes. In general, compounds

quantified as AOC are from the fraction of BDOC composed of organic acids (e.g. acetate), aldehydes, carboxylic acids, and amino acids. Most of these organic compounds are small enough to pass through NF membranes, and thus their retention by NF membranes may be mainly governed by diffusion and electrostatic repulsion. It is also expected that AOC will be poorly removed in feed solution environments which repress electrostatic interactions between charged organic compounds and membranes. This would be the case for groundwater, which would have low pH (after acid pretreatment), high ionic strength, and high hardness. In fact, these solution chemistries are easily created in full-scale operation due to high recovery, explaining the observed low AOC rejection. To verify this hypothesis, a series of well-controlled bench-scale tests using simulated waters, as well as zeta potential measurements of the membrane surface, were systematically conducted.

Membrane surface charge

Increased calcium ion concentrations and lower pH (increased hydrogen ion concentrations) made the zeta potential of TFCS membranes more positive (Figure 3). This was attributed to the higher degree of deprotonation of membrane surface functional groups, such as carboxyl, at high pH. More specifically, when calcium was increased to 0.05 M at either pH = 7.5 or pH = 5.5, the absolute value of the membrane zeta potential was decreased by approximately 5–6 mV. This observation can be explained by effective masking of the membrane surface charge by divalent cations. In addition, specific adsorption of divalent cations to membrane surface functional groups may contribute to the neutralization of the negative charge of the membrane. Similar trends were reported by Hong & Elimelech (1997).

Bench-scale observations

Electrostatic interactions between organic compounds and membranes play a significant role along with diffusion and size exclusion in AOC removal by NF membranes
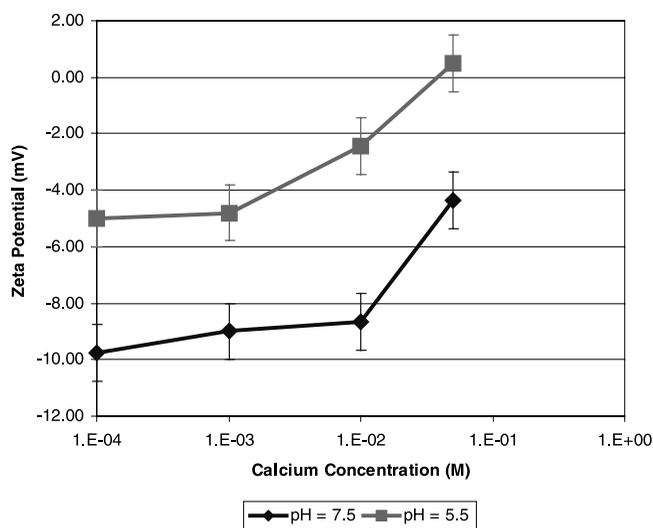

Figure 3 │ Zeta potentials of TFCS membranes when calcium ions were added to the solution with pH=7.5 and 5.5 (background electrolyte solution=10^{-2} M NaCl). Error bars represent one standard deviation between 2 duplicates per experiment.

Table 3 │ Bench-scale AOC relative removal [($AOC_{Raw} - AOC_{Permeate}$)/$AOC_{Raw}$] as a function of hardness and ionic strength addition for TFCS membranes at solution pH=5.5 and 7.5

Ionic strength, M	TDS, mg/l	Hardness, M (mg/l as CaCO$_3$)	AOC relative removal at pH=7.5	AOC relative removal at pH=5.5
0.0040	160	0.0019 (190)	0.93	0.78
0.0050	200	0.0019 (190)	1.00	0.85
0.0053	212	0.0024 (240)	1.00	0.78
0.0063	252	0.0024 (240)	1.00	0.73
0.0665	2,660	0.0269 (2690)	0.07	0.42
0.1040	4,160	0.0019 (190)	0.46	0.27

Note: Full-scale NF bulk feed concentrations: TDS≈2000 mg/l and hardness≈2300 mg/l as CaCO$_3$.

(Table 3; Figure 4). As shown, the AOC removal decreased significantly as the hardness and ionic strength increased. It was also observed that slightly better rejections of AOC were observed at pH = 7.5 than pH = 5.5. From zeta potential measurements, at low pH and high hardness and ionic strength, the membrane surface became less
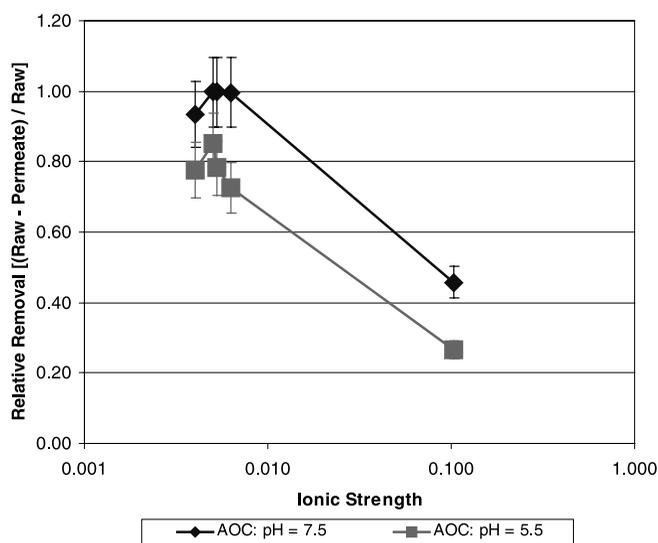
Figure 4 | AOC removal as a function of ionic strength addition for TFCS membranes at solution pH=5.5 and 7.5. Error bars represent one standard deviation.

Figure 5 | Percent AOC rejection [(AOC$_{Feed}$−AOC$_{Permeate}$)/AOC$_{Feed}$] versus feed water AOC for bench- and full-scale results.

negative. Losses in the negative charge of the membrane surface have been observed to cause reductions in electrostatic repulsion between organics and membranes (Braghetta 1995). Thus, charged organic compounds experienced less repulsion near the membrane surface or within pores, leading to a significant increase in passage of AOC through the membrane. This was supported by the high sensitivity of AOC removal to changes in solution chemistry (i.e. pH, hardness, and ionic strength; Table 3). However, it should be mentioned that enhanced removal by charge repulsion can be applicable only to charged AOC compounds such as acetate and might not be important for other uncharged AOC-forming compounds, such as aldehydes.

The decrease in AOC rejection with decreasing pH and increasing hardness and ionic strength may be also explained by changes in configuration of organic compounds. At low pH and high hardness and ionic strength, organic compounds have a more compact, smaller configuration due to reduced interchain charge repulsion (Hong & Elimelech 1997). Smaller configurations of organic compounds allow them to pass through membrane pores more easily, consequently decreasing AOC removal.
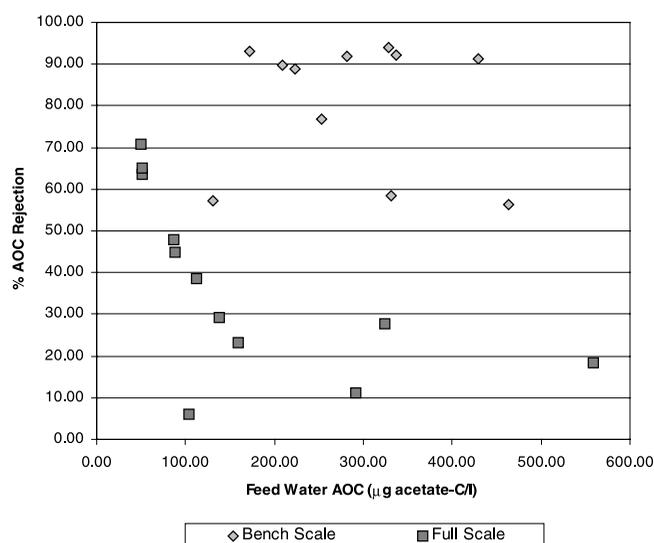
Prediction of AOC removal

Regarding the full-scale data, since AOC rejection decreases as the feed concentration increases, diffusion plays a significant role in the rejection mechanism; on the other hand, the bench-scale data show a nearly constant AOC rejection (90%) for all feed concentrations (Figure 5). The exceptions are the experiments with high ionic strength and/or hardness, where the AOC rejection dropped significantly. Therefore, under conditions of low hardness and ionic strength, size exclusion, diffusion and charge repulsion play significant roles in the rejection of AOC, but as hardness and ionic strength increase, size exclusion becomes the only significant factor (Figure 5).

The bench-scale results for AOC removal by TFCS NF membranes were utilized to predict performance of the full-scale nanofiltration plant. The solute flux (J_S) in diffusion controlled membranes is proportional to the concentration gradient ($\Delta C = C_B - C_P$) across the membrane:

$$J_S = K_S \times (C_B - C_P) \qquad (1)$$

where K_S is solute mass transfer coefficient (cm/sec), and C_B and C_P are feed and permeate solute concentrations,

respectively. In order to correlate bench-scale to full-scale data, the solute mass transfer coefficients for each bench-scale experiment were first determined. These experimental K_S values were then regressed linearly and non-linearly as a function of pH and ionic strength (IS). The best model is shown in Equation 2 which displays a R^2 of 0.81 and MSE of 7.21×10^{-8}, and demonstrates that both pH and ionic strength are statistically significant (F-statistics = 60.712, p-value < 0.0001):

$$K_S = 0.00118 - 0.00017 \times \text{pH} + 0.0132 \times \text{IS} \qquad (2)$$

In addition, the electrical potential of the feed water was calculated using the Nernst equation as a function of total ionic strength including hardness added to the feed water. Finally, the bench-scale AOC rejection was regressed using linear and non-linear models as a function of mass transfer coefficient (K_S) and energy gradient (ΔE) according to Equations (2) and (3), respectively:

$$\Delta E = -\frac{0.059}{1} \times \log\left(\frac{[\text{Na}^+][\text{Cl}^-]}{[\text{NaCl}]}\right) -$$

$$\frac{0.059}{2} \times \log\left(\frac{[\text{Ca}^{2+}][\text{Cl}^-]^2}{[\text{CaCl}_2]}\right) \qquad (3)$$

The best model is shown in Equation 4 (R^2 of 0.92 and MSE of 51.25) and both K_S and ΔE were found to be significant in the prediction of the AOC rejection (F-statistics = 165.383, p-value < 0.0001):

AOC % rejection

$$= 132.2 - 26721.0 \times K_S + 101.4 \times \Delta E \quad (4)$$

Contrary to the bench-scale studies in which recovery (R) was kept at 1–5%, the full-scale water treatment plant operated a multi-stage system at 85% recovery and consequently the local feed solute concentration (C_B) varied from the initial feed (C_{Raw}) to final concentrate concentration (C_C). The prediction of AOC permeate concentration can be improved by accounting for the change in local solute concentrations through the integration with respect to recovery (Mulford 1999):
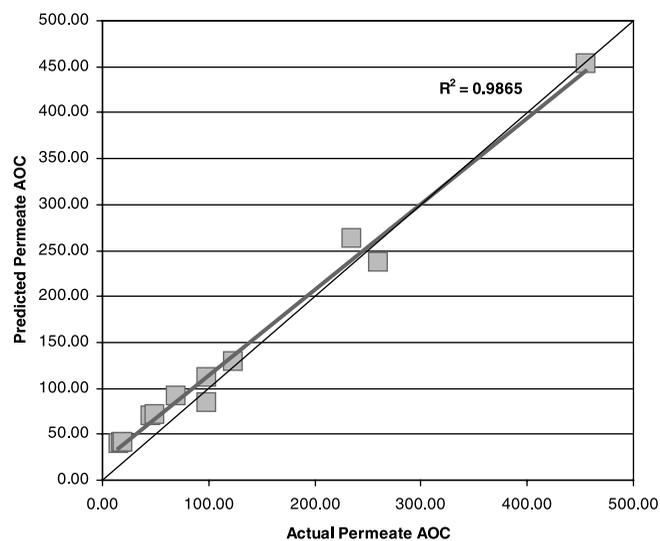

Figure 6 │ Model predicted AOC permeate versus actual full-scale permeate AOC (μg acetate-C/l).

$$C_B = \frac{C_{Raw}}{-\left(\dfrac{RF_w}{F_w + K_S}\right)} \ln\left(1 - \frac{RF_w}{F_w + K_S}\right) \qquad (5)$$

where F_w is an operating water flux. The full-scale dissolved solute concentration (i.e. total ionic strength) was calculated using Equation 5 and was then applied to Equation 2 at pH = 5.5 to determine the full-scale K_S. With the ΔE (-0.62 mV) calculated, the estimated K_S, 1.90×10^{-3} cm/sec, was utilized to predict the AOC rejection for the full-scale plant operation, using Equation 4. The detailed model development is presented elsewhere (Escobar 2000).

Based on a two-tailed t-test assuming unequal variances for the difference between means, it was determined that there was no significant difference between nanofiltrate concentrations obtained from the model and the full-scale plant (p-value = 0.80), indicating that the AOC rejection model developed based on bench-scale experimental data was adequate to predict full-scale operation ($R^2 = 0.98$; Figure 6). Lastly, the model was applied to varying conditions of hardness and total dissolved solids (Figure 7). What the reader should learn is that the model predicts a decrease in AOC rejection as total dissolved solids and/or hardness concentrations increase. It should
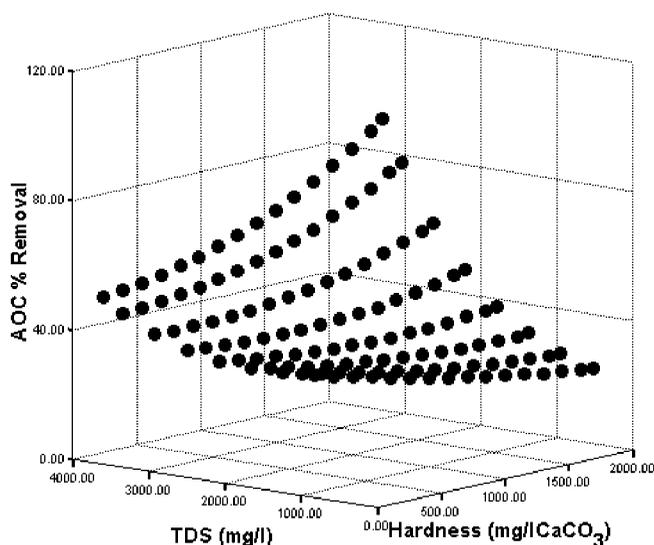
Figure 7 | Application of AOC rejection model to general conditions of hardness and total dissolved solids.

be noted that the model results were specific to the water qualities used in the full- and bench-scale analyses as well as the membranes used.

CONCLUSIONS

It is always difficult to make definitive conclusions from full-scale field studies where no operating variables are truly controlled. This is certainly true for the issue of measuring the biological stability of a large membrane treatment plant. However, comparison of both the full-scale and more controlled bench-scale experiments lead to the impact of water chemistry on the AOC rejection capabilities of membrane filtration systems. This study highlighted the transport mechanisms involved in the rejection of AOC by membrane filtration and gave some preliminary insight on how raw water quality strength and composition affect permeate biostability as measured by AOC and BDOC. The primary observations and conclusions were summarized as follows:

- At full-scale operation, nanofiltration removed 97% of BDOC from the raw water, regardless of feed

BDOC concentrations and solution environments. This suggested that the main mechanism of BDOC removal by NF membranes was size exclusion.

- The majority of AOC was not rejected by nanofiltration at full-scale. Bench-scale analysis demonstrated that the lack of AOC removal by nanofiltration was due to low pH, high hardness, and high ionic strength (particularly in the second stage of the membrane assembly), causing a screening of the negative charge of the membrane surface and/or pores. This charge masking decreased the electrostatic repulsion between the charged AOC-forming compounds and membranes, consequently reducing AOC rejection by NF membranes.

- The empirical AOC rejection model developed based on bench-scale experimental data demonstrated a good predictability of the full-scale operating data, suggesting that AOC compounds in the full-scale plant mainly consisted of small molecular compounds with negatively charged functionality (e.g. acetate).

- Additional research is recommended that would allow variation of flux and recovery, with charge and ionic strength for both amine and acetate based AOC forms.

ACKNOWLEDGEMENTS

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