Comprehensive Bench- and Pilot-Scale Investigation of Trace Organic Compounds Rejection by Forward Osmosis

Nathan T. Hancock,† Pei Xu,† Dean M. Heil,† Christopher Bellona,‡ and Tzahi Y. Cath*‡†

†Department of Civil and Environmental Engineering, Colorado School of Mines, 1500 Illinois Street, Golden, Colorado 80401, United States
‡Department of Civil and Environmental Engineering, Clarkson University, 8 Clarkson Avenue, Potsdam, New York 13699, United States

Supporting Information

ABSTRACT: Forward osmosis (FO) is a membrane separation technology that has been studied in recent years for application in water treatment and desalination. It can best be utilized as an advanced pretreatment for desalination processes such as reverse osmosis (RO) and nanofiltration (NF) to protect the membranes from scaling and fouling. In the current study the rejection of trace organic compounds (TOrCs) such as pharmaceuticals, personal care products, plasticizers, and flame-retardants by FO and a hybrid FO-RO system was investigated at both the bench- and pilot-scales. More than 30 compounds were analyzed, of which 23 nonionic and ionic TOrCs were identified and quantified in the studied wastewater effluent. Results revealed that almost all TOrCs were highly rejected by the FO membrane at the pilot scale while rejection at the bench scale was generally lower. Membrane fouling, especially under field conditions when wastewater effluent is the FO feed solution, plays a substantial role in increasing the rejection of TOrCs in FO. The hybrid FO-RO process demonstrated that the dual barrier treatment of impaired water could lead to more than 99% rejection of almost all TOrCs that were identified in reclaimed water.

1. INTRODUCTION

1.1. Reclamation and Water Reuse and the Presence of Trace Organic Compounds (TOrCs) in Water and Wastewater. A recent report to Congress highlighted the consequences of climate change on water resources in the Western and Southwestern US.1 With expected drier climate, new water resources will be required to fulfill the needs of growing populations and economies. Coastal utilities already use seawater as an unconventional source of drinking water, and inland communities will have to increasingly rely on reclaimed water and desalinated brackish groundwater for nonpotable and indirect potable reuse.2

In the US and around the world water providers are already treating impaired water to supplement their fresh water supplies. Examples include the Water District Groundwater Replenishment System in Orange County, California,3 the Prairie Waters Project in Aurora, Colorado,4 and the NeWater treatment clusters in Singapore.5 These facilities rely on processes such as microfiltration (MF), reverse osmosis (RO), and ultraviolet irradiation with advanced oxidation processes (UV/AOP) to treat impaired water to a high quality. Yet, one of the major concerns related to water reuse is currently the presence of trace organic compounds (TOrCs) in effluents from conventional wastewater treatment facilities and consequently their current prevalence in many water resources.6,7 While RO, NF, UV/AOP, carbon adsorption, and natural systems (i.e., riverbank filtration and aquifer recharge) processes demonstrated efficient removal of TOrCs from impaired and treated water,5–12 new treatment processes might be required to provide multibarrier protection of potable waters.

1.2. Forward Osmosis As a New Process for Reclamation of Impaired Water. Recent advancements in research and development demonstrated that osmosis can be utilized in engineered systems to separate contaminants from water using the forward osmosis (FO) process.13 In FO, clean water can be extracted from contaminated streams utilizing special semi-permeable membranes that have contaminant rejection capabilities similar to those of RO membranes. In the process, water diffuses from the feed stream, through a dense, semipermeable FO membrane, and into a draw solution that has a high osmotic pressure.13 Past studies demonstrated that domestic wastewater, anaerobic digester sludge, food and beverage products, brackish groundwater, and even seawater could be effectively treated with FO.14–16 A recent study also demonstrated the effective dual barrier characteristics of the FO process when hybridized with seawater RO for treatment of secondary and tertiary treated domestic effluents.16 In the hybrid process, impaired water is first treated by an FO membrane and water is drawn into a seawater draw solution, and the diluted draw solution is desalinated by RO to produce a stream of purified water (see Supporting

Received: May 16, 2011
Accepted: August 12, 2011
Revised: August 2, 2011
Published: August 12, 2011
Information, section S1). The rejection of wastewater constituents such as organic carbon, nutrients (i.e., ammonia, nitrate, phosphate), and suspended solids by the two tight barriers was very high (95–99.9%), the FO membranes protected the sensitive RO membranes from fouling and scaling, and energy saving could be achieved.16

1.3. Previous Studies That Employed FO To Remove TOrCs from Impaired Water. An early bench-scale study by Cartinella et al.17 demonstrated the rejection by FO of a limited number of TOrCs from wastewater generated in life support systems. The study investigated the removal of three hormones that were spiked into batches of synthetic wastewater. Results revealed that membrane fouling and the presence of surfactants in the feed solution substantially improved rejection of TOrCs at higher water recoveries. A more recent study by Cath et al.18 compared TOrCs rejection by FO at the pilot- and bench-scale. A pilot-scale FO-RO hybrid system was utilized, and a continuous stream of secondary effluent was used as a feed stream to an FO plate and frame membrane cell. Only a limited number of TOrCs was quantified in the effluent. Bench-scale tests were performed with water spiked with the same TOrCs. Results from short-term experiments (7–14 days) demonstrated that rejection of TOrCs by FO membranes and by the dual barrier FO-RO process are very high (>95%) and can lead to potentially successful incorporation of the FO process in future water reclamation systems for potable reuse. Although the previous studies demonstrated the high efficiency of FO in removal of TOrCs, the experiments were too short, with limited number of compounds, and with a custom-made membrane cell.

Fundamental NF and RO studies8,18–20 have demonstrated that the rejection of TOrCs is primarily governed by steric interactions (i.e., increased rejection with increased molecular size), electrostatic exclusion, and adsorption (often related to solute hydrophobicity); however, other factors such as a solute’s functional groups (e.g., hydroxyl groups, carbonyl groups, amide groups) may play a role in TOrCs rejection.21 A similar systematic investigation is needed to better understand the rejection mechanisms of TOrCs during FO treatment.

1.4. Objectives. The main objective of the current study was to investigate the rejection of TOrCs by FO and by the dual barrier FO-RO processes using mainly seawater as a renewable source of draw solution. This includes testing for extended time (i.e., months) of newer generation FO membranes in a novel spiral wound commercial packaging configuration, with wastewater of different qualities (i.e., tertiary and secondary effluents), and with a larger number of TOrCs having a broader range of physical and chemical properties. Pilot-scale experiments were conducted to assess the performance of commercial FO membrane modules under field conditions, and bench-scale experiments were conducted to further elucidate the mechanisms and conditions controlling rejection of TOrCs by FO membranes. Bench-scale tests were conducted with a flat sheet FO membrane from the same cast, using synthetic feed solutions spiked with similar types and concentrations of TOrCs that were observed in the effluent of the treated wastewater, and with various draw solutions compositions.

2. MATERIAL AND METHODS

2.1. Membranes. FO membranes made from a hydrophilic cellulose-based polymer were acquired from Hydration Technology Innovations (HTI) (Albany, OR). The membranes incorporate a cellulose triacetate (CTA) active layer, and a woven polyester mesh is embedded in the CTA to create a flat sheet membrane.

For the bench-scale study, flat sheet FO membrane coupons were used. For the pilot study the CTA membrane was employed in a spiral wound packaging configuration that improves membrane-packing density (i.e., membrane active surface area per module volume) for commercial applications (additional details presented in Supporting Information, section S2).

Seawater RO spiral wound membranes (SW30 2540, Dow Filmtec, Edina, MN) were used for the pilot RO system. These membranes were chosen for their high salt rejection (>99.4%)22 that enables production of concentrated draw solution for the FO process.

Water permeance and NaCl rejection for the fresh FO membrane were measured during experiments conducted in RO mode and found to be 0.78 ± 0.02 L/m²·h·bar and 93.2 ± 0.9%, respectively. Feed at a constant temperature of 25 °C was either deionized water for permeance tests or a 2,000 mg/L NaCl solution for rejection tests. Tests were conducted with feed pressures of 100 and 150 psig (0.69 and 1.03 MPa). Water permeance and NaCl rejection for the SW30 membrane (1.31 L/m²·h·bar and 99.4%, respectively) were obtained from the manufacturer.22

2.2. Test Systems. 2.2.1. Bench-Scale FO Apparatus. The FO bench-scale apparatus utilized a membrane cell constructed with symmetric flow channels on both sides of the membrane that facilitated parallel, counterflow along the 455-cm² membrane. A programmable logic control (PLC) system was developed to maintain constant experimental conditions (i.e., feed volume of 3 L, draw solution concentration of 30 g/L, and system temperature of 20 °C) and to collect data during the experiments. Feed and draw solution were continuously circulated between their respective tanks and the membrane cell at a flow rate of 1.6 L/min, and feed and draw solution samples were intermittently drawn for analysis. Details about the design and operating conditions and control of the system are provided in our previous publication.23

2.2.2. Pilot-Scale FO-RO System. A pilot-scale FO-RO hybrid system was utilized for the long-term testing of the spiral wound commercial FO membrane. Details about the design and operating conditions and control of the system are provided in our previous publication16 and in the Supporting Information, section S3. In the current study the system was deployed at a wastewater treatment research facility on the campus of the Colorado School of Mines (Golden, CO). Approximately 7000 gallons per day (26.5 m³) of domestic wastewater are treated at the facility by a demonstration scale sequencing batch membrane bioreactor (SBMBR) system (Aqua-Aerobic Systems, Inc., Rockford, IL). Feed to the FO membrane was a continuous side stream from the SBMBR operated with an ultrafiltration (UF) membrane (Puron, KMS, Wilmington, MA). To simulate secondary treated effluent water quality, activated sludge from the SBMBR was dosed into the SBMBR permeate at different rates.

2.3. Water Chemistry. 2.3.1. Draw Solutions. Synthetic sea salt (Instant Ocean, Mentor, OH) was used for preparation of draw solution for all pilot- and two bench-scale experiments. During most of the pilot-scale experiment (approximately three continuous months) the draw solution was maintained at a concentration of approximately 30 g/L sea salt by the RO subsystem. For a limited time, the RO subsystem produced concentrated draw solution of 60 g/L sea salt. In one bench-scale experiments, ACS grade sodium chloride (Fisher Scientific, Atlanta,
GA) was used as draw solution at 30 g/L to elucidate draw solution chemistry effects on TOrCs rejection.

2.3.2. Feed Solutions. SBMBR permeate was the feed to the pilot-scale FO membrane and was continuously pumped into the feed side of the FO spiral wound module at a rate of 12 L/min. The quality of the feedwater (SBMBR effluent with or without activated sludge dosing) to the pilot FO fluctuated throughout the testing period because of the decentralized nature of the SBMBR facility. Fluctuation in the number of users, precipitation events, and constantly changing conditions in the SBMBR system may contribute to varying feedwater quality. Average SBMBR permeate water quality based on 23 samples taken over a 38 day period is summarized in Table 1. Data indicate that the dominant ions in the SBMBR permeate are sulfate, chloride, sodium, calcium, and magnesium. Variable nitrate concentration observed in samples may result from a variety of factors associated with the SBMBR system operation (e.g., aeration cycles and duration) and influent water quality. The concentrations of major constituents that were added to the feedwater during the bench-scale tests are also summarized in Table 1.

2.4. Analytical Methods for TOrCs. TOrCs were quantified using a liquid chromatography tandem mass spectrometry (LC-MS/MS) system assembled with an HPLC system (1200 Series, Agilent Technologies Inc., Santa Clara, CA) coupled to a tandem mass spectrometer (3200 QTrap, Applied Biosystems, Carlsbad, CA) according to the matrix suppression abating method described in Vandeford and Snyder. To alleviate issues induced by matrix suppression of environmental samples, an isotope of each TOrC was spiked into each sample at a known concentration. The absolute recovery of the isotope was used to determine the 12 h stabilization period, each experiment lasted 4 h. Water flux and reverse salt flux from the draw solution to the feed were monitored and recorded throughout each experiment. TOrCs concentrations and water flux were used to conduct mass balance and calculate TOrCs rejection by the FO membranes (Section S5 in the SI). Membrane integrity tests were conducted before and after the set of experiments to confirm that the rejection of ions by the membrane did not change during the experiments. Before each experiment, the feed solution was recirculated on the feed side of the membrane for 12 h to ensure that adsorption of TOrCs to the membrane did not affect mass transport and mass balance calculations. Following the 12 h stabilization period, each experiment lasted 4–5 h.

2.5. Pilot System Experimental Procedure. The pilot-scale system was initially tested with SBMBR permeate as FO feed continuously for 650 h (27 days). Subsequently, the FO feed was

### Table 1. Average Concentrations of Major Constituents and Water Quality Parameters Measured in SBMBR Permeate and Composition of the Feed Solution for the FO Bench-Scale Tests

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Pilot-scale FO Feed</th>
<th>Pilot-scale FO Feed</th>
<th>Bench-scale FO Feed</th>
<th>Bench-scale FO Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>bicarbonate</td>
<td>54.3 ± 1.7</td>
<td>54</td>
<td>O-phosphate</td>
<td>12.3 ± 2.5</td>
</tr>
<tr>
<td>boron</td>
<td>0.08 ± 0.04</td>
<td>-</td>
<td>potassium</td>
<td>11.7 ± 1.7</td>
</tr>
<tr>
<td>barium</td>
<td>0.06 ± 0.02</td>
<td>-</td>
<td>pH</td>
<td>7.1 ± 0.1</td>
</tr>
<tr>
<td>bromide</td>
<td>0.06 ± 0.01</td>
<td>-</td>
<td>silica</td>
<td>10.6 ± 1.1</td>
</tr>
<tr>
<td>calcium</td>
<td>36.1 ± 3.6</td>
<td>35</td>
<td>sodium</td>
<td>54.5 ± 3.6</td>
</tr>
<tr>
<td>chloride</td>
<td>72.0 ± 5.6</td>
<td>97</td>
<td>strontium</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>DOC</td>
<td>3.9 ± 0.7</td>
<td>4#</td>
<td>sulfate</td>
<td>79.8 ± 5.4</td>
</tr>
<tr>
<td>magnesium</td>
<td>10.3 ± 1.0</td>
<td>10</td>
<td>SUVA, L/mg·m</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>nitrate</td>
<td>37.3 ± 15.4</td>
<td>-</td>
<td>TDS</td>
<td>325.0 ± 22.7</td>
</tr>
</tbody>
</table>

# Significance of #

5 mg/L humic acid sodium salt (Aldrich, St. Louis, MO) was added to the feed.

---

dx.doi.org/10.1021/es201654k | Environ. Sci. Technol. 2011, 45, 8483–8490
Table 2. TOrCs Detected by LC-MS/MS in ESI+ and ESI− Modes and Select Physicochemical Properties

<table>
<thead>
<tr>
<th>TOrC</th>
<th>classification</th>
<th>charge</th>
<th>log D @ pH 6a</th>
<th>MW</th>
<th>pilot FO feed,b ng/L</th>
<th>bench FO feed,c ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>amitriptyline</td>
<td>antidepressant</td>
<td>positive</td>
<td>1.45</td>
<td>277.40</td>
<td>3.0 ± 1.1</td>
<td>-</td>
</tr>
<tr>
<td>atenolol</td>
<td>beta-blocker</td>
<td>positive</td>
<td>−2.73</td>
<td>266.34</td>
<td>26.7 ± 10.2</td>
<td>30</td>
</tr>
<tr>
<td>benzophenone</td>
<td>preservative</td>
<td>neutral</td>
<td>3.18</td>
<td>182.21</td>
<td>90.1 ± 22.0</td>
<td>100</td>
</tr>
<tr>
<td>caffeine</td>
<td>stimulant</td>
<td>neutral</td>
<td>−0.13</td>
<td>194.19</td>
<td>32.2 ± 18.0</td>
<td>50</td>
</tr>
<tr>
<td>carbamazepine</td>
<td>anticonvulsant</td>
<td>neutral</td>
<td>2.67</td>
<td>236.27</td>
<td>388 ± 301</td>
<td>500</td>
</tr>
<tr>
<td>DEET</td>
<td>insect repellent</td>
<td>neutral</td>
<td>1.96</td>
<td>191.27</td>
<td>38.8 ± 22.3</td>
<td>50</td>
</tr>
<tr>
<td>diazepam</td>
<td>benodiazepine tranquilizer</td>
<td>neutral</td>
<td>2.96</td>
<td>284.70</td>
<td>0.63 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>dilantin</td>
<td>antiepileptic</td>
<td>neutral</td>
<td>2.52</td>
<td>252.27</td>
<td>133 ± 28</td>
<td>150</td>
</tr>
<tr>
<td>diphenhydramine</td>
<td>antihistamine</td>
<td>positive</td>
<td>1.07</td>
<td>255.36</td>
<td>132 ± 45</td>
<td>150</td>
</tr>
<tr>
<td>fluoxetine</td>
<td>antidepressant</td>
<td>positive</td>
<td>1.03</td>
<td>309.33</td>
<td>18.3 ± 6.0</td>
<td>20</td>
</tr>
<tr>
<td>hydrocortone</td>
<td>analgesic</td>
<td>neutral</td>
<td>−0.61</td>
<td>299.37</td>
<td>14.3 ± 12.4</td>
<td>20</td>
</tr>
<tr>
<td>oxybenzone</td>
<td>ingredient in sunscreens</td>
<td>neutral</td>
<td>3.63</td>
<td>228.24</td>
<td>25.9 ± 8.3</td>
<td>30</td>
</tr>
<tr>
<td>primidone</td>
<td>anticonvulsant</td>
<td>neutral</td>
<td>0.40</td>
<td>218.25</td>
<td>1.6 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>sulfamethoxazole</td>
<td>anti-infective</td>
<td>negative</td>
<td>0.49</td>
<td>253.28</td>
<td>185 ± 175</td>
<td>250</td>
</tr>
<tr>
<td>TCEP</td>
<td>flame retardant</td>
<td>neutral</td>
<td>2.67</td>
<td>250.19</td>
<td>366 ± 152</td>
<td>400</td>
</tr>
<tr>
<td>trimethoprim</td>
<td>anti-infective</td>
<td>positive</td>
<td>−0.42</td>
<td>290.32</td>
<td>21.6 ± 17.6</td>
<td>40</td>
</tr>
</tbody>
</table>

ESI−

<table>
<thead>
<tr>
<th>Compound</th>
<th>Classification</th>
<th>Charge</th>
<th>log D @ pH 6a</th>
<th>MW</th>
<th>Feed concentration ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>bisphenol A</td>
<td>plasticizer</td>
<td>neutral</td>
<td>3.43</td>
<td>228.29</td>
<td>89.6 ± 26.8</td>
</tr>
<tr>
<td>diclofenac</td>
<td>anti-inflammatory agent</td>
<td>negative</td>
<td>2.23</td>
<td>296.15</td>
<td>38.4 ± 33.1</td>
</tr>
<tr>
<td>ibuprofen</td>
<td>anti-inflammatory agent</td>
<td>negative</td>
<td>2.12</td>
<td>206.29</td>
<td>34.1 ± 11.3</td>
</tr>
<tr>
<td>methylparaben</td>
<td>personal care product</td>
<td>neutral</td>
<td>1.86</td>
<td>152.15</td>
<td>23.7 ± 9.0</td>
</tr>
<tr>
<td>naproxen</td>
<td>anti-inflammatory agent</td>
<td>negative</td>
<td>1.81</td>
<td>230.26</td>
<td>74.1 ± 33.9</td>
</tr>
<tr>
<td>trimethoprim</td>
<td>antimicrobial</td>
<td>neutral</td>
<td>5.17</td>
<td>289.54</td>
<td>90.5 ± 23.7</td>
</tr>
<tr>
<td>triclocarban</td>
<td>antimicrobial</td>
<td>neutral</td>
<td>5.74</td>
<td>315.58</td>
<td>267 ± 41</td>
</tr>
</tbody>
</table>

4 Obtained from ACD/Laboratories software version 8.14 (ACD/LABORATORIES, Toronto, Canada). 5 Feed concentration of TOrCs measured in grab samples drawn prior to FO membrane during intervals B through E. 6 Concentration of TOrCs in the feed solution for the FO bench-scale tests.

3. RESULTS AND DISCUSSION

3.1. Bench-Scale Performance: TOrCs Rejection. Bench-scale FO tests were performed to investigate the effect of draw solution composition and organic matter on the rejection of TOrCs in a relatively simple matrix for ease of analysis. TOrC rejection during the three bench-scale experiments is summarized in Figure 1. Because several compounds (i.e., bisphenol A, diclofenac, benzophenone, and trimethoprim) were not quantified in one or more draw solution samples, rejection could not be accurately determined and were not included in Figure 1. Bench-scale FO rejection of TOrCs was between 40 and 98% and depended primarily on molecular size and charge. Rejection of positively and negatively charged TOrCs was greater than 80%, while the rejection of the nonionic TOrCs was more variable, between approximately 40 and 90%. With the exception of TCEP, the rejection of the nonionic TOrCs tended to increase with increasing molecular weight, which is to be expected based on hindered diffusion. The chlorinated flame retardant TCEP, however, exhibited lower rejection than expected based on size. Although TCEP was demonstrated to be highly rejected by RO and NF membranes, rejection of TCEP in our past FO bench scale study was consistently low. While ionic TOrC rejection was greater than 80%, rejection of these compounds was lower than expected.
The addition of humic acid to the feedwater when operating with seawater draw solution had minimal effect on the rejection of TOrCs by the FO membrane. Generally, the type of draw solution employed did not substantially affect rejection of TOrCs during bench-scale experiments. Methylparaben was the only compound that exhibited a substantial increase in rejection with the NaCl draw solution compared to the simulated seawater draw solution (oxybenzone exhibited a statistically insignificant increase as well); however, there is no apparent explanation for this behavior. DEET was detected at a higher concentration in the draw solution than in the feed in samples from the NaCl draw solution experiment, indicating that the sample may have been contaminated during processing for LC/MS-MS analysis.

3.2. Pilot-Scale Performance. 3.2.1. Water Flux. Water flux was continually monitored during the pilot study. Water flux as a function of operation time is shown in Figure 2. Letter indices represent operation intervals enumerated in Table 3. During interval A the pilot system was operated for approximately 250 h with SBMBR permeate as FO feed before reaching a steady-state water flux. This was likely due to interaction of the membrane with various constituents in the feed that changed the surface properties of the virgin FO membrane. Also, a film of organic and biological foulants accumulated on the FO membrane surface during this time interval and further contributed to the flux decline. Membrane cleaning in similar experiments was not able to restore the initial water flux of a new FO membrane.27 During the last 100 h of interval A the water flux was nearly constant.

During interval B the draw solution concentration was doubled, and although the driving force for the process (i.e., the osmotic pressure of the draw solution) was doubled during this interval, water flux did not increase proportionally. This is attributed to internal concentration polarization phenomenon in FO.28 Water flux during this interval was almost constant, and additional flux decline from membrane fouling was not observed. Chemical cleaning of the RO subsystem and draw solution channels in the FO spiral-wound membrane was performed between interval B and C to remove mineral scale within the RO subsystem. During interval C, draw solution concentration was reduced to approximately 30 g/L sea salt. An equivalent water flux to the end of interval A was observed during this time period. During interval D activated sludge was dosed into the FO feed stream to achieve 5 and later 16 mg/L TSS, and a decrease in water flux was observed. During interval E the dosing rate of activated sludge was increased to achieve approximately 50 mg/L TSS in the FO feed, and additional water flux decline was observed.

3.2.2. Pilot-Scale Performance: TOrCs Rejection. Samples were drawn from the feed, draw solution, and product water of the RO pilot system during interval B through E and analyzed by the isotope dilution LC-MS/MS method. Isotope recoveries for TOrCs in each stream are summarized in the Supporting Information, section S4. All isotope recoveries exceeded minimum thresholds for accurate TOrC concentration quantification based on previous research by Vanderford and Snyder.24 Of the 23 compounds detected in the SBMBR permeate (FO feed), 14 are nonionic, four are negatively charged, and five are positively charged at solution pH between 6 and 7 (representative of the draw solution and feed pH, respectively). Nine TOrCs were analyzed for but were not detected in the samples. These include acetaminophen, atrazine, cimetidine, gemfibrozil, ketoprofen, propylparaben, meprobamate, 4-n-nonylphenol, and norfluoxetine.
Average feed concentration of TOrCs with their associated standard deviation is summarized in Table 2. Concentration of TOrCs detected in the feed varied over the 25 day sampling campaign following fluctuations in usage patterns (e.g., diurnal variation) or wastewater treatment. TOrC concentrations varied substantially between different constituents. Dilantin, diphenhydramine, sulfamethoxazole, TCEP, and triclocarban were routinely detected at concentrations exceeding 100 ng/L. Recent studies demonstrated that these compounds are routinely detected in wastewater treatment plant effluents at concentrations significantly greater than LC-MS/MS quantification limits. Other TOrCs, such as amitriptyline, diazepam, and primidone, were detected at very low concentrations (i.e., below 10 ng/L) likely due to their low usage by the residents. Rejection of several TOrCs that were poorly quantified during bench-scale experiments (i.e., bisphenol A, diclofenac, benzophenone, and triclosan) was well characterized during the pilot-scale investigation. There was negligible difference in TOrC concentrations between SBMBR permeate and SBMBR permeate dosed with activated sludge.

Rejection of TOrCs by the hybrid FO-RO process was calculated for all 23 compounds detected in the SBMBR permeate. Rejection of nonionic, nonionic hydrophobic, negatively charged, and positively charged TOrCs by the hybrid process is summarized in Figure 3. TOrCs are divided into classifications based on charge and hydrophobicity. Nonionic hydrophobic compounds are those with log D values greater than two. TOrC molecular weight is indicated in parentheses after the name of each compound. Operation intervals defined in Table 3 are shown above each column of results. (+) corresponds to TOrC concentrations measured below the detection limit for the instrument in the draw solution (red) or RO product water (blue) and rejection cannot be calculated. (⊙) corresponds to instances where TOrCs or their isotopes produced poor chromatographs and a nondetect of that TOrC is recorded in the draw solution (red) or RO product water (blue). (*) designates assumption of 100% rejection because the compound was detected only in the feed and not in the draw solution or RO product water. (cluster of four black diamonds) designates samples where TOrC concentration was measured in the feed and the RO product water but the draw solution sample registered a nondetect. Error bars represent standard deviation derived from four sampling campaigns during interval B, seven sampling campaigns during interval C, nine sampling campaigns during interval D, and three sampling campaigns during interval E.

Figure 3. Rejection of TOrCs by the hybrid process. TOrCs are divided into classifications based on charge and hydrophobicity. Nonionic hydrophobic compounds are those with log D values greater than two. TOrC molecular weight is indicated in parentheses after the name of each compound. Operation intervals defined in Table 3 are shown above each column of results. (+) corresponds to TOrC concentrations measured below the detection limit for the instrument in the draw solution (red) or RO product water (blue) and rejection cannot be calculated. (⊙) corresponds to instances where TOrCs or their isotopes produced poor chromatographs and a nondetect of that TOrC is recorded in the draw solution (red) or RO product water (blue). (*) designates assumption of 100% rejection because the compound was detected only in the feed and not in the draw solution or RO product water. (cluster of four black diamonds) designates samples where TOrC concentration was measured in the feed and the RO product water but the draw solution sample registered a nondetect. Error bars represent standard deviation derived from four sampling campaigns during interval B, seven sampling campaigns during interval C, nine sampling campaigns during interval D, and three sampling campaigns during interval E.
During intervals C, D, and E, the rejection of nonionic compounds (Figure 3) by the RO membrane generally increased with increasing molecular weight in agreement with findings in previous research.\(^8\) Compounds exhibiting average RO rejection less than 90% during one or more operation intervals included methylparaben, caffeine, benzophenone, oxybenzone, bisphenol A, triclosan, and amitryptiline. Several of these compounds, including methylparaben, bisphenol A, and triclosan have phenolic functional groups, which were demonstrated to have lower than expected rejection based on molecular size due to adsorption to and partitioning through membrane materials.\(^32\)–\(^34\) Benzophenone has been quantified in RO permeate samples collected from water reuse facilities, which is likely due to hydrophobic interactions with membrane materials.\(^35\)

Rejection of TOrCs during pilot-scale experiments was significantly greater than observed for bench-scale experiments under all conditions evaluated (Figures 1 and 3). While the exact reason for this disparity is unclear, membrane compaction, the establishment of a fouling layer, and optimized hydrodynamic conditions in the pilot-scale system may result in more efficient rejection. Furthermore, the FO membrane achieved substantial removal of all constituents except for caffeine during interval B and C. It is possible that the relative hydrophilicity of caffeine (log \(D = 0.13\)) and its relatively small molecular weight contribute to its ability to partition into the relatively hydrophilic FO membrane and to diffuse through the active layer.

Hydrophobic nonionic compounds demonstrated lower correlation with molecular weight (e.g., benzophenone and triclosan rejection by RO, and bisphenol A rejection by FO); yet, with the exception of oxybenzone during interval B, high rejection of these constituents by the hybrid process was maintained (Figure 3). Bisphenol-A rejection by the FO membrane was consistently the lowest of all TOrCs among all groups. A relatively high hydrophobicity (log \(D = 3.43\)) and small molecular weight may partially explain the ability of bisphenol A to diffuse through the membrane. It is also possible for the phenolic structure of bisphenol A to more easily associate with the acetylated hydroxyl groups of the CTA membrane, thus enhancing its transport through the membrane by increasing its concentration at the membrane surface.\(^33\) Enhanced rejection of bisphenol A was observed during intervals D and E, when small doses of activated sludge were injected into the FO feed stream. Previous research\(^19\) suggests that a fouling layer on the membrane surface could separate and inhibit the interaction of the bisphenol A molecule with the membrane surface, thus increasing rejection.

Rejection of charged TOrCs was generally high (Figure 3) and is in agreement with previous research.\(^8\),\(^36\),\(^37\) Negatively charged constituents may be rejected by electrostatic exclusion arising from the negative surface charge of the CTA and SW30 membranes. The mechanism for rejection of positively charged compounds is not completely understood; yet, results from previous studies\(^36\)–\(^39\) indicate that constituent rejection in excess of 90% is possible.

The dual barrier FO-RO process was able to achieve consistently high removal of TOrCs from the wastewater feed stream. Accumulation of TOrCs in the draw solution closed loop\(^16\) (Supporting Information, section S3) was observed; however, a mass balance of the water and TOrCs diffusing through the membrane between sampling intervals revealed that a high rejection of these constituents was maintained. TOrC accumulation in the draw solution also challenged the SWRO membrane with greater concentration of these constituents than would be expected in an open loop system (Supporting Information, section S1). Despite the shortcomings associated with operating the system with the draw solution in a closed loop, total system rejection of TOrCs generally exceeded 99%.

### ASSOCIATED CONTENT

#### Supporting Information
Details on the FO-RO dual barrier system for high efficiency water purification, novel spiral wound FO membrane modules, pilot-scale FO-RO system, and TOrCs analysis and rejection calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

**Corresponding Author**
*Phone: (303) 273-3402. Fax: (303) 273-3413. E-mail: tca@mines.edu.

### ACKNOWLEDGMENT

The authors acknowledge the support of California Department of Water Resources (Grant 46-7446-R-08) and the AWWA Abel Wolman Fellowship. Special thanks to Aqua-Aerobic Systems, Inc. and to Hydration Technologies Innovations for providing membranes, systems, and Supporting Information for this study and to Monte Dipalma for his analytical support.

### REFERENCES

12. Xu, P.; Drewes, J. E.; Bellona, C.; Amy, G.; Kim, T.-U.; Adam, M.; Heberer, T. Rejection of emerging organic micropollutants in


