Monitoring the fate of fluorescing substances recycled in ultrafiltration process backwash water
Paul G. Biscardi and Steven J. Duranceau

ABSTRACT
The fate of fluorescing substances during the recycling of membrane backwash water (MBWW) ahead of coagulation, flocculation and sedimentation (CFS) with ultrafiltration (UF) membranes has been investigated. Bench-scale UF membranes were used to generate MBWW from a CFS-treated surface water containing 21 mg/L dissolved organic carbon (DOC) registering a 0.95 cm$^{-1}$ UV$_{254}$ absorbance that had been coagulated with 100 mg/L with polyaluminum chloride. CFS settled water, when processed with UF, produced MBWW containing 9 mg/L DOC registering a 0.25 cm$^{-1}$ UV$_{254}$ absorbance. High performance size-exclusion chromatography using UV$_{254}$ detection demonstrated an analogous UV$_{254}$ reduction as measured by detector response. However, fluorescence excitation emission spectroscopy revealed that protein-like substances, known to be associated with irreversible fouling, had been concentrated in the MBWW. In order to evaluate recycling operations on overall DOC removal in a CFS-UF process, a blend of 30% MBWW with 70% of raw water was treated, resulting in an overall DOC removal of 73%. However, without MBWW recycle, the CFS-UF process removed less of the influent DOC (63%). This work suggests that MBWW recycle operations should consider possible downstream impacts of concentrated protein-like substances not previously detected, as these substances are suspected to contribute to long-term irreversible UF fouling.

Key words | backwash recycling, fluorescence, membrane, surface water, ultrafiltration

INTRODUCTION
The replacement of traditional granular media filters with hollow fiber ultrafiltration (UF) membranes for conventional drinking water treatment filtration can result in more consistent finished water quality with increased rejection of natural organic matter (NOM) (Farahbakhsh et al. 2004; Zularisam et al. 2009). As a result, membrane filtration is considered an important and widely used process in surface water treatment. However, a key barrier to more widespread adoption of UF membranes continues to be membrane fouling from NOM (Huang et al. 2009; Gao et al. 2011). Hydraulic and chemical backwashing can be utilized to mitigate the effects of organic fouling but, if used excessively, these processes can reduce the efficiency of the treatment system since filtered water is wasted when backwashed. Many utilities recycle hydraulic membrane backwash water (MBWW) to reduce waste. However, to the best of our knowledge, the impact of recycling MBWW on the organic foulants has not been studied extensively in the published literature.

In conventional surface water treatment (coagulation-flocculation-sedimentation-media filtration), the recycling of granular media filter backwash water (FBWW) is regulated by the US Environmental Protection Agency Filter Backwash Recycling Rule (FBRR), which requires recycled FBWW to be returned to the head of the water treatment plant (Environmental Protection Agency 2002). The FBRR also requires utilities to keep records of its recycling practices and to report them to their state government.
Furthermore, the FBRR also provides guidance that recommends limiting the recycle of backwash water to 10% to reduce the likelihood of an accumulation of oocysts in the main treatment process. This regulation was developed in response to research that assessed the treatability of FBWW and determined what intermediate processes would be necessary to prevent an accumulation of Giardia and Cryptosporidium as a result of recycling FBWW (Arora et al. 2001; MacPhee et al. 2002).

More recent research by Gottfried et al. (2008) demonstrated that recycling FBWW can increase NOM removal by enhancing coagulation since FBWW contains destabilized particles. As a result, their work also showed that coagulant dosing requirements may be reduced when recycling FBWW. Research has continued on FBWW regarding disinfection by-products (Walsh et al. 2008; McCormick et al. 2010) and NOM removal (Suman et al. 2012). However, despite increasing adoption of membranes in water treatment, there is sparsely available guidance on how to specifically handle MBWW recycling as the research conducted to develop the FBRR guidance did not include consideration of dissolved organic contaminants that could act as foulants to a membrane system. One study conducted by Zhou et al. (2013) characterized and tracked the properties of the NOM found in FBWW through analysis of its molecular weight distribution, hydrophobicity, and fluorescence. This analysis revealed that recycling FBWW could improve overall dissolved organic carbon (DOC) removal but led to increased protein-like matter in treated water. This protein-like matter would be of concern for a membrane process because research has shown that biopolymers consisting of protein-like substances are known to cause irreversible fouling in UF membranes (Haberkamp et al. 2011; Peiris et al. 2013; Yamamura et al. 2014).

Most research on MBWW has been focused on the potential impacts to finished water quality (Gouellec et al. 2004; Walsh et al. 2008; McCormick et al. 2010) or impacts to the efficiency of the coagulation process (Gora & Walsh 2011; Boyd et al. 2012). In one such study, Boyd et al. (2012) determined that carboxylic acids used in chemical backwashes were present in some MBWW and could interfere with coagulation if recycled. While this work demonstrated a potential challenge with regard to recycling MBWW, Gora & Walsh (2011) demonstrated that similar to improved organic removal through coagulation was achieved when the water was initially blended with 10% FBWW or MBWW. Limited research has been conducted on the possibility of recycling backwash water reintroducing concentrated dissolved organic foulants back into the treatment system. In bench-scale work conducted by Cornwell (2001), increased fouling of MF membranes was observed when treating FBWW and concluded that pilot work would be required to further investigate the fouling. Khramenkov et al. (2011) reported that NOM accumulation from FBWW had occurred in a full-scale conventional treatment system which used UF membranes. In their study, a complete discharge of backwash water was tested which resulted in a 10% increase in permeability after only 2 days. Gora & Walsh (2011) did not observe an increase in transmembrane pressure when testing the impact of recycling backwash water at 10% for a bench-scale outside-in UF membrane. However, the focus of their study was on the impact to permeate quality and they concluded that future research would be necessary to assess the impact of recycled MBWW on membrane fouling.

The purpose of this research was to evaluate the effect of recycling MBWW on coagulation performance while simultaneously monitoring the fate of organic foulants throughout the treatment process. Advanced DOC characterization techniques, including fluorescent excitation-emission spectroscopy and high-performance liquid chromatography (HPLC), were applied to identify and compare the components of DOC in processes potentially impacted by recycled MBWW.

**MATERIALS AND METHODS**

**Source water**

Untreated surface water was collected from the Lake Manatee Water Treatment Plant in Manatee County, Florida. This source water was chosen because it is currently treated through conventional surface water treatment with media filtration but is slated to transition to UF membranes (Sethi et al. 2015). Lake Manatee surface water typically contained approximately 20 mg/L DOC during the study.
Bench-scale hydraulic backwashing

The bench-scale assessment of MBWW recycling was conducted in two phases. In the first phase, a solid-contact clarification system was simulated by dosing raw surface water with polyaluminum chloride (PACl) coagulant in a jar tester. The coagulant dose of 100 mg/L PACl was chosen based on information provided by the Lake Manatee Water Treatment Plant. The jar testing apparatus (Phipps and Bird, Richmond, VA) used to conduct the test contained six jars that were filled with 2 L of raw surface water in each jar. The jar testing sequence was chosen to match the conditions of a surface water treatment plant that utilizes a solid-contact clarifier. This sequence consisted of 11 seconds at 300 rpm to simulate a rapid mix, 4 minutes and 14 seconds at 100 rpm to simulate mixing at the inlet works, 8 minutes at 60 rpm to simulate the clarifier mixing zone, 7 minutes at 5 rpm to simulate the clarifier flocculation zone, and 10 minutes at 0 rpm to simulate settling. Six replicate jar test runs were conducted in series to produce enough water for the subsequent steps.

As the jar test runs were completed, the supernatant or settled water from these jar tests (denoted as ‘post-coagulation, flocculation and sedimentation (CFS)’) were collected in a single reservoir used to feed the bench-scale hollow fiber UF membrane. The bench-scale hollow fiber UF membrane was composed of a blend of polyethersulfone (PES) and polyvinylpyrrolidone. The bench-scale membrane module was operated with an inside-out, dead end flow path. The module contained a total of 120 fibers which made up a combined total active area of 0.08 m². Each fiber had a 0.8 mm diameter and was 300 mm in length. The nominal pore size of the membrane was 0.010 μm (0.025 μm absolute) and the molecular weight cut-off was 200,000 Da. The filtration experiments were carried out by pumping feed water to a membrane module using a peristaltic pump.

A digital flow sensor was used to monitor flow and manual adjustments were made as needed to the peristaltic pump to maintain a constant permeate flux of 85 L/m²-hr (50 gal/sf-day) during filtration. Hydraulic backwashing with filtrate at 255 L/m²-hr for 60 seconds was conducted after approximately 45 minutes of filtration. Six backwashes occurred throughout this phase of testing. The MBWW from each filtration cycle was collected and combined in a single reservoir and tested for dissolved organic foulants through analytical methods discussed in a later section.

Bench-scale MBWW recycling

In the second phase of work, jar testing was repeated, however, three of the jars contained 30% MBWW and 70% raw surface water, while the other three jars contained 100% raw surface water. This recycle blend ratio was chosen to exaggerate the effect of recycling MBWW so that water quality changes as a result of recycling MBWW would be amplified. In each of these steps, samples were again taken for organic foulants to track their fate during the overall process both with and without recycle.

After completing the second phase jar tests, the permeability of the organic foulants detected through fluorescence was assessed. This assessment was accomplished by filtering a sample of water collected from each jar through a flat-sheet polyethersulfone UF membrane. This PES membrane was a disc filter with a nominal thickness of 110–150 μm and a 0.03 μm absolute pore size. These membranes were first rinsed with approximately 20 mL of distilled water. A vacuum pump operated at 10 psi was then used to filter 100 mL of sample water. These tests were conducted in triplicate.

Analytical methods

The samples collected during the bench-scale experiments were tested for water quality parameters including pH, turbidity, temperature, and conductivity in accordance with Standard Methods (APHA et al. 2005). Additional parameters which related to organic characterization were determined including DOC, UV-Vis spectra, true color in platinum cobalt color units (PCU), the apparent molecular weight distribution, and fluorescence excitation-emission spectra.

DOC was determined after filtering samples with a pre-washed 0.45 μm membrane filter followed by analysis using a Fusion Total Organic Carbon Analyzer (Teledyne Tekmar Inc., Mason, OH) according to Standard Method 5310 C (APHA et al. 2005). UV-Vis spectra were analyzed using a DR5000 spectrophotometer (Hach, Loveland, CO). Samples were first filtered through a pre-washed 0.45 μm membrane filter before undergoing UV-Vis scans. Each scan was conducted from wavelength 200 to 600 nm in 1-nm intervals.
Fluorescence excitation-emission spectroscopy was conducted to further characterize the dissolved organic matter. Prior to fluorescence analysis, samples were filtered with a 0.45 μm membrane filter to remove particulates. Without further pretreatment, fluorescence excitation-emission matrix (EEM) spectra were collected using a Shimadzu RF-6000 spectrofluorophotometer (Kyoto, Japan). The emission intensity readings were captured in 1-nm wavelength intervals between 280 and 600 nm for excitation wavelengths ranging from 200 to 400 nm in 5-nm intervals. The excitation and emission slits were set to a 10-nm band-pass.

The effect of Raleigh scattering was reduced by subtracting the fluorescence spectra collected from a sample of deionized water. Given that the organic content of the surface water was thought to potentially contain more than 20 mg/L for some samples, it was also important to account for the absorption of light by the DOC of the sample (commonly referred to as the inner filter effect). A correction for the inner filter effect was applied to the blank-subtracted spectra following the method described by Westerhoff et al. (2001).

A data analysis technique developed by Chen et al. (2003) referred to as fluorescence regional integration (FRI) was used to quantify and compare the results of each EEM sample taken. FRI involves dividing an EEM into characteristic regions and subsequently determining a normalized, integrated volume \( \phi_{i,n} \) for each region. A legend of the regions utilized in this study is described in Table 1 and illustrated in Figure 1.

The apparent molecular weight distribution (AMW) of the NOM was determined using high-performance size exclusion chromatography (HPSEC). The details of the HPSEC method employed are provided in detail elsewhere (Chin et al. 1994; Zhou et al. 2000). In brief, a Perkin Elmer Series 200 HPLC system consisting of a pump and autosampler were used. The mobile phase was a phosphate buffer that consisted of 2 mM K₂HPO₄, 2 mM KH₂PO₄, and 0.1 M NaCl. The mobile phase was pumped at a flow rate of 1 mL/min. The sample injection volume was 150 μL. The size exclusion column used was a Protein-Pak 125 (Waters Inc., Milford, MA). Calibration was achieved with molecular weight standards prepared from HPLC-grade acetone, salicylic acid, and sodium polystyrene sulfonate (PSS) standards (Scientific Polymer Products Inc., Ontario, NY) with molecular weights of 1.6, 5.2, 7.4, 16, and 34 kDa. Prior to HPSEC analysis, samples were filtered with a 0.45 μm membrane filter and adjusted to an ionic strength and pH similar to the mobile phase using sodium chloride, K₂HPO₄, and KH₂PO₄ to prevent undesired interactions between the sample and the column media that would exaggerate retention times.

RESULTS AND DISCUSSION

MBWW and raw water characteristics

Raw surface water was jar tested (without blending recycled MBWW) which reduced the DOC from approximately 21 to

<table>
<thead>
<tr>
<th>EEM region</th>
<th>Excitation range</th>
<th>Emission range</th>
<th>Description</th>
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<tbody>
<tr>
<td>Region I</td>
<td>200–250</td>
<td>280–330</td>
<td>Aromatic protein-like</td>
</tr>
<tr>
<td>Region II</td>
<td>200–250</td>
<td>330–380</td>
<td>Aromatic protein-like</td>
</tr>
<tr>
<td>Region III</td>
<td>200–250</td>
<td>380–600</td>
<td>Fulvic acid-like</td>
</tr>
<tr>
<td>Region IV</td>
<td>250–340</td>
<td>280–380</td>
<td>Soluble microbial by-product-like</td>
</tr>
<tr>
<td>Region V</td>
<td>250–400</td>
<td>380–600</td>
<td>Humic acid-like</td>
</tr>
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Figure 1 | Fluorescence regional integration legend.
7.3 mg/L, or 65% removal. The UV$_{254}$ absorbance, true color, turbidity, and other water quality measurements taken during this test are shown in Table 2.

The DOC and UV$_{254}$ absorbance of the post-CFS and filtrate water were similar, indicating that little to no removal of organics was occurring on the surface of the membrane. However, it was apparent that some removal was occurring because after backwashing, an elevated DOC was detected in the MBWW.

The backwash water quality shown in Table 2 is for the combined backwash water collected from the six backwash events that took place during the testing. It was important to also compare the MBWW water quality to the raw water since the point of blending would occur at the head of the plant if MBWW backwashing were practiced. While the backwash water did have a relatively high turbidity of 16.6 NTU, the MBWW initially did not appear to have dissolved components that were concentrated higher than the raw surface water. The UV$_{254}$, DOC, and true color were lower in the MBWW than in the raw water. As previously mentioned, the DOC in the MBWW was 9.9 mg/L C which was higher than the 7.5 mg/L C found in the filtrate. However, the specific UV absorbance (SUVA) was slightly reduced in MBWW, indicating that the organics concentrated in the MBWW were of similar overall aromaticity compared to the filtrate.

HPSEC results shown in Figure 2 revealed that the apparent molecular weight distribution of UV$_{254}$ absorbing constituents in MBWW was similar to that of the post-CFS samples. The magnitude of the HPSEC response was below that of the raw water suggesting that there was no particular size fraction of UV$_{254}$ absorbing constituents present at a higher concentration than the raw surface water. Overall, the HPSEC results demonstrated an analogous UV$_{254}$ difference between the raw surface water and the MBWW. This suggested that the MBWW did not contain a particular size-fraction of UV$_{254}$ absorbing components that was concentrated relative to the raw water.

However, the fluorescent EEMs, shown in Figure 3(a) and 3(b), revealed that protein-like substances (regions I and II) were in fact concentrated in the MBWW and were clearly producing a higher response than in the raw surface water. This figure compares raw water with MBWW because MBWW would blend with raw water during recycling operations and components that are in a higher concentration in the MBWW as compared to the raw water could potentially accumulate in the treatment system. This concentration is quantified by the FRI integrated volumes ($\phi_{i,n}$) shown in Figure 4. Figure 4 revealed that MBWW was concentrated with aromatic protein like matter (Regions I and II) as compared to the raw water.

### Table 2: Water quality data from the first phase of the bench-scale testing during the generation of MBWW

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw water</th>
<th>Post-CFS</th>
<th>Hollow fiber UF filtrate</th>
<th>Hollow fiber UF backwash</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.6</td>
<td>5.8</td>
<td>5.9</td>
<td>6.0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2.35</td>
<td>2.03</td>
<td>0.06</td>
<td>16.6</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>157</td>
<td>188</td>
<td>188</td>
<td>230</td>
</tr>
<tr>
<td>True color (PCU)</td>
<td>202</td>
<td>17</td>
<td>16</td>
<td>&lt;5</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>21</td>
<td>7.3</td>
<td>7.3</td>
<td>9.9</td>
</tr>
<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
<td>0.95</td>
<td>0.20</td>
<td>0.19</td>
<td>0.25</td>
</tr>
<tr>
<td>SUVA</td>
<td>4.5</td>
<td>2.7</td>
<td>2.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**Effect of MBWW recycle**

In the second phase of testing, the jar testing was repeated with a 30% recycle of MBWW revealing an increased
removal of turbidity, true color, DOC, and UV<sub>254</sub> absorbance as shown in Table 3. As seen in Figure 5(a) and 5(b), the post-CFS samples from the test with recycle showed reduced fluorescence compared to the post-CFS from the test without recycle. This is true specifically for Regions I and II as shown in Figure 4. This indicated that the incorporation of MBWW improved removal of fluorescent organic compounds. Overall process DOC removal was 63% during the test without recycle and was 73% during the test with recycle.

While others such as Gottfried et al. (2008) have previously demonstrated that recycling backwash can result in increased NOM removal, their study did not consider the characteristic components of the NOM. Notably, the EEMs from this set of jar tests revealed that the coagulation process with MBWW recycle removed protein-like substances to a greater degree than the control test without MBWW recycle. As a result, the protein-like substances did not accumulate in the overall bench-scale treatment system with MBWW recycle in with the surface water from Lake Manatee.

Similar results were observed for the UF filtrate samples. As seen in Figure 5(c) and 5(d), the filtrate samples from the test with recycle showed reduced fluorescence compared to the filtrate from the test without recycle. The DOC in the filtered water from the test without MBWW recycle was 7.7 mg/L C compared to

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Water quality data from MBWW recycling experiment</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>0% Recycled backwash</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2.71</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>231</td>
</tr>
<tr>
<td>Apparent color (PCU)</td>
<td>87</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>8.2</td>
</tr>
<tr>
<td>UV254 (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.22</td>
</tr>
<tr>
<td>SUVA</td>
<td>2.7</td>
</tr>
</tbody>
</table>
5.7 mg/L C in the filtrate water from the experiment with MBWW recycle. This does not suggest that the filtration step performed better or worse in isolation. Rather, what was made clear was that the overall process yielded a lower DOC finished water when incorporating an internal backwash recycle. Others have seen similar results. Gora & Walsh (2011) demonstrated that similar to improved organic removal through coagulation when recycling MBWW, but did not take into account that a component of the organics may have been selectively concentrated in

Figure 5 | Fluorescence EEMs for post-CFS without (a) and with recycle (b), filtrate without (c) and with recycle (d), and differential EEMs (post-CFS minus filtrate) for samples without (e) and with recycle (f).
MBWW and confirm its removal in the subsequent CFS or filtration steps.

In this work, differential EEMs were calculated by subtracting the filtrate EEM from the associated post-CFS EEM are shown in Figure 5(e) and 5(f) for testing without and with recycled MBWW respectfully. These plots illustrate the types of organic compounds that were retained by the membrane. Less organic matter was retained on the flat sheet membrane during the recycle experiment. Notably, the protein-like substances peak shown on the differential EEM for the test without MBWW recycle (Figure 5(e)) corresponds to the peak found in the MBWW in regions I and II (Figure 5(b)). This provided additional evidence that the protein-like substances were being concentrated in UF backwash water due to their tendency to be selectively rejected during filtration. However, their subsequent removal during CFS indicates that a 30% recycle blend under the conditions tested in this study would not likely lead to protein-like substance accumulation. However, the detection of concentrated dissolved foulants in MBWW nevertheless suggests that future research should further investigate their fate under additional treatment scenarios.

**CONCLUSIONS**

In this research, the fate of protein-like substances during the recycling of MBWW ahead of CFS with UF membranes was investigated. The major findings of this study are as follows:

- MBWW generated during the bench-scale testing was concentrated with protein-like substances suspected to be associated with membrane foulants.
- Recycling MBWW at a 30% blend ratio improved the coagulation process at a PACI dose of 100 mg/L for a surface water containing 21 mg/L DOC.
- The improved coagulation process performance removed concentrated protein-like substances which reduced the likelihood of accumulation occurring as a result of MBWW recycling for the evaluated source water.
- The protein-like substances concentrated in the MBWW were found to be rejected by the UF membrane which is known to cause irreversible fouling. Therefore, caution should be exercised when evaluating the incorporation of MBWW recycle in membrane treatment systems.
- Future research should investigate the fate of protein-like substances under additional treatment scenarios as well as investigate their impact on long-term, irreversible fouling rate of UF membranes used in conventional surface water treatment.

**ACKNOWLEDGEMENTS**

Funding for this project was provided by Harn R/O Systems (Venice, Florida) and the Alameda County Water District (Alameda County, CA) under UCF project agreement 16208088. The authors are grateful for the contributions of University of Central Florida students Maria Arenas, Martin Coleman, Cassidy Conover, Ari Hadar, Carlyn Higgins, Hadi Toure, and David Yonge. The authors are also grateful for the laboratory support of Maria Real-Robert. This work would not have been possible without the source water provided by Bruce MacLeod and Katherine Gilmore of the Lake Manatee Water Treatment Plant.

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