

Characterization of performance of full-scale tertiary membranes under stressed operating conditions


Sara Abu-Obaid, Pierre Bérubé  and Wayne J. Parker 

ABSTRACT

This study sought to identify factors responsible for enhanced fouling of ultrafiltration membranes used in tertiary wastewater treatment under challenging conditions of high flow and low temperature. A detailed analysis of full-scale membrane operating data was conducted, and this was supported by data gathered through a field sampling campaign. Higher average fouling rates and average recoveries were observed during periods of highest flows and lowest temperatures. The results demonstrated that the negative impact of seasonal changes on short-term fouling are readily reversible, while hydraulically irreversible fouling, which is responsible for intermediate and long-term fouling rates, is not effectively recovered by maintenance cleans (MCs) but is recovered by recovery cleans (RCs). An examination of membrane feedwater quality revealed that high fouling rates correlated to an increase in dissolved organic carbon (DOC) concentrations, with the biopolymer fraction of the DOC being most important. Increased capillary suction time (CST) values, which indicate reduced sludge dewaterability, were also observed during high fouling events. It was concluded that seasonal variations result in the increased release of extracellular polymeric substances (EPS) by microorganisms, which leads to higher membrane fouling and worsened dewaterability of the activated sludge.

Key words | flow, fouling, seasonal variation, temperature, ultrafiltration membranes, wastewater tertiary treatment

Sara Abu-Obaid (corresponding author)

Wayne J. Parker 

Department of Civil and Environmental Engineering,

University of Waterloo,

200 University West, N2 L 3G1, Waterloo, Ontario, Canada

E-mail: ssabuoba@uwaterloo.ca

Pierre Bérubé 

Department of Civil Engineering,

University of British Columbia,

6250 Applied Science Lane, V6T 1Z4, Vancouver, British Columbia,

Canada

ABBREVIATIONS

BP	Back-pulse	TCP	Temperature corrected permeability
cBOD ₅	Carbonaceous biological oxygen demand	TMP	Trans-membrane pressure
COD	Chemical oxygen demand	TOC	Total organic carbon
CST	Capillary suction time	UF	Ultrafiltration
DOC	Dissolved organic carbon	WPCP	Water pollution control plant
EPS	Extracellular polymeric substances		
FI	Fouling index		
HRT	Hydraulic retention time		
LC-OCD	Liquid chromatography–organic carbon detection		
MBR	Membrane bioreactor		
MC	Maintenance clean		
NOM	Natural organic matter		
NR	Net recovery		
R	Recoveries in permeability		
RC	Recovery clean		
SMP	Soluble microbial products		
SRT	Solids residence time		

INTRODUCTION

Membrane technologies are increasingly being employed in wastewater treatment applications to meet stringent regulations on suspended solids and pathogen concentrations, often in support of water reuse initiatives (Torà-Grau *et al.* 2015). Membranes can be incorporated in the treatment train downstream of activated sludge – tertiary membranes – or as membrane bioreactors (MBRs) (Kent *et al.* 2011). Although membrane technology has proven to be effective in producing high-quality effluent, membrane

fouling has limited its widespread use as it leads to increased operational costs and a decline in overall performance (Ma *et al.* 2013). Increased fouling also leads to the need for membrane cleaning, which requires the use of chemicals, increasing costs of operation and shortening membrane life-span (Abdullah & Bérubé 2013).

Membrane fouling can be divided into two categories: short-term hydraulically reversible fouling, which can be mitigated by physical membrane cleaning such as backwashing, and hydraulically irreversible fouling, which cannot be mitigated by physical membrane cleaning and thus needs chemical membrane cleaning (Chang *et al.* 2002). Although similar membranes are used for MBRs and tertiary filtration, it is anticipated that the systems will have somewhat different fouling mechanisms. This is expected because the membranes in MBRs interact with a range of potential foulants that span from materials present in raw wastewater to biological solids and products (Rosenberger *et al.* 2006). In contrast tertiary membranes are exposed to mainly soluble (i.e. non-settleable) components.

There are very few studies focused on fouling of tertiary membranes. Prior studies of tertiary membrane applications have primarily focused on average operating conditions and have not addressed dynamic changes in operating conditions. Subsequent conditions, such as low temperatures and short hydraulic residence times (HRTs), may stress the upstream bioreactor (Citulski *et al.* 2009; Soler-Cabezas *et al.* 2015). Hence, literature on MBRs operating under such conditions was reviewed to identify mechanisms that may impact tertiary membranes.

Fluctuations in operating conditions, such as temperature, flow, and raw wastewater characteristics can affect bioreactor performance and consequently the foulant characteristics in membrane feed streams. Several studies of deterioration of membrane performance in MBRs under low operating temperatures have been reported (Rosenberger *et al.* 2006; Al-Halbouni *et al.* 2008; van den Brink *et al.* 2011; Sun *et al.* 2014). Fouling under low operating temperatures has been attributed to the presence of elevated concentrations of supernatant organics (humics, polysaccharides, and proteins), differences in water viscosity with temperature (Ma *et al.* 2013; Sun *et al.* 2014), and reduced recovery of flux after membrane cleaning (Martín-Pascual *et al.* 2015). Further, in prior studies of membrane fouling in drinking water applications, biopolymers, which consist of polysaccharides, proteins, and protein-like substances, were reported to be the fraction of dissolved natural organic matter (NOM) which contributed most to fouling of low-pressure membranes (Croft 2012).

The operation of MBRs under cold water conditions has been reported to lead to changes in sludge characteristics that could be used as indicators of membrane fouling potential. Lyko *et al.* (2007) demonstrated that temperature impacted the mixed liquor carbohydrate concentration, corresponding to changes in sludge dewaterability. Al-Halbouni *et al.* (2008) observed a negative impact on sludge dewaterability with an increase of soluble extracellular polymeric substance (EPS) concentration. Further, Le-Clech *et al.* (2006) revealed a direct relationship between soluble carbohydrates, fouling rates, and capillary suction time (CST). The results of these studies highlight the value of monitoring sludge properties when studying the effects of seasonal variation on fouling of tertiary membranes. Consequently, it may be expected that components (primarily soluble) released from the activated sludge process would impact on the downstream membranes.

The goal of the present study was to investigate seasonal variations in the performance of tertiary membranes and determine the underlying cause of observed performance deterioration (increased fouling or reduced cleaning efficiency). The study sought to identify critical operating conditions leading to fouling, and to obtain an improved understanding of foulant characteristics under such conditions. This was achieved through the analysis of historical data generated over a two-year period (2016–2017) and through a 17-month field sampling campaign of the full-scale tertiary membranes employed at the Keswick Water Pollution Control Plant (WPCP) in the Region of York, Ontario, Canada. This plant treats municipal wastewater and has reported substantial deterioration in the performance of tertiary membranes during the early spring period of March to May. This period is characterized by low wastewater temperatures and elevated flows. The Keswick WPCP was used as a case study to obtain insight into the interaction between dynamic operating conditions and membrane performance.

MATERIALS AND METHODS

Keswick WPCP

The Keswick WPCP has a design capacity of 18,000 m³/d and treats municipal wastewater using an extended aeration activated sludge process – median solids residence time (SRT) of 14 days, HRT of 21 hours – that is followed by tertiary ultrafiltration (UF) membrane filtration system. The dissolved oxygen concentration in the aeration tanks is

controlled to achieve a minimum of 1.0 mg/L during peak load periods and 2–3 mg/L during average load periods. A plant schematic is provided in Figure 1. The tertiary treatment consists of a flocculation tank followed by micro-screens and five UF membrane trains. Alum is dosed just prior to the flocculation tank to create phosphorous precipitates that are subsequently captured by the UF membrane system. Each membrane train consists of six cassettes with 48 modules in each cassette. The trains contain bundles of ZeeWeed 1,000 v4 (Suez) hollow-fiber membranes operating under negative pressure created within the hollow fibers by permeate pumps. The membranes remove relatively large particles, such as microbes, bacteria and macromolecules, with molecular weights greater than about 300,000 Da.

The UF trains are operated at a predetermined net maximum production flow of 405 m³/h/train (flux of 29 L/m² h). Depending on plant demand, an UF train proceeds to production and then back-pulse (BP) modes. This continues until the permeate flow demand decreases, placing the train on standby. As a result, the number of

trains permeating at any time depends on plant flow. Treated water is used to BP the membranes (i.e. backwash) to maintain stable trans-membrane pressure (TMP) in the trains. The membranes are backpulsed using pumps with a maximum capacity of 805 m³/h and aerated using membrane blowers. The membranes are also periodically chemically cleaned using maintenance cleans (MCs) and recovery cleans (RCs) to restore permeability. The trains undergo MCs and RCs according to a set schedule that is modified when the membranes' TMP approaches a maximum value. At the start of the MCs and RCs the membranes are backpulsed to remove solids prior to adding chemicals to improve the cleaning effectiveness. For MCs, the membranes are soaked in 100 mg/L of a hypochlorite solution for 15 min. For RCs, the membranes are normally soaked in 500 mg/L of a hypochlorite solution for 6 hours, and occasionally soaked in 2,000 mg/L of citric acid for the same duration. After cleaning, the membranes are backpulsed with permeate water, and the spent chemical solution and backpulse water are flushed to a cleaning tank.

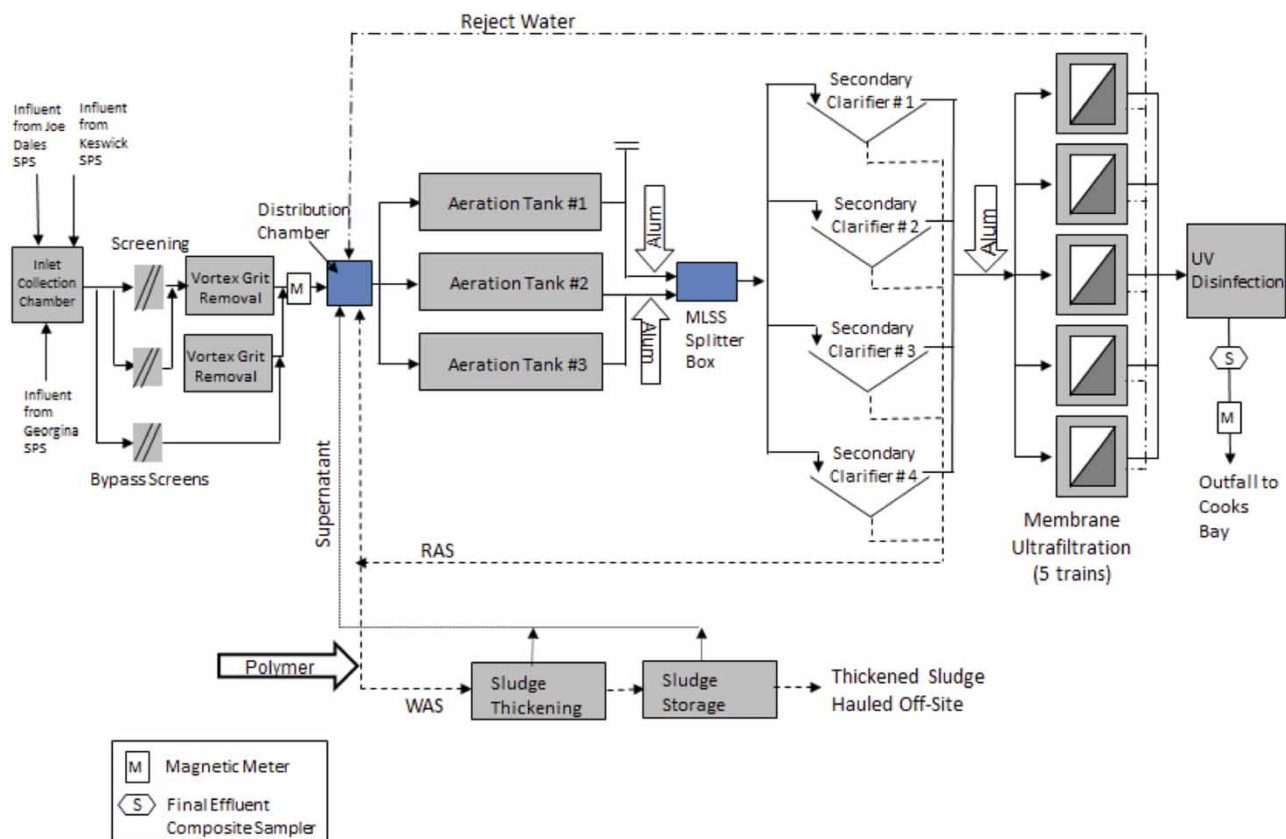


Figure 1 | Keswick WPCP schematic.

Historical data analysis

Detailed historical data of membrane operations were analyzed to obtain a comprehensive understanding of membrane performance over time at the Keswick WPCP. The historical data was obtained from the InSight[®] asset performance management (APM) tool (Suez Water Technologies and Solutions). At the Keswick WPCP, InSight[®] is used to provide real-time data on the performance of the membrane trains. InSight[®] allows for visualization of membrane key performance indicators (KPIs). Within the software, membrane permeability values are calculated from measured flux and TMP values and then corrected to reflect the impact of temperature on water viscosity. Equation (1) was used to calculate temperature corrected permeabilities (TCP) to a standard temperature of 20 °C. The viscosity of water was calculated using Equation (2).

$$TCP = \frac{\mu_T}{\mu_{20}} * P_T \quad (1)$$

where:

μ_T : Viscosity of water at temperature T (cP)

μ_{20} : Viscosity of water at 20 °C (cP)

P_T : Observed permeability at temperature T (Lmh/bar)

$$\mu_T = 1.415 \times 10^{-7} T^4 - 2.079 \times 10^{-5} T^3 + 1.395 \times 10^{-3} T^2 - 5.992 \times 10^{-2} T + 1.786 \quad (2)$$

where:

μ_T : Viscosity of water at temperature T (cP)

T: Water temperature (°C)

The rates of fouling between consecutive BPs, MCs and RCs, and the recoveries of permeability that were achieved in the various cleaning processes were quantified. In the analysis, a cycle was defined as the production period between two successive cleans. Fouling indices (FI) were employed to quantify the rates of fouling (i.e. decrease in membrane permeability) for each operating cycle. Fouling indices between successive BPs (FI_{BP}), MCs (FI_{MC}), and RCs (FI_{RC}) were calculated for two representative trains (UF1 and UF4) to confirm the reproducibility of the data. Sun et al. (2014) and Ma et al. (2013) suggested that declines in permeability during cold water periods was the result of changes in water viscosity with temperature. Hence, TCPs were used to calculate FI values in the current study to account for changes in viscosity. TCP values that were estimated before (B), after (A), and during (D) a BP were used

for the calculation of FI metrics. Fouling indices between consecutive BP (short-term fouling), representing hydraulically reversible fouling, were calculated using Equation (3).

$$FI_{BP} = \frac{A_N - B_{N+1}}{\Delta t} \quad (3)$$

where:

FI_{BP} : Fouling index between two BPs (Lmh/bar·min)

A_N : TCP immediately after BP (Lmh/bar)

B_{N+1} : TCP immediately before subsequent BP (Lmh/bar)

Δt : Length of permeation between consecutive BP (min)

Fouling indices between consecutive MCs (intermediate fouling) and RCs (long-term fouling), representing hydraulically irreversible fouling, were calculated using Equation (4). For all calculations involving MCs or RCs, the TCP values observed during BPs were used to estimate FI values as this ensured that the fluxes employed in the calculations were consistent.

$$FI_{MC} \text{ or } FI_{RC} = \frac{D_{N+1(C)} - D_{N-1(C+1)}}{\Delta t} \quad (4)$$

where:

FI_{MC} : Fouling index between two MCs (Lmh/bar·min)

FI_{RC} : Fouling index between two RCs (Lmh/bar·min)

$D_{N+1(C)}$: TCP during BP for initial BP after clean (MC or RC) (Lmh/bar)

$D_{N-1(C+1)}$: TCP during BP for the last BP before subsequent clean (Lmh/bar)

Δt : Length of permeation between consecutive MCs or RCs (min)

Recoveries in permeabilities (R) were estimated to quantify the efficiency of the different membrane cleaning approaches and to determine if R values were affected by the operational conditions. R values reflected the improvement in TCP after membrane cleans and were calculated using Equation (5) for BPs (R_{BP}), which are frequent and expected to affect short-term fouling. Recovery in permeability values for MCs (R_{MC}) and RCs (R_{RC}), which are infrequent and expected to affect intermediate and long-term fouling respectively, were calculated using Equation (6).

$$R_{BP} = A_N - B_N \quad (5)$$

where:

R_{BP} : Recovery in permeability due to BP (Lmh/bar)

A_N : TCP after BP (Lmh/bar)

B_N : TCP before BP (Lmh/bar)

$$R_{MC} \text{ or } R_{RC} = D_{N+1(c)} - D_{N-1(c)} \quad (6)$$

where:

R_{MC} : Recovery in permeability due to MC (Lmh/bar)

R_{RC} : Recovery in permeability due to RC (Lmh/bar)

$D_{N+1(c)}$: TCP during BP for initial BP after clean (MC or RC) (Lmh/bar)

$D_{N-1(c)}$: TCP during BP for the last BP before clean (MC or RC) (Lmh/bar)

Net recovery (NR) values were calculated to determine if the permeability lost within a cycle was fully recovered by membrane cleaning at the end of the same cycle. NR values were calculated for each cleaning type (NR_{BP} , NR_{MC} , NR_{RC}) as the difference between each R value and the numerator of the corresponding FI value. Equations (7) and (8) were used to calculate NR for BP, and for MC and RC respectively.

$$NR_{BP} = R_{BP} - (A_{N-1} - B_N) \quad (7)$$

where:

NR_{BP} : Net recovery in permeability due to BP (Lmh/bar)

R_{BP} : Recovery in permeability due to BP (Lmh/bar)

A_{N-1} : TCP immediately after previous BP (Lmh/bar)

B_N : TCP immediately before BP (Lmh/bar)

$$NR_{MC} \text{ or } NR_{RC} = R_{MC \text{ or } RC} - (D_{N+1(C-1)} - D_{N-1(C)}) \quad (8)$$

where:

NR_{MC} : Net recovery in permeability due to MC (Lmh/bar)

NR_{RC} : Net recovery in permeability due to RC (Lmh/bar)

$R_{MC \text{ or } RC}$: Recovery in permeability due to MC or RC (Lmh/bar)

$D_{N+1(C-1)}$: TCP during BP for initial BP after previous clean (MC or RC) (Lmh/bar)

$D_{N-1(C)}$: TCP during BP for the last BP before clean (MC or RC) (Lmh/bar)

A custom [MATLAB \(2018\)](#) application was developed to extract the parameters used in Equations (3)–(8) from the historical data and to calculate the FIs, Rs, and NR. Data describing the permeate temperature and raw wastewater daily flow were also extracted from the database over the study period using a custom MATLAB application.

The reduction in permeability over an extended period of operation can result from an increase in the rate of fouling, and/or a decrease in the efficiency of cleaning. Historical FIs were used to identify increases in fouling, while R and NR values were used to identify potential decreases in cleaning efficiency. A two-year operating period (2016–2017) was examined and this resulted in a large dataset available for interpretation ([Table 1](#)).

Field sampling and characterization

To supplement the results of the historical data analysis, the membrane feedwater was characterized over an extended period of time. The sampling programme was developed to generate data on changes in membrane feedwater composition and characteristics and, therefore, samples were collected at an increased frequency during periods of high fouling and reduced frequency during low fouling periods. Triplicate grab samples were collected from the effluent of the micro-screens (influent to the UF membranes) on a weekly basis between January and May 2017 (early spring). The sampling frequency was then reduced to once per month during the subsequent period to develop a baseline of operations. The sampling frequency reverted to a weekly basis for the period between January and May 2018 to obtain a detailed characterization of fouling under the second early spring period.

Samples of additional process streams were collected to gain further insight into potential causes of fouling. Triplicate samples of the raw wastewater entering the plant (influent to bioreactor) were collected between October 2017 and May 2018 to assist with identification of the source of foulants. Samples were collected once per month between October and December 2017, then biweekly

Table 1 | Number of membrane performance indicator values considered

Indicator	Number
FI_{BP}	6,593
FI_{MC}	569
FI_{RC}	59
R_{BP}	7,371
R_{MC}	509
R_{RC}	65
NR_{BP}	3,158
NR_{MC}	257
NR_{RC}	37

from January to May 2018. In addition, duplicate grab samples of the mixed liquor from the plant's north and south aeration basins were collected at the same frequency as the membrane feed, to gain insight into the activated sludge characteristics during the study.

Samples of the membrane feedwater were characterized with respect to a number of water quality parameters that were anticipated to have potential impacts on membrane permeability (Table 2). Saravia *et al.* (2006) reported a significant influence of ionic strength, especially of calcium ions, on the permeability of membranes in an MBR. Hence, the concentrations of various cations and anions were measured for this study. Nitrogen species concentrations were also measured as they were considered to be indicators of the state of nitrification in the biological process. The remaining parameters – total organic carbon (TOC), dissolved organic carbon (DOC), carbonaceous biological oxygen demand (cBOD₅), chemical oxygen demand (COD), turbidity – were included as measures of colloidal and dissolved organic matter which are suspected to foul UF membranes (Citulski *et al.* 2009)

The water quality parameters described in Table 2 were analyzed by the York-Durham Regional Environmental Laboratory as per Standard Methods (APHA 2017). Temperature, pH, and turbidity were measured on site using HACH probes, while samples for the remaining analytes were transported on ice to the laboratory for analysis.

Membrane feedwater and raw wastewater samples were transported to the University of Waterloo for further testing. The samples collected were analyzed for NOM sub-

fractions, using liquid chromatography coupled with organic carbon detection (LC-OCD) (Huber & Frimmel 1991; Lankes *et al.* 2009). Samples were filtered through 0.45 µm PES filters within 24 hours of sampling and stored at a temperature of 4 °C before processing (generally conducted within 48 hours of sampling).

The dewaterability of the mixed liquor was characterized to obtain an indirect measure of changes in floc properties, a potential result from changes in EPS content, which is a potential membrane foulant. Samples of the activated sludge mixed liquor were analyzed using the CST method. A Triton Electronics Ltd Type 304M CST analyzer was used for this study.

Statistical analysis

Various statistical tools were used to assist with identifying critical operating conditions leading to membrane performance deterioration and changes to foulant characteristics. Regression analysis was used to determine the relationship between operating parameters, water quality characteristics, and fouling indices, using Microsoft Excel's (16.23) Regression Tool. Correlation coefficients were calculated to determine the strength of relationships between selected variables (Montgomery & Runger 2002). Multivariable linear regression was used to assess whether fouling was dependent on the concentration of the five fractions of dissolved NOM determined by LC-OCD. Additionally, a two-tailed t-test – using Microsoft Excel's (16.23) Regression Tool – was used to determine if there was a significant statistical difference between two datasets.

Table 2 | Water quality parameters measured

Parameter	Units
pH	–
Conductivity	µS/cm
Temperature	°C
Turbidity	NTU
Total organic carbon (TOC)/dissolved organic carbon (DOC)	mg/L
Carbonaceous biological oxygen demand (cBOD ₅)	mg/L
Chemical oxygen demand (COD)	mg/L
Dissolved organic nitrogen (DON)	mg/L
Cation concentrations (Ca ⁺ , Mg ⁺² , K ⁺ , Na ⁺)	mg/L
Anion concentrations (Br ⁻ , Cl ⁻ , F ⁻ , SO ₄ ⁻ P)	mg/L
Nitrogen species concentrations (NH ₄ , NO ₃ ⁻ , NO ₂ ⁻ , total)	mg/L
Total Kjeldahl nitrogen (TKN)	mg/L

RESULTS

Membrane performance

In order to obtain a comprehensive understanding of membrane performance over time, the FI, R and NR values that were observed between BPs, MCs, and RCs were analyzed below to identify patterns in performance and compare the responses obtained in the two observation years.

Fouling indices

FI values were estimated for each cycle of membrane operation to describe the rate of deterioration of membrane permeability over the two year observation period. The fouling patterns of two operating trains (UF1 and UF4) were

initially assessed to evaluate reproducibility between membrane modules. The results of a correlation analysis between UF1-FI_{BP} and UF4-FI_{BP} are presented in Figure S1 (Supplementary Material). As illustrated in Figure S1, the relationship between both trains was linear; with slopes of 0.9615 ($r^2 = 0.774$) and 0.9337 ($r^2 = 0.6673$) for 2016 and 2017, respectively. The similar performance patterns between both trains were observed for all other performance indicators. Hence, it was concluded that membrane performance was independent of the train used and only the results of one train are presented in the remainder of the paper.

In this study, membrane fouling was examined between BP operations (FI_{BP} referred to as short-term fouling), maintenance cleans (FI_{MC} referred to as intermediate-term fouling) and recovery cleans (FI_{RC} referred to as long-term fouling) and the resulting values are presented in Figure 2. From Figure 2 it can be observed that in the 2016 period (Figure 2(a) and 2(c)), all FI metrics substantially increased for an extended period of time (March to May) and this appeared to correspond to periods of seasonally low temperature and high flow. Short-term fouling in 2016 was lowest during the period from July to October. In contrast,

in 2017, the FI metrics demonstrated several peaking events with shorter durations. The most significant fouling event was observed during the month of May as this was the period when all three FI metrics increased. While the patterns in short-term fouling rates differed between 2016 and 2017, the water temperature patterns were nearly identical (Figure S2). As shown in Figure S2, seasonal variation in temperature in 2016 and 2017 were similar. By contrast, the seasonal variation in flows differed between the two observation years, with an extended period of higher flows observed between March and May for 2016 ($>12,000 \text{ m}^3/\text{d}$), and multiple shorter duration periods of elevated flow for 2017. For both observation years, the lowest water temperatures ($<13 \text{ }^\circ\text{C}$) occurred between March and May. Viewed collectively, the results suggested a dependence of fouling on operating conditions, which was then subsequently examined in greater detail.

Permeability recovery

The previously described analysis of FI metrics suggested that there were periods of the year when membrane fouling

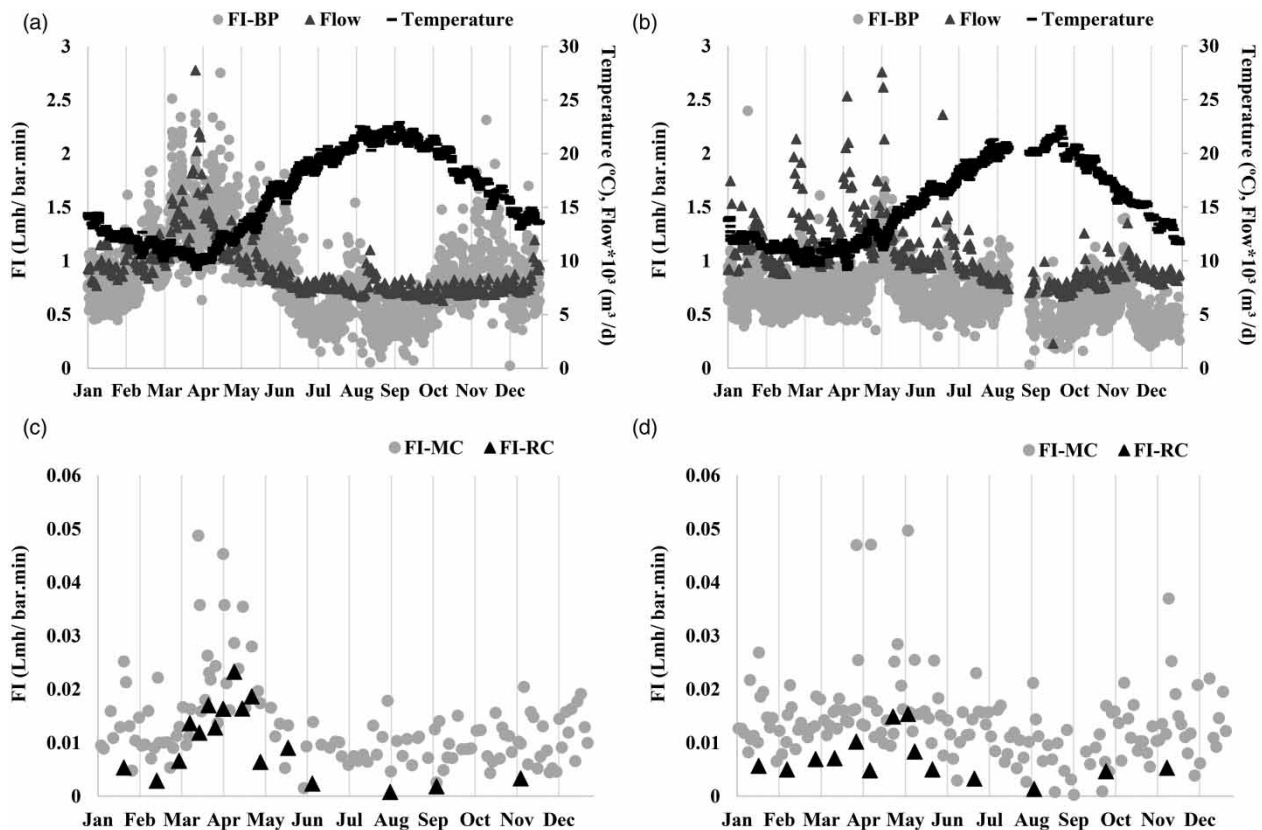


Figure 2 | Fouling index metrics, operating temperature and wastewater flow for (a) BP 2016, (b) BP 2017, (c) MC and RC 2016, (d) MC and RC 2017.

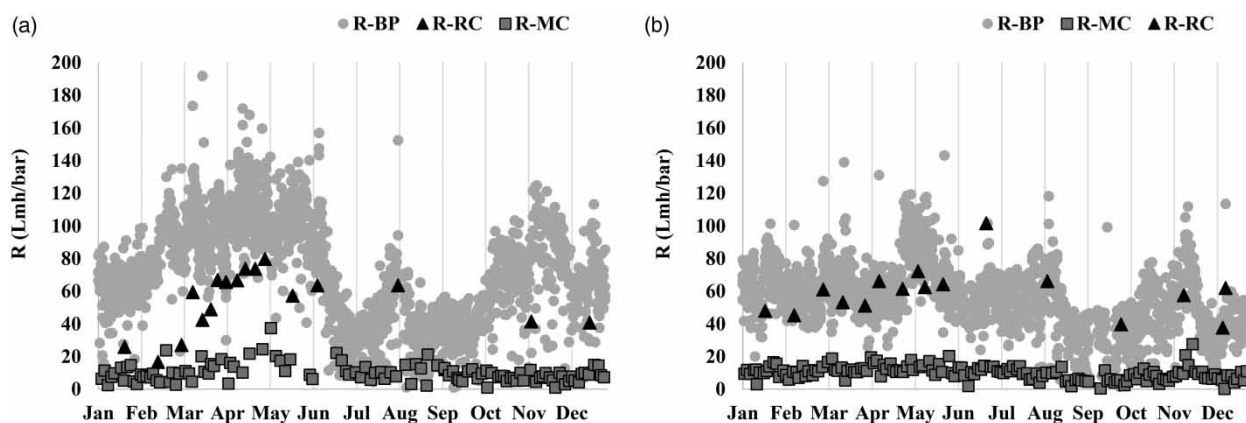


Figure 3 | Recovery in permeability after BP, MC, and RC for 2016 (left) and 2017 (right).

was enhanced. However, it was possible that reductions in permeability during these periods were also due to reduced effectiveness of membrane cleaning operations. Hence, the recovery of permeability due to back-pulsing (R_{BP}), maintenance cleans (R_{MC}) and recovery cleans (R_{RC}) was examined in detail. A preliminary comparison of the FI_{BP} values (Figure 2) with the corresponding R_{BP} values (Figure 3) suggested that the negative impact of seasonal changes in short-term fouling were readily recoverable and did not impact membrane performance in the lower fouling period. This was quantitatively examined in the ‘Net recoveries’ section. In contrast, the trends in recovery of permeability during MC and/or RC did not follow short-term, intermediate, or long-term fouling rates as closely. R_{MC} values were relatively constant throughout each year, while R_{RC} values increased in response to the increase in long-term fouling (FI_{RC}). However, when the fouling decreased after the month of May of each year, R_{RC} values remained relatively high well into the summer (i.e. July

and August). These results suggested that the negative impacts of seasonal changes on intermediate fouling were not readily recoverable, or they impacted on membrane performance over an extended period.

Net recoveries

NR values were calculated to determine if permeability lost to short, intermediate, and long-term fouling was fully recovered by BP, MC and RC. As illustrated in Figure 4, BP recovered short-term fouling consistently for 2016 and 2017 – indicated by NR_{BP} values that did not deviate substantially from zero (± 10 Lmh/bar). By contrast, negative NR_{MC} values were observed in the period between March and May of 2016, and during May of 2017 (Figure 4), indicating that intermediate fouling was not entirely recovered by MC during this period. As shown in Figure 3, the recovery in permeability by MC was constant during the entire year and did not significantly improve during periods of

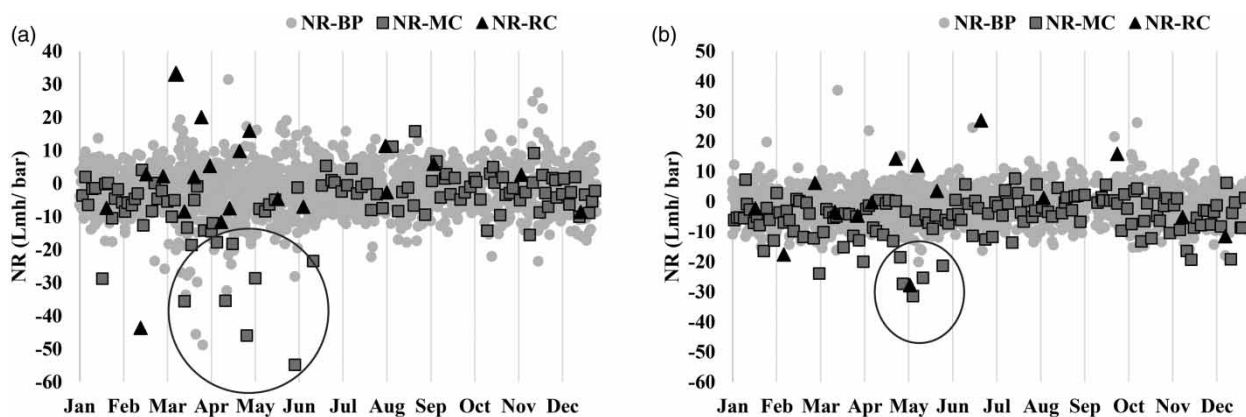


Figure 4 | Net recoveries by BP, MC, and RC for 2016 (left) and 2017 (right).

higher intermediate fouling. This may have been due to the fixed, relatively short duration of maintenance cleaning (15 min). The results suggest that this duration was sufficient to recover fouling during the summer but not during the spring.

The results suggest that the deterioration in performance during the spring season may have been due to changes in foulant characteristics during this period. The effectiveness of BP and RC were not affected by changes in foulant characteristics, but the effectiveness of MC in removing the elevated levels of foulants decreased. Changes in foulant characteristics during spring are further investigated in the 'Foulant characteristics' section.

Impact of operating conditions

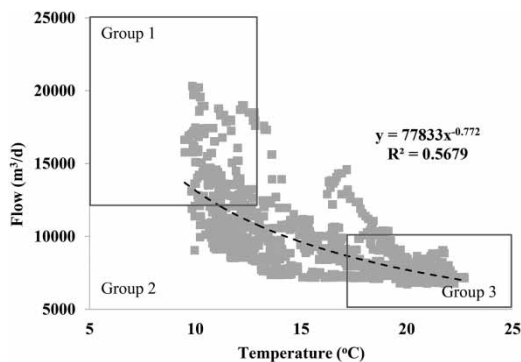
Membrane performance indicated that both temperature and flow affected membrane performance, hypothesizing that this may have resulted from their impact on the performance of the activated sludge process. To gain additional insight into the interaction between temperature and plant wastewater flow, the historical data for these parameters from the two observational years were plotted against each other, resulting in a non-linear inverse relationship (Figure 5). As shown in Figure 5, the periods of lowest temperatures were generally characterised by highest flows, and periods of highest temperatures were characterized by lowest flows. The strong relationship between flow and temperature on fouling made it challenging to separately assess the impact of these operating parameters on membrane fouling.

Since it was not possible to isolate the impacts of temperature and flow on membrane performance, it was elected to compare membrane performance metrics between 'bins' of operating conditions. Each bin reflected a combination of temperature and flow. The bins were selected based on a visual inspection of the extreme highs and lows in temperatures and flows demonstrated in Figure 2. The

membrane metrics were clustered into the three groups summarised in Figure 5. Average values of the metrics FI, R, and NR associated with BP, MC, and RC were calculated for Group 1 and Group 3. These represent the extremes in operating conditions, summarised in Figure 5. This approach facilitated a quantitative assessment of the relationship between the fouling metrics and the operating conditions.

From Figure 6(a) it can be observed that the average short, intermediate, and long-term fouling rates were highest for Group 1 conditions of lowest temperatures and highest flows. The average fouling rates were lowest for Group 3, which represented periods of lowest flows and highest temperatures. Using a two-tailed t-test, the fouling rates (FI_{BP} , FI_{MC} and FI_{RC}) for Groups 1 and 3 were determined to be statistically different ($P < 0.05$). The average recoveries also followed a similar pattern, with relatively higher recoveries for Group 1 that decreased for Group 3. However, as demonstrated in Figure 6(b), the average R_{MC} was relatively low when compared to R_{BP} and R_{RC} values. The average R_{MC} value was higher for Group 1 and it decreased for Group 3; these values were relatively low for both groups when compared to R_{BP} and R_{RC} . There was a significant statistical difference between R_{BP} and R_{MC} for Groups 1 and 3 ($P < 0.05$, t-test). However, this was not the case for R_{RC} ($P = 0.1406$, t-test).

The NR metric provided insight into the ability of cleaning exercises to recover the permeability that was lost to fouling in an operational period (Figure 6(c)). The average NR_{BP} , NR_{MC} , and NR_{RC} values for all groups were relatively close to 0; except for NR_{RC} which had a value of 4.1 (Lmh/bar-min) for Group 3, and NR_{MC} which had a value -12 (Lmh/bar-min) for Group 1. However, similar to average recoveries, there was a significant statistical difference between R_{BP} and R_{MC} for Groups 1 and 3 ($P < 0.05$, t-test) but not for R_{RC} ($P = 0.3955$, t-test). This indicated that the permeability decrease due to intermediate fouling was substantially higher than permeability recovered by MCs during Group 1 conditions. The



	Flow (m ³ /d)	Temperature (°C)
Group 1	>12000	<13
Group 3	<10000	>17

Figure 5 | Relationship between temperature and flow.

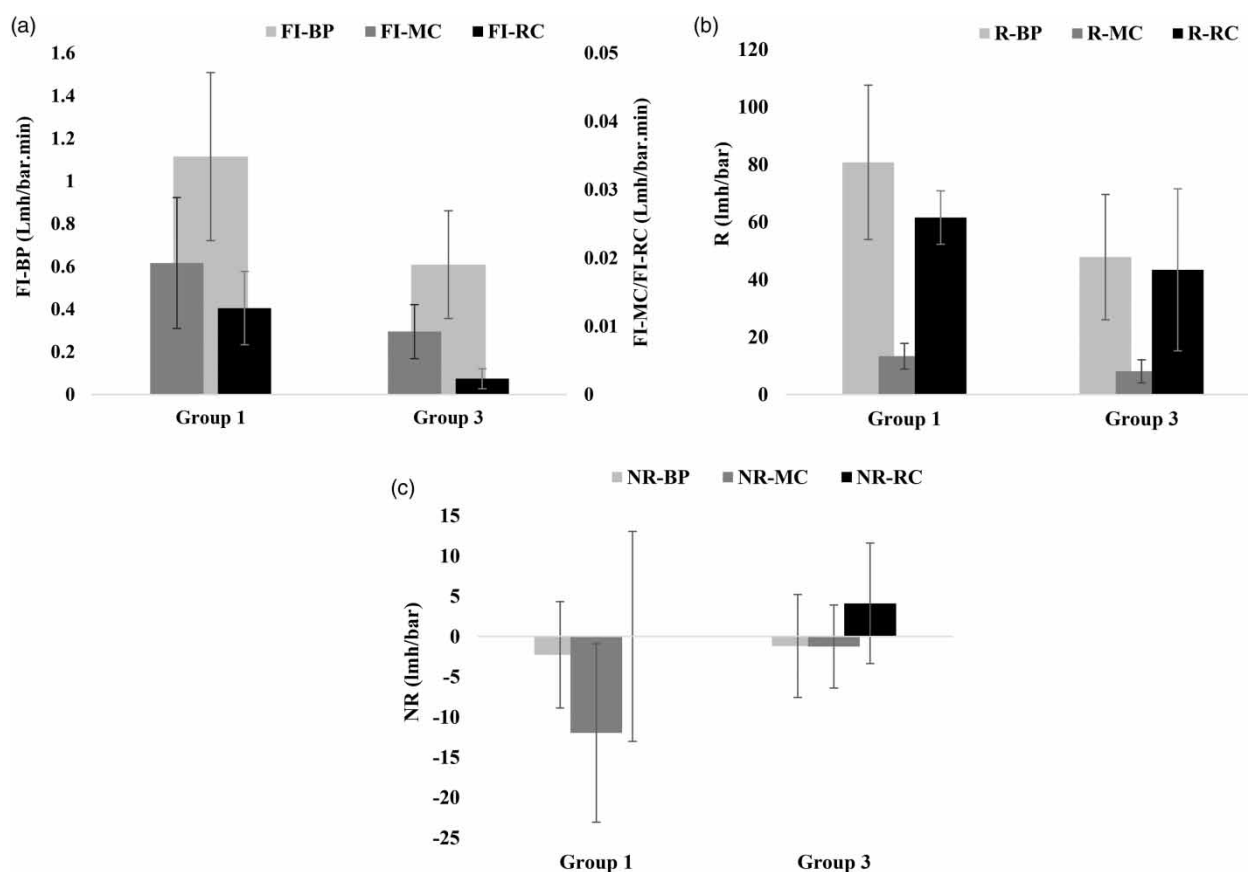


Figure 6 | Grouped average (a) fouling rates, (b) recoveries, and (c) net recoveries.

results of this analysis confirmed that MCs were not effectively recovering permeability during periods of highest flows and lowest temperatures. Therefore, it is anticipated that seasonal variation in membrane performance is due to an increase in hydraulically reversible and irreversible fouling. Hydraulically reversible fouling is fully recovered by backwashing. However, hydraulically irreversible fouling is more persistent, and is only recoverable by RCs, which are relatively long and use higher chemical concentrations when compared to MCs.

Foulant characteristics

In order to obtain a greater insight into the mechanisms of fouling, the feed to the membranes was characterized with respect to a range of water quality parameters for a period of 17 months (January 2017–May 2018) (Figure S3). Average FI_{BP} values were calculated for each sampling day to directly compare the feedwater characteristics with the fouling responses. As previously described, the FI_{BP} , FI_{MC} , and FI_{RC} values followed similar patterns for a given year.

Hence, FI_{BP} was chosen to represent periods of higher fouling as BP events occurred more frequently each day. The average FI_{BP} values were regressed against all of the measured water quality parameters using a linear regression model. The regression analysis revealed that relationships between FI_{BP} and DOC and nitrate concentrations (Figure 7) were statistically significant ($P < 0.05$).

From Figure 7, it can be observed that FI_{BP} values increased (slope = 0.13) as the concentrations of DOC increased ($r^2 = 0.2785$). In contrast, FI_{BP} values decreased (slope = -0.0196) as nitrate concentrations increased ($r^2 = 0.2123$). The r^2 value is a measure of the percentage of total variation in the dependant variable that is accounted for by the independent variable (Montgomery & Runger 2002). Therefore, a low r^2 of a statistically significant model (low P -value) could be an indication that the model does not contain all relevant predictors to explain the outcome. However, the independent variable explains some of the variability in the dependent variable, and the relationship is statistically significant. The positive relationship

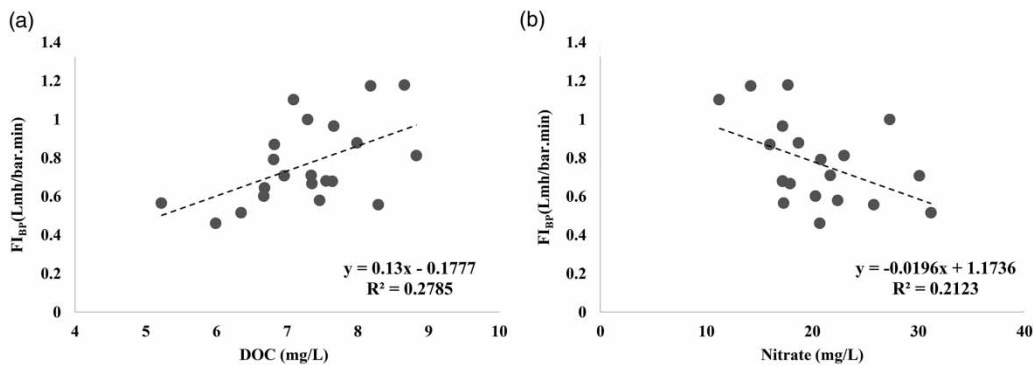


Figure 7 | Fouling index versus (a) DOC and (b) nitrate.

between FI_{BP} and DOC concentration was consistent with prior studies of MBRs that reported that membranes were mainly fouled by polysaccharides, proteins, and organic colloids (Rosenberger *et al.* 2006; Al-Halbouni *et al.* 2008; Wang *et al.* 2010; van den Brink *et al.* 2011; Sun *et al.* 2014). Subsequently, the results suggest that UF membranes in a tertiary configuration are impacted by similar foulants as those present in MBRs. It was, however, not possible to assess whether the rate or extent of fouling differed between tertiary and MBR configurations.

The decline in FI_{BP} values with increases in nitrate concentrations (Figure 7(b)), was attributed to the dependency of both of the following responses on wastewater flow. Nitrate is a product of nitrification in wastewater treatment and its effluent concentration depends on the concentration of TKN in the raw wastewater. During high flow periods, TKN concentrations in raw wastewater become more dilute and decrease (correlation coefficient = -0.6199) with flow and, thus, the concentrations of nitrate in the secondary effluent also decreases (correlation coefficient = -0.8312). Correspondingly, the dependence of FI_{BP} on nitrate concentrations was interpreted to result from the common impact of flow on both of these responses. Lower nitrate concentrations may also result from reduced nitrification during periods of lower temperatures, but the data indicated that the plant was able to maintain full nitrification throughout the observation period and, hence, this cause of the observed response was discounted.

The relationship between the presence of elevated DOC and FI_{BP} had a relatively low correlation coefficient. The literature (Lankes *et al.* 2009; van den Brink *et al.* 2011; Sun *et al.* 2014) suggests that fouling can be attributed to a specific DOC fraction. Therefore, five fractions of DOC that were determined by the LC-OCD analysis were investigated with respect to their impact on fouling. It was hypothesized that this would provide insight into whether seasonal changes in

the fractionation of organic material could impact membrane performance, providing direction on how fouling might be mitigated. A multivariable linear regression model was used to assess the relationship between fouling (i.e. FI_{BP}) and the concentrations of the various organic fractions. The regression model (Table S1) was found to be statistically significant ($r^2 = 0.6716$, P -value of $F = 0.0027$), and demonstrated that only the biopolymer fraction made a significant contribution to the overall model. Hence, it was concluded that the biopolymer fraction of DOC was a significant contributor to FI_{BP} and a better predictor of fouling in tertiary membranes than bulk DOC.

Source of foulants

The literature reveals conflicting hypotheses regarding the source of membrane foulants under cold temperatures. Krzeminski *et al.* (2012) attributed the increased concentration of foulants to reduced hydrolysis of raw wastewater components while Rosenberger *et al.* (2006) and Gao *et al.* (2013) suggested that biomass-generated soluble microbial product (SMP) concentrations increased as a result of biological or mechanical stress. The foulant sources in the current study were assessed by comparing the biopolymer concentrations in the raw wastewater and membrane feed streams. The FI_{BP} values were plotted versus the corresponding relationship between ratios of the concentration of biopolymers in the feed stream and biopolymers in raw wastewater ($C_{\text{feed}}/C_{\text{raw}}$) (Figure 8). Figure 8 reveals that during periods of higher fouling (>0.8 Lmh/bar.min), the concentrations of biopolymers in the membrane feed stream exceeded that in the raw wastewater ($C_{\text{feed}}/C_{\text{raw}} > 1$). The results suggest that the foulants were being generated by the biomass in the activated sludge process during the periods of higher fouling, due to concentrations during this period being greater than those observed in the raw wastewater.

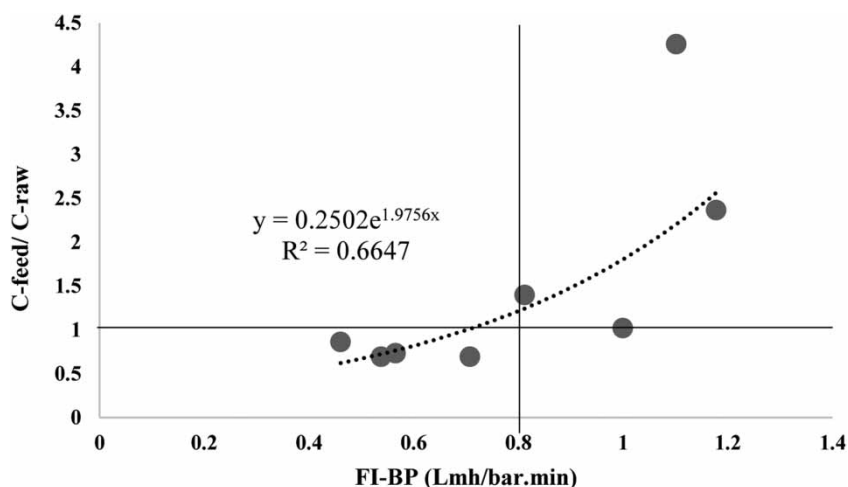


Figure 8 | Relationship between ratios of the concentration of biopolymers in feed stream and biopolymers in raw wastewater versus fouling index.

Sludge characteristics

The results from the field sampling campaign indicated that increased fouling was observed during periods when microbially excreted biopolymers were enhanced. This was consistent with the literature as it is widely recognized that the main foulants of aerobic MBRs are EPS excreted from cells (Gkotsis *et al.* 2014). These results were also consistent with prior studies (Le-Clech *et al.* 2006; Al-Halbouni *et al.* 2008; Lyko *et al.* 2008) that have shown that low temperature operation of activated sludge processes can lead to a reduction in sludge dewaterability, as attributed to an increase in mixed liquor carbohydrate concentrations. Therefore, the relationship between FI_{BP} and CST was investigated and found to have a significant correlation ($r^2 = 0.6085$; $P = 0.0001$, slope = 0.0321).

In addition, the relationship between biopolymer concentration and CST was investigated and found to have a significantly positive relationship ($r^2 = 0.4627$; $P = 0.001$, slope = 0.0042). Subsequently, when viewed collectively, it was concluded that CST could be used as an indirect indicator of membrane fouling potential in tertiary membrane processes as there were significant relationships between this response and all of the previously described indicators of membrane fouling.

CONCLUSIONS

This study investigated seasonal variations in the performance of tertiary membranes to determine the underlying

cause of observed performance deterioration (increased fouling or reduced cleaning efficiency). The patterns in performance indicators (i.e. FI_{BP} , FI_{MC} , FI_{RC} , R_{BP} , R_{MC} , R_{RC}) differed between the two observation years, with higher short, intermediate, and long-term fouling rates between March and May for 2016, and higher fouling rates in May for 2017. Regardless of the year, the recoveries in permeability during BP were observed to be proportional to short-term fouling rates, suggesting that the negative impact of seasonal changes on short-term fouling were readily reversible. The recovery in permeability during MC was relatively low and remained constant during the whole year. It was concluded that the hydraulically irreversible fouling, which is responsible for intermediate and long-term fouling rates, is not effectively recovered by MC but rather recovered by RC. It appears that the relatively short duration of MC (15 min) is sufficient to recover hydraulically irreversible fouling during the summer, but not during the spring. Also, higher average fouling rates – short, intermediate, and long-term – and average recoveries were observed during periods of highest flows and lowest temperatures. It was concluded that seasonally variable membrane performance is due to an increase in hydraulically reversible and irreversible fouling. Hydraulically reversible fouling is fully recovered by backwashing. However, hydraulically irreversible fouling is more persistent, and is only recoverable by RCs, which are relatively long and use higher chemical concentrations when compared to MCs.

The high fouling rates were observed to be correlated to an increase in DOC concentrations with the biopolymer

fraction of the DOC being most important. Higher concentrations of biopolymers were observed in the membrane feed in comparison to raw wastewater during higher fouling periods (>0.8 Lmh/bar-min). This indicated that some foulants are produced by biomass in the activated sludge process during periods of higher fouling. A strong correlation between CST values and biopolymer concentrations was observed, suggesting that biopolymers were the common contributor to both increased membrane fouling and reduced dewaterability.

The results of this study enhance the overall understanding of patterns in fouling behaviour and foulant characteristics of tertiary membranes operating under stressed conditions. This knowledge can be employed to assist with the design of mitigation strategies to reduce costs of these types of systems. Furthermore, the greater the insight gained into the operational challenges associated with operating such systems, the more confident we will be with their incorporation into our treatment systems, thus allowing us to continuously improve the quality of discharged wastewater to protect the environment and to support water reuse initiatives.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at <https://dx.doi.org/10.2166/wst.2020.140>.

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