

Integrating bench- and full-scale nanofiltration testing for two surface waters

Rupa Lamsal, Mike Chaulk, Emily Zevenhuizen, Margaret E. Walsh and Graham A. Gagnon

ABSTRACT

This study investigated the nanofiltration (NF) fouling behavior by two surface waters that serve as source waters for full-scale integrated membrane systems (IMS) of the Tatamagouche and Collins Park drinking water treatment plants (WTPs) in Nova Scotia, Canada. Bench-scale NF fouling experiments conducted under controlled laboratory conditions showed a flux decline of 25% with the Collins Park source water compared with a flux decline of 15% with the Tatamagouche source water over 96 hours of operation. The higher rate of flux decline observed was related to the water quality parameters observed in the Collins Park source water. Membrane autopsies were conducted on virgin and fouled membranes using different techniques to compare the fouling propensity of the two feed waters. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) results showed considerable difference between the fouled membranes fed with two source waters. Analyses of full-scale NF fouling data from the two IMS plants reveal higher fouling in the Collins Park WTP. Full- and bench-scale NF fouling observations provide consistent results that together support ongoing membrane cleaning practices in the Collins Park WTP.

Key words | integrated membrane systems, membrane fouling, nanofiltration, small water systems, ultrafiltration

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INTRODUCTION

Membrane filtration technology has been gaining increased usage in the drinking water industry because of its superior removal of disinfection by-product (DBP) precursors, minimal use of chemicals, reduction in sludge production and potential for use in a compact treatment train system while being economically feasible, particularly in small-scale systems (Pressdee *et al.* 2006). Low pressure microfiltration (MF) and ultrafiltration (UF) membranes are mostly used for the removal of particulate matter, and high pressure nanofiltration (NF) and reverse osmosis (RO) membranes are used for the removal of organic substances, multivalent ions and micro pollutants. Integrated membrane system (IMS), using low pressure (MF/UF) membranes followed by high pressure (NF/RO) membranes, has been used as a multi-barrier approach in drinking water treatment. The

NF membrane is of particular interest in drinking water treatment applications because of capabilities for high rejection of dissolved organic compounds and multivalent ions and operation at much lower pressure than the RO membranes.

Despite continued advances in membrane filtration technologies, membrane fouling is the major expense in the operation of membrane processes in water treatment. In full-scale operations, NF/RO membranes are exposed to different water constituents such as inorganic ions, natural organic matter (NOM) and biological compounds such as microorganisms and soluble microbial product which can contribute to membrane fouling. Among these NOM present in the source water plays a vital role as primary foulant (Nilson & DiGiano 1996; Cho *et al.* 1999; Schäfer *et al.* 2001).

The flux decline and NOM rejection in the NF membrane are mostly dependent on NOM properties including size (e.g. molecular weight), characterization (e.g. hydrophobic vs. hydrophilic), charge density (functional groups) (Nilson & DiGiano 1996; Mänttari *et al.* 2000; Tang *et al.* 2007; Her *et al.* 2008) and the chemistry of the feed water (i.e. ionic strength, pH and concentration of monovalent and divalent ions) (Braghetta 1995; Childress & Elimelech 1996; Hong & Elimelech 1997; Seidel & Elimelech 2002; Jarusutthirak *et al.* 2007). The rate of NF/RO membrane fouling increases with an increase in electrolyte concentration, decrease in solution pH and addition of divalent cations (Hong & Elimelech 1997; Jarusutthirak *et al.* 2007).

Numerous previous studies have been conducted to understand the effect of feed water properties on NF membrane fouling using synthetic feed waters (Childress & Elimelech 1996; Braghetta *et al.* 1997; Hong & Elimelech 1997; Her *et al.* 2004; Lee *et al.* 2005; Tang *et al.* 2007). Of those studies utilizing real source waters, most have either used single source water or have conducted experiments only at bench-scale level (Nilson & DiGiano 1996; Jarusutthirak *et al.* 2007; Her *et al.* 2008; Makdissy *et al.* 2010). While bench-scale studies performed under controlled laboratory-scale conditions can provide insights into various aspects of membrane fouling, they may not represent the actual condition of a full-scale membrane system. A combination of bench- and full-scale studies would help understand the effect of feed water properties on NF membrane fouling and understand the actual conditions of NF membrane fouling.

There are existing studies (Escobar *et al.* 2000, 2002; Bellona *et al.* 2008, 2010) that have compared or incorporated bench-scale results with full-scale results. However, the focus of these studies was specifically on the removal of assimilable organic carbon (AOC) and biodegradable organic carbon (BDOC) (Escobar *et al.* 2000, 2002) and applicability of NF/RO membranes in water reuse (Bellona *et al.* 2008, 2010) applications. Therefore, further studies on effect of feed water properties on NF membrane fouling are needed both at bench- and full-scale level.

This study addresses fouling in commercial polyamide NF membrane by two surface source waters in Nova Scotia, Canada. The surface waters used in this study serve as source waters for two small-scale IMS drinking water

treatment plants (WTPs) that utilize two different types of spiral wound NF membrane modules. Bench-scale NF fouling experiments were investigated under similar operating and NF membrane type conditions for the two source waters and results were compared. Membrane autopsies were conducted on virgin and fouled membranes using different techniques to characterize the properties of fouled membranes. In addition, full-scale NF fouling data collected from the two IMS plants were compared in order to understand the real NF fouling conditions in these water treatment plants.

MATERIALS AND METHODS

Description of small systems and raw water characteristics

This research was based in two small communities in Nova Scotia: (1) Tatamagouche, a village within the Municipality of the County of Colchester; and (2) Collins Park, a subdivision within the Halifax Regional Municipality. Both communities are provided with municipal drinking water from public utilities. Both the Tatamagouche and Collins Park water treatment plants are based on integrated membrane systems that are designed to minimize chemical handling and ease operational duties to reflect operational challenges associated with small systems.

The source water for the Tatamagouche WTP is the French River. The French River is a shallow river that flows through the surrounding agricultural and natural land-use areas. The water quality of the river is degraded during periods of high precipitation and seasonal changes during the spring and fall associated with run-off events. Two source water samples used in this study were collected in the fall 2010 during a period when water quality had not deteriorated following a heavy rainfall event. Each water quality parameter was measured in triplicate and standard deviation was reported. The water quality characteristics of the French River water are provided in Table 1.

Both the UF and NF membrane filtration modules utilized in the Tatamagouche IMS plant design were manufactured by GE Water and Process Technologies. Figure 1 shows a schematic of the treatment process in the

Table 1 | Feed waters characteristics

Analytes	Tatamagouche WTP – French River	Collins Park WTP – Fletcher Lake
pH	6.7 ± 0.04	6.6 ± 0.02
UV ₂₅₄ , cm ⁻¹	0.064 ± 0.001	0.164 ± 0.001
Conductivity, μS cm ⁻¹	74.7 ± 1.9	93.07 ± 5.0
DOC, mg L ⁻¹	2.8 ± 0.04	4.5 ± 0.11
SUVA, L mg ⁻¹ m ⁻¹	2.2 ± 0.04	3.6 ± 0.07
Na, mg L ⁻¹	4.0 ± 0.01	17.5 ± 0.53
Ca, mg L ⁻¹	4.7 ± 0.22	5.62
Mg, mg L ⁻¹	0.74 ± 0.03	0.92 ± 0.03
NO ₃ ⁻ , mg L ⁻¹	0.38	0.80
PO ₄ ⁻ , mg L ⁻¹	2.02	8.41
Cl ⁻ , mg L ⁻¹	4.96	22.10

Tatamagouche plant. Raw water is pumped from the French River to two redundant UF skids, each containing 18 Zee-Weed[®] 1000 UF modules. Each UF module has a membrane surface area of 41.8 m²; therefore, total area of each UF skid is 752.4 m². The units operate in parallel and each is designed to produce a continuous output of $8.883 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ (533 L min⁻¹) with a net raw water flow of $9.350 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ (561 L min⁻¹) at 95% recovery. Under design operating conditions the net operating flux is $5.92 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ (21.3 L m⁻² h⁻¹). The UF permeate is directed to an intermediate transfer tank which provides

storage and feed water to redundant NF units operated in parallel.

Each NF unit (GE Osmonics PRO-100NF) is equipped with 1.0 μm cartridge pre-filtration for membrane protection prior to a 4-2 membrane array consisting of six pressure vessels, each containing 4 × 200 mm diameter NF modules (OSMO PRO RO365). Each membrane element has a surface area of 33.9 m² which provides a total area of 813.6 m² per skid. Permeate production from each NF unit is designed at $6.317 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ (379 L min⁻¹) at 75% recovery, or an operating flux of $7.75 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ (27.9 L m⁻² h⁻¹). The overall system recovery is designed at 71% recovery. Details on design and operating conditions of the NF membrane are presented in Table 2.

Raw water supplied to the Collins Park WTP is from Fletcher Lake. The lake is part of the Shubenacadie watershed, one of the largest and most developed watersheds in Nova Scotia. The lake receives primary inflow from the south, via Lake Thomas. Fletcher Lake is used for many recreation purposes and is largely developed along the eastern and southwestern edges with residential properties and light commercial businesses. Developments along the eastern lakefront include onsite water and wastewater systems. There are also two municipal wastewater treatment plants located along the southern lakefront which discharge treated effluent into the lake. Storm water flowing from properties, highways and the surrounding catchment area

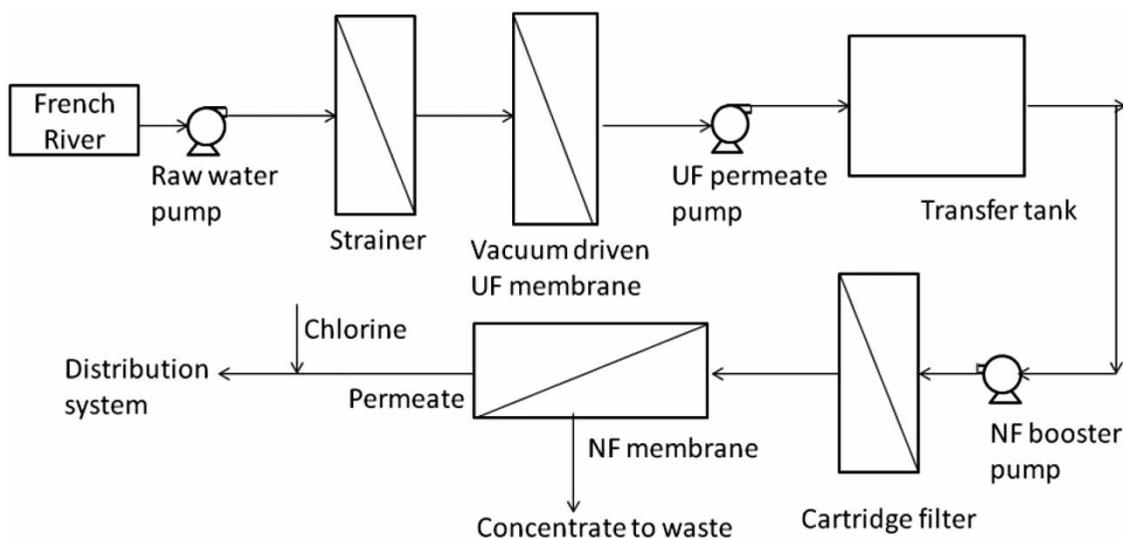
**Figure 1** | Process diagram of the Tatamagouche water treatment plant.

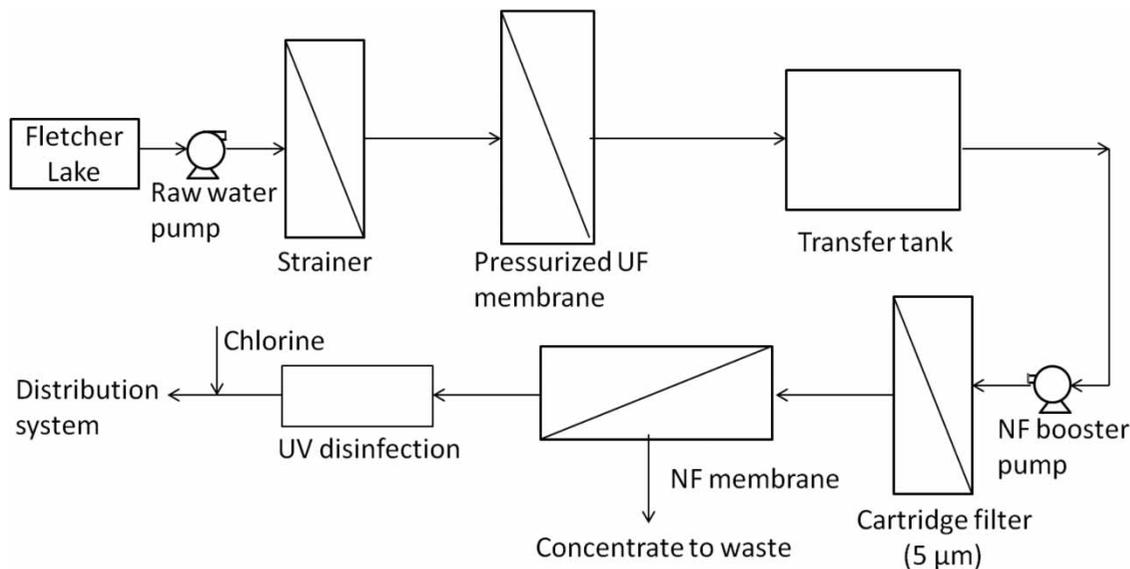
Table 2 | NF membrane type and operating conditions in full-scale plants

Membrane design and operating conditions	Tatamagouche WTP	Collins Park WTP
NF manufacturer and module	GE-Osmonics, OSMO-MUNI-NF 365	Hydranautics –ESPA4
Membrane material	Proprietary polyamide thin-film (TFM [®])	Aromatic composite polyamide
Module area (m ²)	33.9	37.1
Number of skids	2	1
Total modules per skid	24	8
Total membrane area (m ²)	813.6	296.8
Array	4-2	1-1
Permeate flow rates m ³ s ⁻¹ (L min ⁻¹)	0.0063 (378.5)	0.0018 (109.8)
Recovery (%)	75	80
Inlet flowrate m ³ s ⁻¹ (L min ⁻¹)	0.0084 (503.5)	0.0023 (137.4)
Total flowrate m ³ s ⁻¹ (L min ⁻¹)	0.011 (643.5)	0.003 (182.8)
Average design flow per module m ³ s ⁻¹ (L min ⁻¹)	0.00026 (15.8)	0.00023 (13.7)
Range of feed pressure (Pa)	5.9 × 10 ⁵ –9.2 × 10 ⁵	6.3 × 10 ⁵ –8.4 × 10 ⁵
Range of temperature (°C)	2.6–13.0	4.6–14.4

also discharge to the lake. As source water for municipal drinking water, the general water characteristics of Fletcher Lake are typical of those found in many similar surface supplies in Nova Scotia, and are summarized in Table 1.

Figure 2 shows a schematic of the treatment process in the Collins Park WTP. The Collins Park WTP treatment train includes an integrated UF-NF membrane system with redundant UF trains and a single NF train. Raw water is

pumped from the lake through 50 micron self-cleaning strainers into two parallel UF module racks. Each rack contains four HYDRAcap UF modules (Nitto Denko/Hydranautics Corporation, Oceanside, USA), with an active membrane surface area of 46.5 m² per module. The modules operate in a dead-end filtration mode at a design flowrate of $3.18 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ (191.2 L min⁻¹) per rack at a flux of $2.58 \times 10^{-5} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ (93 L m⁻² h⁻¹) and recovery of 95.7%.

**Figure 2** | Process diagram of the Collins Park water treatment plant.

Permeate from the UF modules is stored in an intermediate transfer tank that is used as NF feed water.

The NF system consists of pre-filtration through a 5 µm cartridge filter and a 1-1 membrane array of two pressure vessels, each containing 4 × 200 mm NF modules (Hydronics ESPA4). Each NF module has a surface area of 37.1 m² providing a total NF membrane area of 296.8 m². The permeate production rate from the system is 1.83 × 10⁻³ m³ s⁻¹ (110 L min⁻¹) at a recovery of 80% and average per module flux of 6.14 × 10⁻⁶ m³ m⁻² s⁻¹ (22.1 L m⁻² h⁻¹).

Bench-scale NF membrane fouling tests

Bench-scale NF fouling experiments were conducted under laboratory conditions. The purpose of the bench-scale tests was not to simulate the full-scale conditions, but rather to understand full-scale NF fouling with bench-scale observations that will help isolate the role of water quality in observed differences in full-scale data.

Bench-scale commercially available DK-NF membrane test sheets (GE Osmonics, Minnetonka, MN) were used in this study. The DK-NF membrane is a thin-film composite membrane with a three-layered structure with a porous polysulfone support and an active polyamide layer (Al-Amoudi et al. 2007). The DK-NF membrane test sheets were purchased in a flat sheet and pre-cut form (14.6 cm × 9.5 cm) from the manufacturer. The properties of this membrane are presented in Table 3.

Table 3 | Properties of DK NF test membrane

Properties	Value
Skin layer material	Cross-linked aromatic polyamide
Typical flux/pressure	1.04 × 10 ⁻⁵ m ³ m ⁻² s ⁻¹ @ 6.89 × 10 ⁵ Pa
pH range	2–11 ^a
Salt rejection	98% MgSO ₄ ^a
Molecular weight cut-off	400 Da ^b
Contact angle	40.6° ± 5.2° ^c
Root mean square roughness	16.4 ± 3.1 nm ^c
Zeta potential at pH 9	-18.5 mV ^c

^aNominal value reported by manufacturer.

^bLi et al. (2008).

^cTang et al. (2007).

A bench-scale, cross-flow filtration unit (SEPA II, GE-Osmonics, Minnetonka, MN) was used in the NF fouling experiments. The membrane cells were fitted with feed and permeate spacers in an attempt to simulate the hydrodynamics of spiral-wound membrane elements. Specifically, the thickness of the feed spacer was set at approximately 0.2 mm (65 mil). Virgin test membrane sheets used in the experiments were soaked in milli-Q water for 24 hours prior to loading into the bench-scale NF module. The milli-Q water was refreshed four times during this membrane pre-soak procedure. The membrane test sheets were then pre-compacted with milli-Q water overnight in the test-unit prior to commencing the fouling experiments.

The source water from the French River and Fletcher Lake used in the fouling experiments was pre-filtered through a mixed cellulose ester 0.45 µm membrane (GN-6 Metrice, Pall, East Hills, NY) to remove larger particles prior to NF treatment at the bench-scale. Since most organic matter is dissolved and is much smaller than 0.2 µm in size, the organic removal by 0.45 µm and 0.2 µm filters is virtually the same. The pre-filtration step was intended for turbidity removal. The filtered water was pumped at a flowrate of 1.33 × 10⁻⁵ m³ s⁻¹ (800 mL min⁻¹) (cross-flow velocity = 0.09 m s⁻¹) into the NF membrane cell body with a constant flow diaphragm pump (Hydracell, Wanner Engineering, Inc., Minneapolis, MN) equipped with variable speed motor and variable frequency drive (Baldor Electric Co., Fort Smith, AR). The bench-scale NF test unit was operated at constant pressure, variable flux mode with a transmembrane pressure (TMP) of 4.96 × 10⁵ Pa maintained during the entire filtration cycle of each experiment.

The bench-scale NF apparatus was operated in recycle mode, in which concentrate and permeate were returned to the feed water tank. To maintain constant temperature (24 ± 2 °C) of the feed water, the concentrate line was passed through a water refrigerated bath (Thermo Scientific NESLAB RTE Series, P/N U00694) before recycling into the feed tank. The membrane fouling experiments were conducted for 4 days (96 hours) for both source waters. The permeate flow rate was monitored regularly by measuring the volume of water collected in each hour in a graduated cylinder.

Full-scale data were normalized by membrane-specific temperature correction factor (TCF). Because the temperature correction factor is dependent on membrane and

manufacturer (USEPA 2003), two different equations were used for calculating TCF. Collins Park and Tatamagouche NF membrane permeate flow rates were corrected according to Equations (1) (GE Infrastructure 2008) and (2) (Sharma *et al.* 2003) respectively.

$$Q_{25^{\circ}\text{C}} = Q_T \times [0.35 + (0.026 \times T)] \quad (1)$$

$$Q_{25^{\circ}\text{C}} = Q_T \times \exp\left[2918\left[\frac{1}{298} - \frac{1}{273 + T}\right]\right] \quad (2)$$

Here T is the membrane operating temperature, Q_T is the permeate flow rate at temperature T and $Q_{25^{\circ}\text{C}}$ is the permeate flow rate at 25°C .

Water samples were collected from the feed and the permeate tanks of the bench-scale NF apparatus every two hours to measure UV_{254} , dissolved organic carbon (DOC), conductivity, trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP). Percentage DOC rejection was calculated as follows:

$$\text{Percentage DOC rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p and C_f are the DOC concentrations of NF permeate and feed waters respectively.

Water quality analysis

Water samples (feed water and permeate) were characterized in terms of pH, ultraviolet absorbance at 254 nm (UV_{254}), DOC, conductivity, THMFP, HAAFP, cations (sodium, calcium, magnesium) and anions (phosphate, chloride, nitrate). THMFP and HAAFP were determined using the uniform formation conditions (Summers *et al.* 1996). The pH, UV_{254} and DOC were measured following the procedure as described in Lamsal *et al.* (2011). The concentrations of anions were measured using an Ion Chromatogram (Metrohm 761 Compact IC, Fisher Scientific) and dissolved metals were measured using ICP-MS (Thermo Scientific X-Series 2). High performance size exclusion chromatography (HPSEC) (Perkin Elmer, Series 200) with UV/VIS detector was used to determine molecular weight distribution of NOM present in two source waters. Detailed analytical

descriptions can be found in the supplementary materials provided in Lamsal *et al.* (2011).

Microbiological enumeration and microscopy analysis

Heterotrophic plate counts (HPCs) of the feed waters and the fouled membrane layers were determined using the spread plate method on R2A agar (Standard Methods, APHA 1995). Serial dilutions were prepared from each sample analyzed to yield 30 to 300 colonies per plate. The Petri plates were incubated at room temperature (20°C) for 7 days and then enumerated using a colony counter.

At the end of the fouling experiments (i.e. after 4 days), the membrane test sheets were carefully removed from the SEPA-Cell test unit and cut in half using sterilized gloves and tools. One half of the fouled membrane test sheet was placed in 250-mL Erlenmeyer flasks containing 200 mL of sterilized water, covered with aluminum foil, and then placed on a shaker table (Barnstead E-Class, Model 2000, Fischer Scientific) operated at a speed of 1,200 rpm for 1 minute. A 1 mL of sample was collected and serial dilutions were prepared and 1 μL of each diluted sample was poured into R2A agar plates (Standard Methods, APHA 1995). The normalized HPC results are presented as numbers of microbes per unit membrane area (cells/m^2) as reported in previous studies (Sanna *et al.* 1998; Speth *et al.* 1998). Control runs were made with the virgin membrane samples.

The second half of the membrane was stored in a sterilized beaker and covered with aluminum foil. The small pieces of membrane coupons were subjected to scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses. For SEM analysis, sections of the virgin and dried fouled test membranes were first coated with gold/palladium by utilizing a SC7620 Mini Sputter Coater under vacuum. The thickness of the coating was approximately 367 Å. A model Hitachi S-4700 field emission scanning electron microscope equipped with Oxford Inca x-sight EDS system was used to observe and analyze the surface morphology of virgin and fouled membranes.

AFM analysis was used to obtain images and roughness of the surfaces of the test membrane sheets. The analysis was performed in acoustic mode at a scanning speed of 1 Hz with an Agilent 5500 instrument (Agilent, Santa Barbara,

CA) using high frequency (300 kHz) silicon cantilevers with a tip radius of 2–5 nm (TESP-SS, Veeco, Santa Barbara, CA). Images were analyzed using the software Gwyddion (<http://gwyddion.net/>). Surface roughness of the membrane test sheets was quantified as average roughness, which is defined as the arithmetic average of the absolute values of the surface height deviations measured from the center plane. The root mean squared (RMS) roughness is the average of the measured height deviations from the mean surface taken within the evaluation area (Huang *et al.* 2007; Macdonald *et al.* 2012). Three different images were taken at $10\ \mu\text{m} \times 10\ \mu\text{m}$ scan at different spots of the membrane with a resolution of 512×512 points and average roughness values were calculated.

RESULTS AND DISCUSSION

Impact of feed water characteristics on membrane fouling and NOM rejection

Figure 3 shows permeate flux declines for the Tatamagouche and Collins Park source waters with the DK-NF test sheet membranes at constant pressure of 4.96×10^5 Pa. The initial permeate flux for both source waters was approximately $1.03 \times 10^{-5}\ \text{m}^3\ \text{m}^{-2}\ \text{s}^{-1}$ ($37.01\ \text{L}\ \text{m}^{-2}\ \text{h}^{-1}$). The flux

decline trend with the two different source waters was almost identical during the first 12 hours of filtration. After 24 hours of operation, the Fletcher Lake source water showed slightly higher flux decline than the French River water.

At the completion of the 96-hour filtration run time, the percentage flux decline for the Fletcher Lake water (i.e. 25%) was found to be higher than that of the French River water (i.e. 15%). The higher organic content of the Fletcher Lake water compared with the French River water may have influenced the flux decline patterns observed. The Fletcher Lake water has a much higher DOC concentration ($4.5\ \text{mg}\ \text{L}^{-1}$) and SUVA value ($3.6\ \text{L}\ \text{m}^{-1}\ \text{mg}^{-1}$) than the French River water (DOC = $2.9\ \text{mg}\ \text{L}^{-1}$ and SUVA = $2.2\ \text{L}\ \text{m}^{-1}\ \text{mg}^{-1}$). Braghetta *et al.* (1998) also observed increased flux decline with increased TOC concentration in bench-scale NF fouling experiments conducted with Suwanne River humic acid as a model foulant. The conductivity of the Collins Park source water was slightly higher ($96.6\ \mu\text{S}\ \text{cm}^{-1}$) than that of the Tatamagouche source water ($86.1\ \mu\text{S}\ \text{cm}^{-1}$). Li & Elimelech (2004) observed increased rates of NF fouling with increasing ionic strength (i.e. conductivity) owing to a reduction in the repulsive electrostatic forces between the colloids and the membrane surface. At high ionic strength, the electric potential and energy of interaction decrease owing to double layer compression and charge

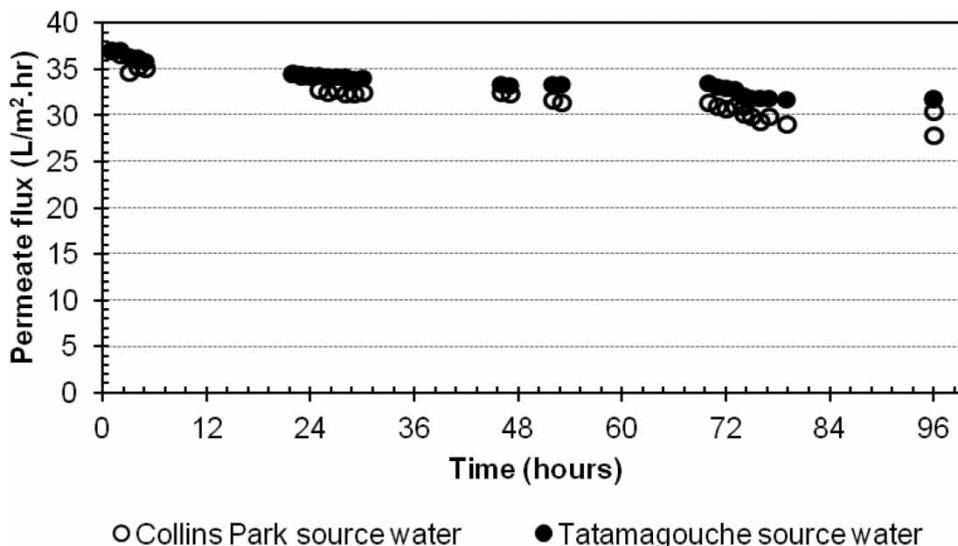


Figure 3 | Permeate flux during bench-scale NF experiments.

screening, resulting in a decrease in electrostatic repulsion between the membrane surface and NOM.

The higher concentration of selected cations (i.e. Ca^{2+} and Mg^{2+}) observed in the Collins Park source water compared with the Tatamagouche source water may also have contributed to increased flux decline observed with the Collins Park source water compared with the Tatamagouche source water through the combined effect of NOM complexation with those cations. As presented in Table 1, calcium, magnesium and sodium concentrations were 16, 24 and 77% higher, respectively, in the Collins Park source water compared with those measured in the Tatamagouche source water samples. Li & Elimelech (2004) reported the synergetic effect of model dissolved organic carbon and calcium and magnesium cations on permeate flux decline. Other studies have also found increased flux decline rates in the presence of Ca^{2+} and Mg^{2+} and emphasized the dramatic effect of Ca^{2+} in enhancing the flux decline rates by an intermolecular bridging mechanism (Hong & Elimelech 1997; Li & Elimelech 2004). Another possible explanation for the differences observed in flux decline may be potential differences in NOM composition between the two source waters.

The NOM rejection achieved with treatment of the source waters through the bench-scale NF apparatus was evaluated in terms of DOC, UV_{254} , conductivity, THMFP and HAAFP for the Fletcher Lake and the French River waters (Table 4). Samples were taken every two hours during the daytime operation of the bench-scale NF apparatus over a 4 day operational period and values were averaged. For both source waters, significant DOC rejection was achieved. Results of the Fletcher Lake water experiments showed a slightly higher rejection (up to 83%) of DOC than that found in the French River water experiments (80%). Results of the bench-scale NF study also showed significant reduction (i.e. $\geq 99\%$) of UV-absorbing organics with both source waters. The reduction of SUVA is the indication of removal of humic and/or larger molecular weight NOM over non-humic and/or lower molecular weight NOM. Siddiqui et al. (2000) observed similar results in bench-scale NF fouling experiments with low turbidity surface waters.

As expected with the significant decreases in DOC and UV_{254} after NF treatment, significant reductions in DBP

Table 4 | NOM removal during NF fouling experiments with the source water from the Tatamagouche WTP and Collins Park WTP

WTP	UV_{254} (cm^{-1})		Cond. ($\mu\text{S cm}^{-1}$)		DOC (mg L^{-1})		THMFP ($\mu\text{g L}^{-1}$)		HAAFP ($\mu\text{g L}^{-1}$)	
	C_F	C_P	C_F	C_P	C_F	C_P	C_F	C_P	C_F	C_P
Tatamagouche source water	0.122 ± 0.011	0.0005 \pm 0.0007	78.3 ± 5.1	4.1 ± 2.9	$4. \pm 0.6$	0.8 ± 0.22	236.0 ± 4.6	19.1 ± 0.3	203.1 ± 50.8	1.6 ± 2.0
Collins Park source water	0.186 ± 0.017	0.001 ± 0.0007	158.8 ± 15.9	5.3 ± 0.9	5.3 ± 0.5	0.9 ± 0.08	306.3 ± 4.4	9.0 ± 0.1	272.7 ± 10.0	0.5 ± 0.7

formation were observed on NF permeate samples of both source waters. The results of the Uniform Formation Conditions tests showed 92 and 97% reductions in THMFP for the French River and Fletcher Lake source waters, respectively. Results of this study are consistent with the 90 to 99% reduction of THMFP and HAAFP observed in other NF studies with natural source waters (Edwards 1988; Conlon & McClellan 1989; Siddiqui *et al.* 2000; Ates *et al.* 2009). Lower reductions in THMFP (65 to 70%) have been reported in a NF bench-scale study of Colorado River water (Amy 1990). However, the lower rejections found in that study were concluded to be related to the low molecular weight (MW) characteristics of organic precursor material in that source water (i.e. significant amount of precursor material corresponded to MW \leq 500 Da).

Organic molecular weight distribution analysis

Figure 4 presents the HPSEC chromatogram measured with UVA detector as a function of retention time for the two source water samples used in this study. Although the intensity of the peak for the Collins Park source water was higher than that of the Tatamagouche source water, the overall trend of the spectra (i.e. presence of peaks at set retention times) was found to be the same for both source waters. The higher molecular weight UV-absorbing organics were eluted

in the column first before the lower MW UV-absorbing organics. Note that since the UV detector can only measure the UV-absorbing organic compounds, the HPSEC results presented in this study are limited to UV-absorbing organics only.

Table 5 shows the MW of each peak for both samples. The first peak with high MW organics (\sim 58,000 Da) most likely represents protein-type organic molecules as polysaccharides are not detected by UV detection. Peaks 2 and 3 may be associated with fulvic acid-like substances (Her *et al.* 2002; Wu *et al.* 2007). Wu *et al.* (2007) identified the humic acid and fulvic acid fractions in Harp Lake, Ontario, water based on MW calibration, and determined that the MW of humic acid was higher than 4,500 Da and that of fulvic acid was slightly lower than 4,500 Da. MW results found in this study indicate that both the source waters have a high percentage of low MW organics (i.e. $<$ 4,500 Da) possibly representing higher constituents of fulvic acid fractions. Previous studies have demonstrated a strong relationship between the MW profile and the physico-chemical properties of DOC and humic/fulvic substances (Chin *et al.* 1994; Her *et al.* 2002). Those studies demonstrated that larger MW fractions have been related to higher levels of hydrophobicity while smaller MW fractions have been related to higher hydrophilicity (Cabaniss *et al.* 2000). Further, a previous study that focused on NOM fractionation of water samples taken from the French River

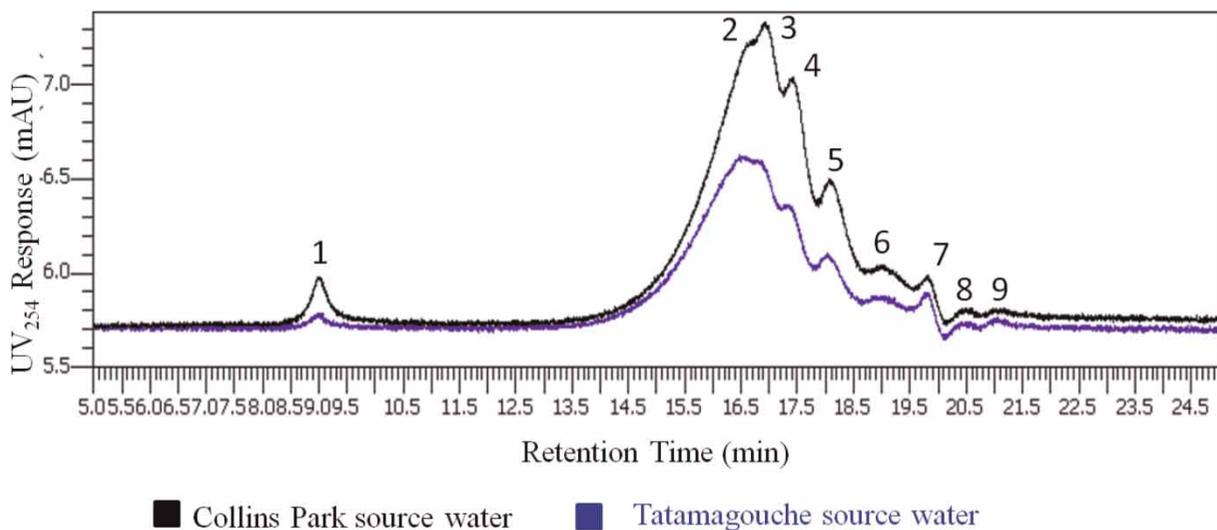


Figure 4 | Molecular weight distribution of organic compounds.

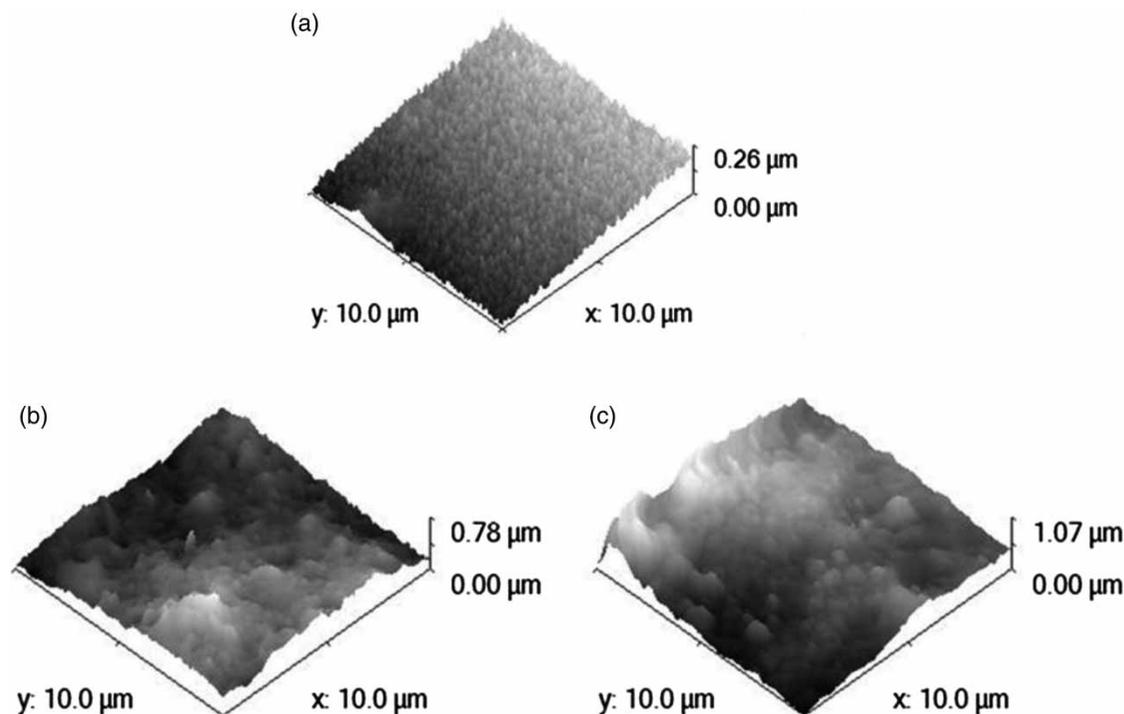
Table 5 | Molecular weights of assigned peaks in HPSEC analysis

Peak number from chromatogram	Molecular weights (Daltons)	
	Tatamagouche source water	Collins Park source water
1	58,300	58,600
2	2,060	1,930
3	1,210	1,180
4	912	864
5	637	625
6	405	410
7	290	291
8	213	206
9	145	154

showed that a higher percentage (~58%) of the organic material was hydrophilic in nature (Lamsal *et al.* 2012).

Roughness of foulant layer by AFM analysis

The AFM images for virgin and fouled membrane samples are presented in Figure 5. The three-dimensional images were taken in each case with scan size of $10\ \mu\text{m} \times 10\ \mu\text{m}$.

**Figure 5** | AFM images (a) virgin NF membrane, (b) fouled with the Tatamagouche source water and (c) fouled with the Collins Park source water.

A significant difference was observed between the surface morphologies of the virgin and fouled membranes. The virgin membrane exhibited an average roughness (Ra) and root mean squared (RMS) roughness of 46.0 and 55.0 nm, respectively. The test membrane that had been fouled through NF filtration runs with the Tatamagouche source water resulted in Ra and RMS roughness of 100.3 and 119.5 nm, respectively (Figure 5(b)), whereas, the test membrane samples that were fouled with the Collins Park source water had Ra and RMS of 173 and 211 nm, respectively. The maximum height of the peaks on the fouled layer (Ry) was also found to be higher (i.e. $1.07\ \mu\text{m}$) for the membrane samples fouled with Collins Park source water. The Ry for the French River membrane samples was $0.78\ \mu\text{m}$ (Figure 5(b)). Visually, the foulant layer was noticeably thicker on the NF test sheet that processed the Collins Park source water than the test sheets that processed the Tatamagouche source water.

Morphological analysis of foulant layer by SEM

Figure 6 provides the SEM images of the virgin and fouled test sheet membranes after 96 hours of treatment with the Collins

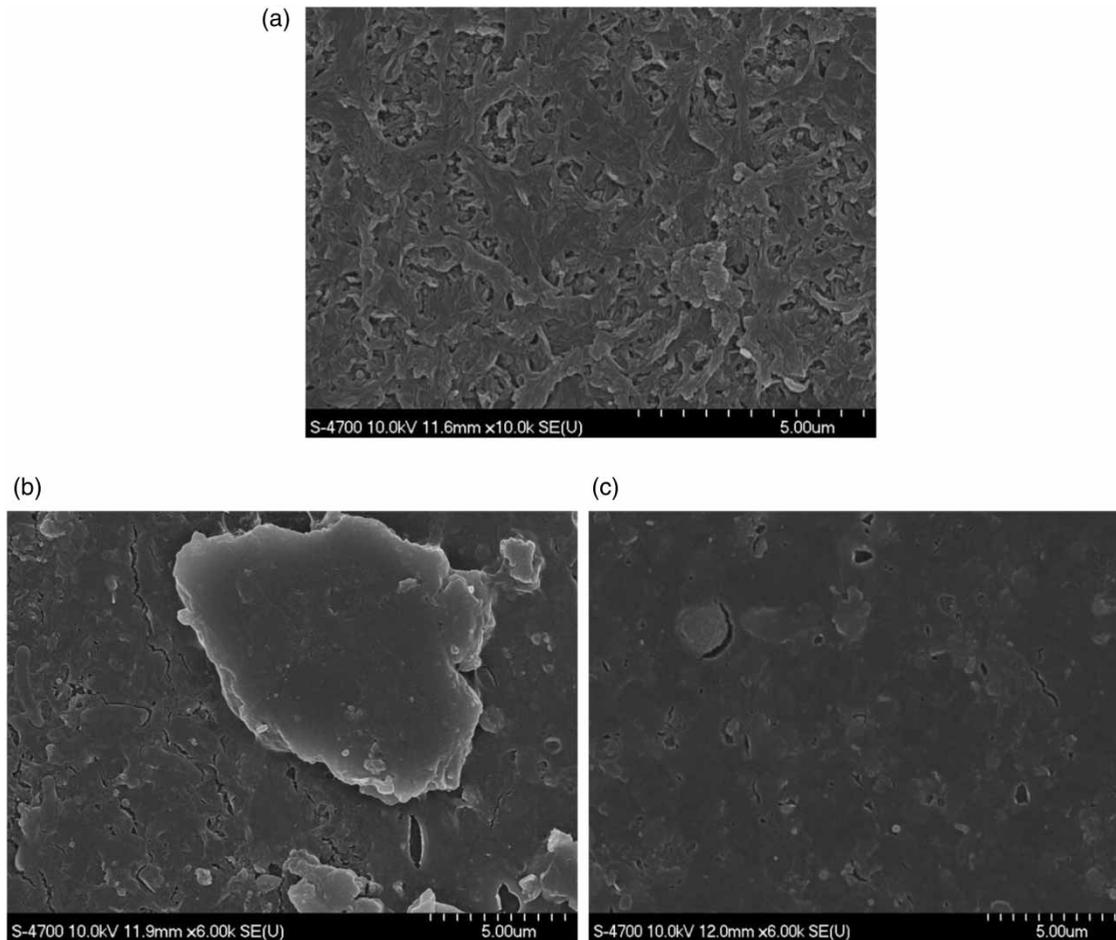


Figure 6 | SEM images (a) virgin NF membrane, (b) fouled membrane with the Tatamagouche source water and (c) fouled membrane with the Collins Park source water.

Park source water and the Tatamagouche source water. The SEM images of the virgin membrane demonstrate the network-like structure typical of a membrane polyamide layer (Mukherjee *et al.* 1996), while images of the fouled membranes showed different morphologies. The visual observations obtained from these SEM photos support the theory that surface adsorption is the dominant mechanism in NF fouling (Li & Elimelech 2004). The SEM images of the membrane fouled after treatment of the Collins Park source water showed a more homogeneous and dense foulant layer than the membrane fouled with the Tatamagouche source water.

Microbiological enumeration

Heterotrophic plate counts (HPCs) of the NF feed water and membrane foulant layers are presented in Figure 7. HPCs of

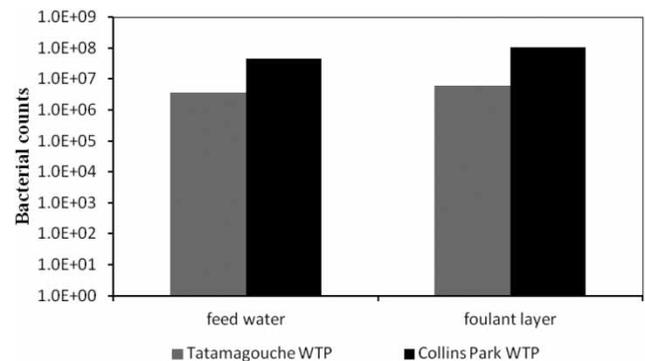


Figure 7 | Heterotrophic bacteria in the feed waters (CFU m⁻¹) and microbial cell counts in the foulant layers (CFU m⁻²).

the source waters were observed in the range 10⁶–10⁷. HPCs in both source waters are consistent with the range of values of HPC reported by Sanna *et al.* (1998) and Speth

et al. (1998) for surface waters. HPCs of the Collins Park source water were found to be more than an order of magnitude higher than those of the Tatamagouche source water. HPCs enumerated in the fouled membrane with the Collins Park source water were also an order of magnitude higher than HPCs quantified from the fouled membrane with the Tatamagouche source water.

Full-scale NF fouling analysis

Plant operational data were collected from 26 October to 19 December 2010 from both the Tatamagouche and Collins Park WTPs to evaluate NF fouling behavior of the two source waters at full-scale. Data were collected in real-time by the plant Supervisory Control and Data Acquisition (SCADA) system (VTSCADA, Trihedral Engineering

Limited, Bedford, Nova Scotia) and online instrumentation. Data were collected every two hours. The operational hours of the Collins Park NF membrane were much longer (412 hours) than for the Tatamagouche NF membrane (244 hours). The NF membrane at the Collins Park WTP was cleaned twice and the membrane at the Tatamagouche WTP was not cleaned.

Feed water temperature, membrane operating pressures and permeate flux data collected for this study from both plants are presented in Figure 8. The overall increase in feed pressure of the NF membranes in Collins Park and Tatamagouche WTPs were 25 and 5%, respectively. The feed pressure of the NF membrane in Collins Park increased from 6.3×10^5 Pa at 84 hours (on 9 Nov) to 8.4×10^5 Pa at 380 hours (on 13 Dec) in 296 hours of operation within one cleaning cycle. A second cleaning was performed at

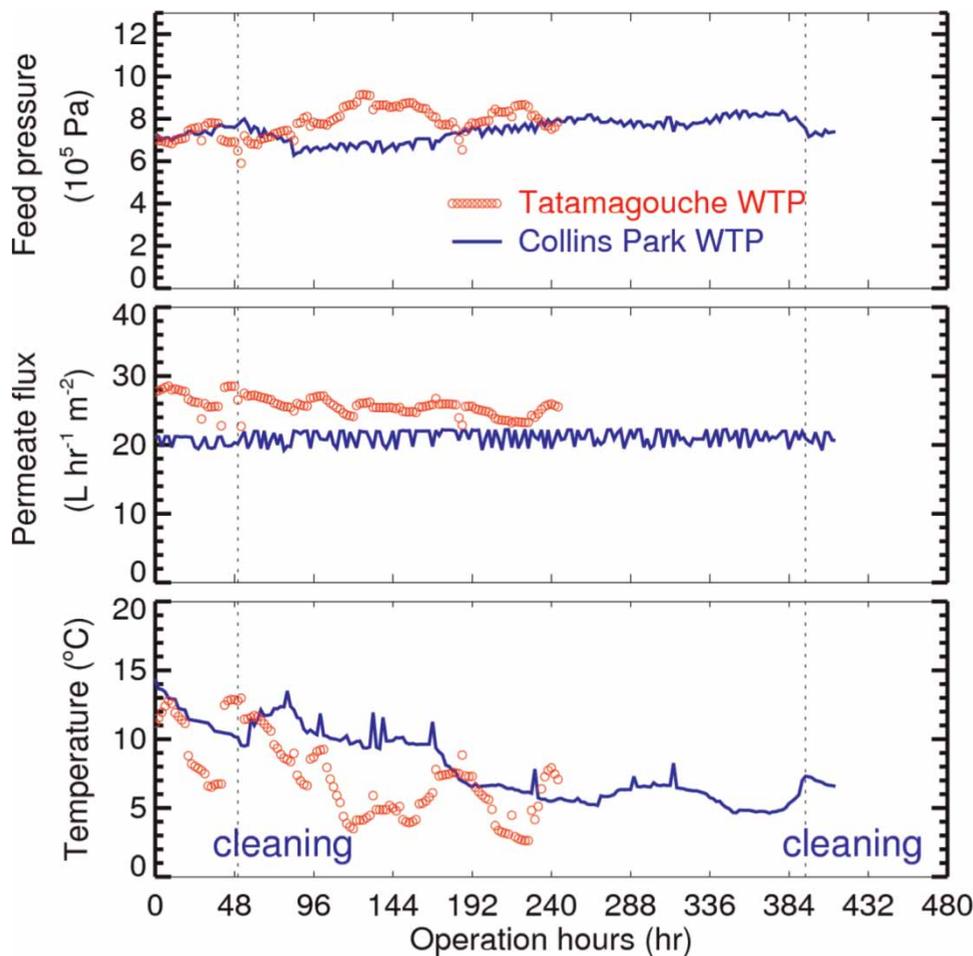


Figure 8 | Actual feed pressure and permeate flux of NF units at the Collins Park and Tatamagouche water treatment plants.

400 hours (on 15 Dec) since the feed pressure exceeded the maximum operating pressure 8.27×10^5 Pa. The feed pressure in the Tatamagouche WTP was varied from 5.9×10^5 Pa to 9.1×10^5 Pa in 244 hours of operation within the study period. As evident in Figure 8, the permeate flux of the NF membrane in the Collins Park WTP was almost constant. In principle, the NF system is designed to operate at constant permeate flux, and the feed pressure is adjusted to compensate for water flux changes when temperature changes. However, permeate flux at the Tatamagouche WTP appears to be changing over time following the trend of water temperature (approx. 0.58 correlation).

Temperature-corrected feed pressure of Collins Park within one complete cycle was nearly constant (Figure 9). This suggests that the increase in feed pressure was mostly associated with the decrease in water temperature because the viscosity of water increases with decreasing temperature (Sharma *et al.* 2003). The temperature-corrected feed pressure of the Tatamagouche WTP was almost constant to 4.2×10^5 Pa, suggesting that there was no significant NF fouling during the study period. The normalized permeate flux at 25 °C for the Collins Park WTP was $12.5 \text{ L h}^{-1} \text{ m}^{-2}$

at 48 hours before the first cleaning. The permeate flux increased to $13.8 \text{ L h}^{-1} \text{ m}^{-2}$ at 60 hours after the first cleaning was performed. This was followed by a gradual decrease in permeate flux to $10.3 \text{ L h}^{-1} \text{ m}^{-2}$ on 13 Dec during 380 hours of operation. After the second cleaning at 400 hours (on 15 Dec) the permeate flux was recorded as $10.9 \text{ L h}^{-1} \text{ m}^{-2}$ (on 16 Dec) which indicates that the cleaning procedure did not immediately return the permeate flux back to the initial value (i.e. $13.8 \text{ L h}^{-1} \text{ m}^{-2}$). Data collected from the Tatamagouche WTP also showed decreases in the normalized permeate flux at 25 °C. Review of the operator logs from both of the full-scale UF-NF facilities has shown that the NF membranes in the Collins Park WTP have been chemically cleaned almost every month in the spring and fall period, whereas the NF modules in the Tatamagouche WTP have been cleaned only once in the last 2 years of operation. Anecdotally, this showed that the source water quality contributed to membrane fouling at the Collins Park WTP. Based on the cleaning regime in full-scale, the primary NF fouling in the Collins Park WTP is due to organics and/or biological growth. The bench-scale NF fouling results provide evidence that biofouling could be a mechanism of fouling at the Collins Park WTP.

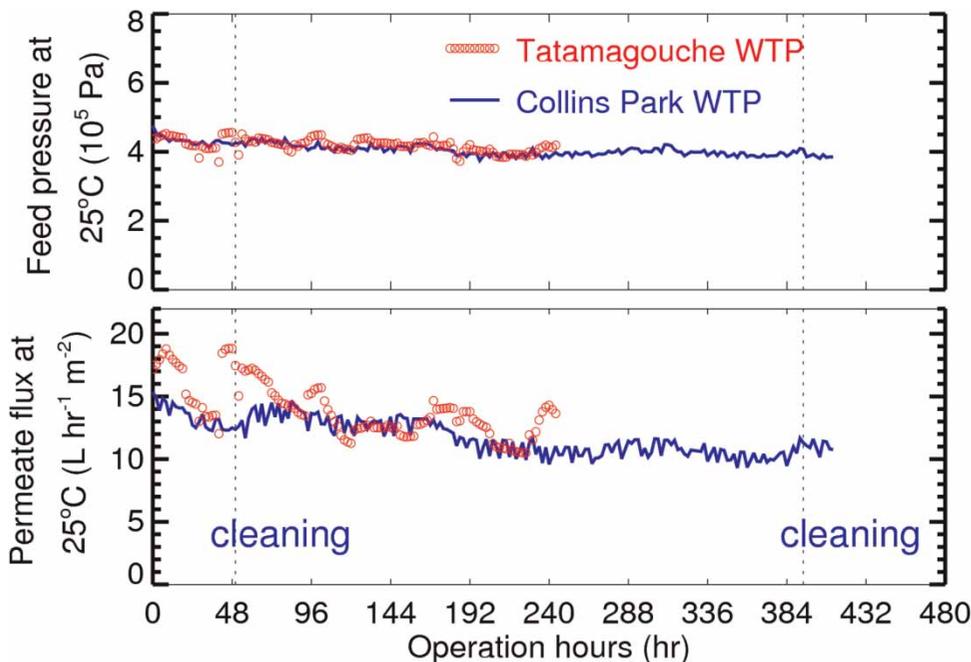


Figure 9 | Normalized permeate flux and feed pressure of NF units at the Collins Park and Tatamagouche water treatment plants.

CONCLUSIONS

The purpose of this study was to examine the impact of feed water characteristics on fouling behavior of commercial polyamide NF membranes by two surface source waters in Nova Scotia, Canada. The surface waters used in this study serve as source waters for two small-scale IMS drinking water treatment plants that utilize two different types of spiral wound NF membrane module.

Bench-scale NF fouling experiments were investigated under similar operating and NF membrane type conditions for the two source waters and results were compared. Results of the bench-scale study showed that Collins Park source water caused more NF fouling than the Tatamagouche source water. The AFM analysis showed higher average and root mean squared foulant layer roughness, the SEM analysis indicated a dense foulant layer, and microbiological enumeration revealed higher heterotrophic plate counts in membrane fouled with the Collins Park source water.

In addition, full-scale NF fouling data collected from the two IMS plants were compared in order to understand the real NF fouling conditions in these water treatment plants. Analyses of the full-scale NF fouling data showed that the overall trend of increase in the feed pressure of the Collins Park WTP was higher than the Tatamagouche WTP. Decrease in normalized permeate flux indicated a real NF fouling issue in the Collins Park WTP, while no clear fouling was observed in the Tatamagouche WTP. These observations support the current practices of regular membrane cleaning almost every month in the Collins Park WTP. Both the bench- and full-scale NF fouling studies suggested that the higher rate of NF fouling with the Collins Park source water was due to the higher concentration of DOC, conductivity and concentrations of ionic species.

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REFERENCES

- Al-Amoudi, A., Williams, P., Mandale, S. & Lovitt, R. W. 2007 Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability. *Separation Science and Technology* **54**, 234–240.
- Amy, G. 1990 Removal of dissolved organic matter by nanofiltration. *Journal of Environmental Engineering-ASCE* **116**, 1046–1062.
- APHA 1995 *Standard Methods for the Examination of Water and Wastewater*, 19th edition. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.
- Ates, N., Yilmaz, L., Kitis, M. & Yetis, U. 2009 Removal of disinfection by-product precursors by UF and NF membranes in low-SUVA waters. *Journal of Membrane Science* **328** (1–2), 104–112.
- Bellona, C., Drewes, J. E., Oilker, G., Luna, J., Filteau, G. & Amy, G. 2008 Comparing nanofiltration and reverse osmosis for drinking water augmentation. *Journal of American Water Works Association* **1000**, 102–116.
- Bellona, C., Marts, M. & Drewes, J. E. 2010 The effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes. *Separation and Purification Technology* **74**, 44–54.
- Braghetta, A. 1995 The influence of solution chemistry operating conditions on nanofiltration of charged and uncharged organic macromolecules. PhD dissertation.
- Braghetta, A., DiGiano, F. A. & Ball, W. P. 1997 Nanofiltration of natural organic matter: pH and ionic strength effects. *Journal of Environmental Engineering-ASCE* **123** (7), 628–641.
- Braghetta, A., DiGiano, F. A. & Ball, W. P. 1998 NOM accumulation at NF membrane surface: impact of chemistry and shear. *Journal of Environmental Engineering* **124** (11), 1087–1098.
- Cabaniss, S. E., Zhou, Q., Maurice, P. A., Chin, Y. -P. & Aiken, G. R. 2000 A log-normal distribution of model for the molecular weight of aquatic fulvic acids. *Environmental Science and Technology* **34**, 1103–1109.
- Childress, A. E. & Elimelech, M. 1996 Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science* **119** (2), 253–268.
- Chin, Y. P., Alken, G. & Loughlin, E. O. 1994 Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environmental Science and Technology* **28**, 1853–1858.
- Cho, J., Amy, G. & Pellegrino, J. 1999 Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. *Water Research* **33** (11), 2517–2526.
- Conlon, W. J. & McClellan, S. A. 1989 Membrane softening: a treatment process comes of age. *Journal of American Water Works Association* **81** (11), 47–51.

- Edwards, E. 1988 THM control using membrane technology. In *Proceedings, Joint FS/AWWA, FPCA, and FW&PCOA*, Fort Lauderdale, FL.
- Escobar, I. C., Hong, S. & Randall, A. A. 2000 Removal of assimilable organic carbon and biodegradable dissolved organic carbon by reverse osmosis and nanofiltration membranes. *Journal of Membrane Science* **175**, 1–17.
- Escobar, I. C., Randall, A. A., Hong, S. K. & Taylor, J. S. 2002 Effect of solution chemistry on assimilable organic carbon removal by nanofiltration: full and bench scale evaluation. *Journal of Water Supply: Research and Technology-AQUA* **51** (2), 67–76.
- GE Infrastructure 2008 Operation and Maintenance Manual, Water and Process Technologies, SWRO-200C System.
- Her, N., Amy, G., Foss, D., Cho, J., Yoon, Y. & Kosenka, P. 2002 Optimization of method for detecting and characterizing NOM by HPLC-size exclusion chromatography with UV and on-line DOC detection. *Environmental Science and Technology* **36**, 1069–1076.
- Her, N., Amy, G., Park, H.-R. & Song, M. 2004 Characterizing algogenic organic matter (AOM) and evaluating associated NF membrane fouling. *Water Research* **38** (6), 1427–1438.
- Her, N., Amy, G., Chung, J., Yoon, J. & Yoon, Y. 2008 Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. *Chemosphere* **70** (3), 495–502.
- Hong, S. & Elimelech, M. 1997 Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science* **132**, 159–181.
- Huang, X. J., Ryu, S.-W., Im, H.-S. & Choi, Y.-K. 2007 Wet chemical needlelike assemblies of single-walled carbon nanotubes on a silicon surface. *Langmuir* **23**, 991–994.
- Jarusutthirak, C., Mattaraj, S. & Jiratananon, R. 2007 Influence of inorganic scalants and natural organic matter on nanofiltration membrane fouling. *Journal of Membrane Science* **287**, 138–145.
- Lamsal, R., Walsh, M. E. & Gagnon, G. A. 2011 Comparison of advanced oxidation processes for the removal of natural organic matter. *Water Research* **45**, 3263–3269.
- Lamsal, R., Montreuil, K. R., Kent, F. C., Walsh, M. E. & Gagnon, G. A. 2012 Characterization and removal of natural organic matter by an integrated membrane system. *Desalination*, in press.
- Lee, S., Cho, J. & Elimelech, M. 2005 Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling. *Journal of Membrane Science* **262**, 27–41.
- Li, Q. & Elimelech, M. 2004 Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms. *Environmental Science and Technology* **38**, 4683–4693.
- Li, Y., Shahbazi, A., Williams, K. & Wan, C. 2008 Separate and concentrate Lactic acid using combination of nanofiltration and reverse osmosis membranes. *Applied Biochemistry and Biotechnology* **147**, 1–9.
- Macdonald, T., Gibson, C. T., Constantopoulos, J., Shapter, J. G. & Ellis, A. V. 2012 Functionalization of vertically aligned carbon nanotubes with polystyrene via surface initiated reversible addition fragmentation chain transfer polymerization. *Applied Surface Science* **258**, 2836–2843.
- Makdissy, G., Huck, P. M., Reid, M. M., Leppard, G. G., Haberkamp, J., Jekel, M. & Peldszus, S. 2010 Investigating the fouling layer of polyamide nanofiltration membranes treating two different natural waters: internal heterogeneity yet converging surface properties. *Journal of Water Supply: Research and Technology-AQUA* **59** (2–3), 164–178.
- Mänttari, M., Puro, L., Nuortila-Jokinen, J. & Nyström, M. 2000 Fouling effects of polysaccharides and humic acid in nanofiltration. *Journal of Membrane Science* **165**, 1–17.
- Mukherjee, D., Kulkarni, A. & Gill, W. 1996 Chemical treatment for improved performance of reverse osmosis membranes. *104* (3), 239–249.
- Nilson, J. A. & DiGiano, F. A. 1996 Influence of NOM composition on nanofiltration. *Journal of American Water Works Association* **88** (5), 53–66.
- Pressdee, J. R., Veerapaneni, S., Darby, H. L. S., Clement, J. A. & Hoek, J. P. V. d. 2006 Integration of membrane filtration into water treatment systems. AWWA Research Foundation, Denver, CO.
- Sanna, N., Gianturco, F. A., Pikramenou, Z., Baker, J. S. & Dudley, L. Y. 1998 Biofouling in membrane systems: A review. *Desalination* **118** (1), 81–89.
- Schäfer, A. I., Fane, A. G. & Waite, T. D. 2001 Cost factors and chemical pretreatment effects in the membrane filtration of waters containing natural organic matter. *Water Research* **35**, 1509–1517.
- Seidel, A. & Elimelech, M. 2002 Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: implications for fouling control. *Journal of Membrane Science* **203**, 245–255.
- Sharma, R. R., Agrawal, R. & Chellam, S. 2003 Temperature effects on sieving characteristics of thin-film composite nanofiltration membranes: pore size distributions and transport parameters. *Journal of Membrane Science* **223**, 69–87.
- Siddiqui, M., Amy, G., Ryan, J. & Oden, W. 2000 Membranes for the control of natural organic matter from surface waters. *Water Research* **34** (13), 3355–3370.
- Speth, T. F., Summers, R. S. & Gusses, A. M. 1998 Nanofiltration foulants from a treated surface water. *Environmental Science and Technology* **32**, 3612–3617.
- Summers, R. S., Hooper, S. M., Solarik, G. & Owen, D. 1996 Assessing DBP yield: uniform formation conditions. *Journal of American Water Works Association* **81** (7), 80–93.
- Tang, C. Y., Kwon, Y.-N. & Leckie, J. O. 2007 Fouling of reverse osmosis and nanofiltration membranes by humic acid: Effects of solution composition and hydrodynamic conditions. *Journal of Membrane Science* **290** (1–2), 86–94.
- USEPA 2003 Membrane Filtration guidance manual, Proposal Draft, EPA, 815-D-03-008. 1–87.
- Wu, W. C., Evans, R. D., Dillon, P. J. & Cai, Y. R. 2007 Rapid quantification of humic and fulvic acids by HPLC in natural waters. *Applied Geochemistry* **22**, 1598–1605.