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# Understanding the organic micropollutants transport mechanisms in the fertilizer-drawn forward osmosis process

Youngjin Kim <sup>a</sup>, Sheng Li <sup>a,b</sup>, Sherub Phuntsho <sup>c</sup>, Ming Xie <sup>d</sup>, Ho Kyong Shon <sup>c\*</sup>, Noredine Ghaffour <sup>a\*</sup>

<sup>a</sup> King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Division of Biological & Environmental Science & Engineering (BESE), Thuwal 23955-6900, Saudi Arabia

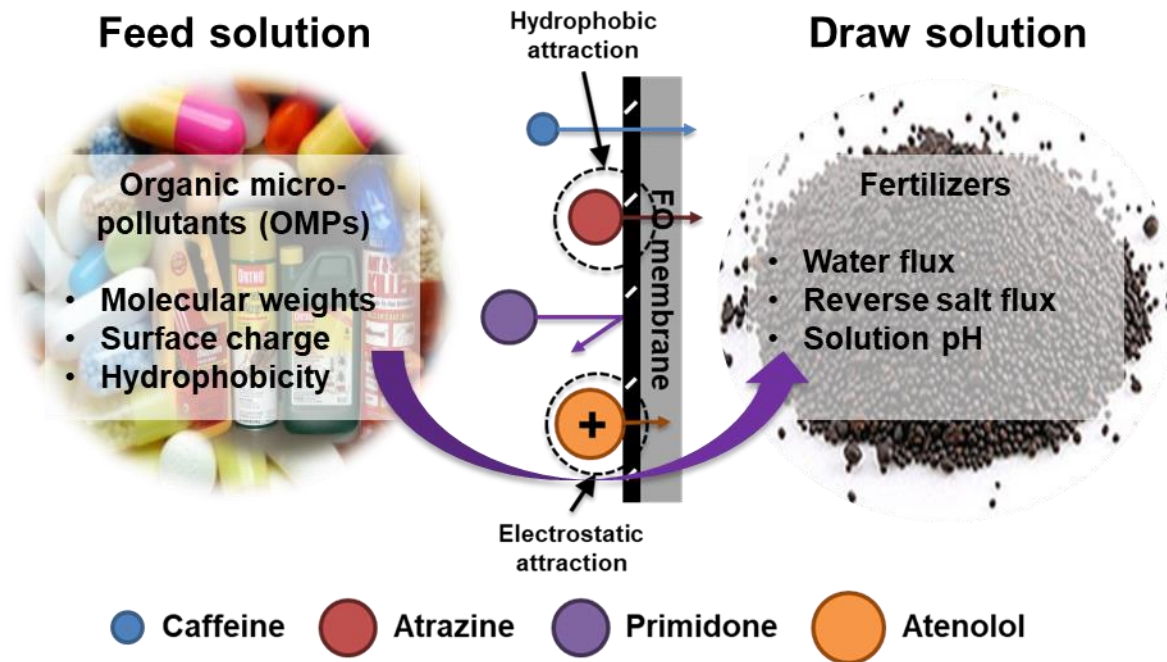
<sup>b</sup> Guangzhou Institute of Advanced Technology, Chinese Academy of Science, Haibin Road #1121, Nansha district, Guangzhou, China

<sup>c</sup> Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia

<sup>d</sup> Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK

\* Co-corresponding authors: Ho Kyong Shon, Tel.: +61-2-9514-2629; E-mail: [Hokyong.Shon-1@uts.edu.au](mailto:Hokyong.Shon-1@uts.edu.au), Noredine Ghaffour. Tel. +966-128082180, E-mail: [noredine.ghaffour@kaust.edu.sa](mailto:noredine.ghaffour@kaust.edu.sa)

## Graphical abstract



## Highlights

- Performance of FDFO was significantly affected by the property of fertilizer DS.

- 21 • OMPs transport was governed by physicochemical property at low water flux and RSF.
- 22 • DAP reduced OMPs flux due to enhanced steric hindrance by increased FS pH and RSF.
- 23 • Transport of OMPs having high molecular weight was readily hampered by high RSF.
- 24 • The pore hindrance model could be helpful in understanding OMPs transport in FDFO.

25

## 26 **Abstract**

27 We systematically investigated the transport mechanisms of organic micropollutants (OMPs) in a  
28 fertilizer-drawn forward osmosis (FDFO) membrane process. Four representative OMPs, i.e.,  
29 atenolol, atrazine, primidone, and caffeine, were chosen for their different molecular weights and  
30 structural characteristics. All the FDFO experiments were conducted with the membrane active  
31 layer on the feed solution (FS) side using three different fertilizer draw solutions (DS): potassium  
32 chloride (KCl), monoammonium phosphate (MAP), and diammonium phosphate (DAP) due to  
33 their different properties (i.e., osmotic pressure, diffusivity, viscosity and solution pH). Using KCl  
34 as the DS resulted in both the highest water flux and the highest reverse solute flux (RSF), while  
35 MAP and DAP resulted in similar water fluxes with varying RSF. The pH of the FS increased with  
36 DAP as the DS due to the reverse diffusion of  $\text{NH}_4^+$  ions from the DS toward the FS, while for  
37 MAP and DAP DS, the pH of the FS was not impacted. The OMPs transport behavior (OMPs flux)  
38 was evaluated and compared with a simulated OMPs flux obtained via the pore-hindrance transport  
39 model to identify the effects of the OMPs structural properties. When MAP was used as DS, the  
40 OMPs flux was dominantly influenced by the physicochemical properties (i.e., hydrophobicity and  
41 surface charge). Those OMPs with positive charge and more hydrophobic, exhibited higher  
42 forward OMP fluxes. With DAP as the DS, the more hydrated FO membrane (caused by increased  
43 pH) as well as the enhanced RSF hindered OMPs transport through the FO membrane. With KCl  
44 as DS, the structural properties of the OMPs were dominant factors in the OMPs flux, however the  
45 higher RSF of the KCl draw solute may likely hamper the OMPs transport through the membrane  
46 especially those with higher MW (e.g., atenolol). The pore-hindrance model can be instrumental  
47 in understanding the effects of the hydrodynamic properties and the surface properties on the  
48 OMPs transport behaviors.

49

50 *Keywords:* FDFO; Organic micropollutants; Fertilizer properties; OMPs properties; Pore-  
51 hindrance model.

52

## 53 **1. Introduction**

54 Organic micropollutants (OMPs), such as pharmaceutical and personal care products, pesticides,  
55 herbicides, household chemicals, have become a growing risk to public health and the environment  
56 in the past decades (Arslan et al., 2017; Snyder et al., 2003; Tang et al., 2013). Despite the  
57 significant possible impact of OMPs, no legal discharge limits have been set by most countries.  
58 Only a few countries monitor and manage OMPs discharge through a watch list (Barbosa et al.,  
59 2016). While wastewater reuse can sustain freshwater resources and provide necessary nutrients  
60 for plants (Jeong et al., 2016), the presence of OMPs in raw sewage (Escher et al., 2014) directly  
61 influences and reduces its reuse, particularly in the agricultural sector. A more efficient process  
62 for the removal of OMPs from wastewater could facilitate the reuse and discharge of wastewater.

63 [The OMPs removal efficiencies of conventional biological wastewater treatment technologies,](#)  
64 [such as the activated sludge process, are reported to range from 0% to 90% depending on OMPs](#)  
65 [properties, sludge properties, and operating conditions \(Grandclément et al., 2017\).](#) Such variation  
66 limits the consistent and safe reuse of wastewater (Bernhard et al., 2006; Carballa et al., 2004;  
67 Clara et al., 2005; Grandclément et al., 2017; Pérez et al., 2005). To enhance the efficiency of  
68 biological treatments, a membrane bioreactor (MBR), which combined a bioreactor with  
69 microfiltration (MF) or ultrafiltration (UF), was proposed (Krzeminski et al., 2017). This MBR  
70 advertised a small environmental footprint, high effluent quality, and complete rejection of  
71 suspended solids, and could be effective in the treatment of OMPs that were not readily removed  
72 by the activated sludge treatment process (Bernhard et al., 2006; Clara et al., 2005; Hai et al., 2011).  
73 However, this MBR technology did not meet the permissible limits, e.g., 1 µg L<sup>-1</sup> for irrigation  
74 reuse ((NSW), 2004), for adequate water-reuse quality.

75 Wastewater reclamation and reuse is considered more cost-effective and environmentally  
76 friendly than seawater desalination for solving water-scarcity issues because it has low energy  
77 requirements and additional water does not need to be transferred to inland regions (Shannon et  
78 al., 2008). Advanced membrane processes, such as nanofiltration (NF) or reverse osmosis (RO),  
79 have been widely employed in wastewater reuse to improve the efficiency of OMPs removal, since

80 even very low concentrations of many OMPs may have a harmful impact on the environment  
81 (Fujioka et al., 2015; Radjenović et al., 2008; Snyder et al., 2003). Ionic or charged OMPs are  
82 rejected more easily by RO membranes with a negative surface charge, while hydrophobic  
83 nonionic OMPs are rejected at decreasing rates with operation (Xu et al., 2005). Also, the rejection  
84 of negatively charged OMPs was observed to be higher than that of positively charged OMPs,  
85 despite similar molecular weights (Fujioka et al., 2015). While both the NF and RO membranes  
86 achieved high rejections of OMPs, they also failed to retain some OMPs, implying that the reuse  
87 of wastewater treated with these membranes may pose a risk (Radjenović et al., 2008).  
88 Furthermore, pressure-driven membrane-based desalting processes have many disadvantages, e.g.,  
89 high energy demands and severe membrane fouling caused by high hydraulic pressure (Chong et  
90 al., 2015; Ghaffour et al., 2013; Xie et al., 2015).

91 To overcome these problems, forward osmosis (FO) was recently presented as a potential  
92 alternative to the conventional, pressure-driven membrane processes used for desalination (Lee et  
93 al., 2010). FO uses a high concentration gradient as its driving force, which not only generates a  
94 high water flux, but also reversely diffuses the draw solutes towards the feed solution (FS). As the  
95 reverse solute flux (RSF) moves in the opposite direction of the OMPs solute flux, it hinders the  
96 OMPs flux. Thus, the FO process was reported to have a higher OMPs removal efficiency than the  
97 RO process (Kim et al., 2012; Xie et al., 2012a).

98 Operational conditions (i.e., water flux, solution pH, membrane orientation, and working  
99 temperature) also significantly affect OMPs rejections (Jamil et al., 2016; Jin et al., 2012; Xie et  
100 al., 2013). The OMPs removal of the FO process was much less efficient when the active layer of  
101 the membrane was facing the draw solution (DS), i.e., AL-DS, than when the active layer was  
102 oriented towards the feed solution (FS), i.e., AL-FS (Jin et al., 2012; Xie et al., 2012b). In the AL-  
103 FS orientation, an internal concentration polarization (ICP) occurred, which not only increased the  
104 OMPs concentration inside the membrane support layer, but also severely restricted the backward  
105 diffusion (mass transfer) of the OMPs into the bulk FS. Thus, the OMPs flux was enhanced and  
106 the efficiency of its removal was reduced (Alturki et al., 2013; Jin et al., 2012). At high FS  
107 temperatures, the OMPs rejection decreased due to the enhanced OMPs diffusivity; the opposite  
108 effect was observed at high DS temperatures. The OMPs rejection increased at high DS  
109 temperatures because the enhanced water flux had a diluting effect and the slightly elevated reverse

110 solute flux had a hindrance effect (Xie et al., 2013). The solution pH also significantly influenced  
111 the ionic OMPs rejection (Xie et al., 2012b). The thin-film composite (TFC) FO membrane based  
112 on polyamide (PA) was reported to have a much better OMPs rejection due to pore hydration than  
113 FO membranes based on cellulose triacetate (CTA), even though TFC membranes have larger pore  
114 sizes (Xie et al., 2014b). Membrane fouling also significantly influenced OMPs rejection, and a  
115 previous study observed that the initial FO water flux played a key role in both membrane fouling  
116 and OMPs rejection (Jin et al., 2012; Xie et al., 2014a). [Interfacial interactions between foulants  
117 and membrane are decisive forces to membrane fouling \(Qu et al., 2018; Teng et al., 2019\),  
118 potentially affecting OMPs rejection.](#) The surface characteristics of the fouling layer in a fouled  
119 FO membrane could also influence OMPs rejection (Valladares Linares et al., 2011). [The  
120 characteristics of the fouling/cake layer may be an important factor affecting OMPs rejection due  
121 to their different resistance depending on their composition \(Teng et al., 2018; Zhang et al., 2018\).](#)  
122 However, since the FO process simply converts a concentrated DS into a diluted DS, additional  
123 desalting processes are needed to produce pure water while the diluted DS is reconcentrated and  
124 regenerated for a sustainable operation (Chekli et al., 2016).

125 The fertilizer-drawn forward osmosis (FDFO) process has received significant attention  
126 because a diluted fertilizer DS can be directly applied in irrigation with no need for DS separation  
127 (Kim et al., 2018; Kim et al., 2017d). FDFO was employed in irrigation reuse by integrating it  
128 with an anaerobic MBR (AnMBR) (Kim et al., 2016), and was successful in concentrating  
129 municipal wastewater (Chekli et al., 2017b). However, one of the major concerns with FDFO is  
130 the high reverse diffusion of inorganic fertilizers towards the bioreactor, as it negatively impacts  
131 the anaerobic microorganisms, reducing biogas production (Kim et al., 2017a; Li et al., 2017b).  
132 Also, biofouling on the osmotic membrane surface is considerably influenced by the properties of  
133 the fertilizers used as the DS (Li et al., 2017a). Despite these drawbacks, FDFO was found to be  
134 feasible for wastewater treatment, and it has exhibited high OMPs removal during the treatment  
135 of AnMBR effluent (Kim et al., 2017c). When commercial hydroponic fertilizer solutions were  
136 evaluated for use as the DS, the fertilizer solution diluted by a pilot-scale FDFO system was found  
137 to be appropriate for a hydroponic application (Chekli et al., 2017a). Though many studies have  
138 attempted to understand the FDFO process for wastewater treatment, the OMPs transport  
139 mechanisms in the FDFO process have not yet been well elucidated.

140 Therefore, the aim of this study is to investigate the transport mechanisms of the OMPs in the  
 141 FDFO process. Four different OMPs (atenolol, atrazine, primidone, and caffeine) were used to  
 142 investigate the effects of molecular weight and physicochemical properties such as hydrophobicity  
 143 and surface charge. Caffeine and primidone were compared due to their different molecular  
 144 weights and similar surface physicochemical properties (i.e., neutral surface charges and similar  
 145 hydrophobicity). Atrazine and primidone were examined since they have different  
 146 hydrophobicities, but similar molecular weights and neutral surface charges. Finally, atenolol was  
 147 examined to determine the effect of a positive surface charge on the OMPs transport behaviors.  
 148 For evaluation, three different fertilizers potassium chloride (KCl), monoammonium phosphate,  
 149 i.e.,  $\text{NH}_4\text{H}_2\text{PO}_4$  (MAP), and diammonium phosphate, i.e.,  $(\text{NH}_4)_2\text{HPO}_4$  (DAP)) were employed as  
 150 draw solutes in this study because they have the different properties and performances (i.e., water  
 151 flux, RSF, and a pH change of the FS) as reported the FDFO process (Kim et al., 2017c). To  
 152 identify the effect of the physicochemical properties of the OMPs surfaces on their transport, the  
 153 pore-hindrance transport model, which has been utilized to estimate rejections by size exclusion  
 154 (Rodgers and Miller, 1993), was employed and compared to the experimental data.

155

## 156 2. Materials and methods

### 157 2.1. Representative organic micropollutants (OMPs)

158 Four different OMPs, i.e., atenolol, atrazine, caffeine, and primidone, were provided by Sigma  
 159 Aldrich in a powder form. Their key physicochemical characteristics are presented in **Table 1**. The  
 160 diffusivity of the solute was calculated based on the Wilke and Chang equation, while the Stokes-  
 161 Einstein equation was used to calculate the Stokes radius (Wilke and Chang, 1955). To prepare a  
 162  $4 \text{ g L}^{-1}$  stock solution, 4 mg OMPs were added to 1 mL methanol; the stock solution was stored  
 163 until use at about  $4 \text{ }^\circ\text{C}$ .

164

165 **Table 1:** Key physicochemical characteristics of the OMPs used in this study.

|                                    | Caffeine                                      | Atrazine                              | Primidone  | Atenolol   |
|------------------------------------|---|---------------------------------------|--|--|
| Application                        | Stimulant                                     | Herbicide                             | Anticonvulsant                                   | Beta-blocker                                     |
| Formula                            | $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ | $\text{C}_8\text{H}_{14}\text{ClN}_5$ | $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$ | $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$ |
| Molecular weight<br>(g/mol)        | 194   | 216                                   | 218  | 266  |
| Charge <sup>a</sup><br>(at pH 6.5) | Neutral                                       | Neutral                               | Neutral  | Positive   |

|   |       |      |       |       |
|---|-------|------|-------|-------|
| Log $D^{a, b}$<br>(at pH 6.5)                             | -0.63 | 2.64 | 0.83  | -2.09 |
| $pK_a^a$  | 0.52  | 2.27 | 12.26 | 9.6   |
| Diffusivity <sup>c</sup> ( $\times 10^{-10}$<br>$m^2/s$ ) | 6.46  | 6.10 | 6.07  | 5.46  |
| Stokes radius <sup>d</sup><br>(nm)                        | 0.33  | 0.35 | 0.35  | 0.39  |

<sup>a</sup> Information about the surface charge, Log  $D$ , and  $pK_a$  was adopted from the ChemSpider website (<http://www.chemspider.com>).

<sup>b</sup> High Log  $D$  values indicate high hydrophobicity.

<sup>c</sup> Diffusivity at 20 °C was calculated based on the Wilke and Chang equation (Wilke and Chang, 1955).

<sup>d</sup> Stokes radius was calculated based on the Stokes-Einstein equation (Wilke and Chang, 1955).

166

## 167 2.2. FO membrane and draw solutions (DS)

168 CTA FO membranes from HTI (Hydration Technology Innovations, USA) were used in the  
 169 present study. The membrane transport parameters were adopted from our previous study (Kim  
 170 et al., 2016), and are presented in **Table S1**, Supplementary Data. The average pore radius and  
 171 structural factors of FO membranes (**Table S2**, Supplementary Data) from another study (Xie et  
 172 al., 2014b) were employed and utilized to solve the pore-hindrance transport model. The surface  
 173 characteristics of the FO membrane, such as contact angle, zeta potential, and roughness of the  
 174 selective layer, are presented in **Table 2**. A Sigma 701 microbalance (KSV Instrument Ltd.,  
 175 Finland) was used to determine the surface contact angle. The zeta potential of the membrane  
 176 surface was measured using a streaming current electrokinetic analyzer (SurPass, Anton Paar  
 177 GmbH, Austria). The roughness of the membrane surface was characterized using atomic force  
 178 microscopy (AFM) (Dimension Icon, Germany). *At least three measurements were taken for  
 179 each membrane sample and the average value was used.*

180

181 **Table 2.** Surface characteristics of an HTI CTA FO membrane. The zeta potential was measured  
 182 at pH 6.5 with 0.01 M KCl as the background electrolyte solution. The contact angle and the  
 183 roughness were determined at pH 6.5 and room temperature. (Average  $\pm$  standard deviation)

|                 | Contact angle        | Zeta potential      | Roughness           |
|-----------------|----------------------|---------------------|---------------------|
| CTA FO membrane | $79.5 \pm 5.2^\circ$ | $-6.87 \pm 2.07$ mV | $13.33 \pm 2.89$ nm |

184

185 Three reagent-grade fertilizers (KCl, MAP and DAP) were used as received from Sigma  
 186 Aldrich for the DS. The DS was prepared by dissolving an appropriate amount of fertilizer salt in



187 deionized (DI) water. The thermodynamic properties of the fertilizer chemicals are presented in  
188 **Table S3**, Supplementary Data.

189

### 190 2.3. FDFO experimental studies

191 For all the experimental studies, a lab-scale FO unit consisting of two variable-speed gear pumps  
192 (Cole-Parmer, USA), a standard membrane cell, two flow meters, and a balance was used. The FO  
193 membrane cell contained two symmetric flow channels (100 mm length  $\times$  20 mm width  $\times$  3 mm  
194 depth) for the FS and DS, and the FO membrane was installed between these two channels. The  
195 FO membrane cell was operated at a crossflow rate of 8.5 cm s<sup>-1</sup> in the direction of the co-current  
196 crossflow. The FO process was operated in batch mode, meaning that both the FS and DS were  
197 recirculated back to their respective solution tanks, which were maintained at a constant  
198 temperature of 20  $\pm$  1 °C using a temperature control system. The experiments were carried out  
199 for a duration of 10 hours, using a fertilizer DS (either 1 M or 2 M) with the AL-FS membrane  
200 orientation. The OMPs transport mechanism was investigated by adding 10  $\mu$ L OMPs stock  
201 solution (1g L<sup>-1</sup> each OMPs) into 1 L FS to achieve a 10  $\mu$ g L<sup>-1</sup> concentration of each OMP. The  
202 change in the diluted DS volume was recorded by placing the DS tank on a digital weighing scale  
203 (Mettler Toledo, USA) connected to a PC for data logging; these data were used to calculate the  
204 water flux using **Eq. (1)**,

$$205 \quad J_w = \frac{\Delta V_{DS}}{A_m t}, \quad (1)$$

206 where  $J_w$  refers to the measured water flux (L m<sup>-2</sup> h<sup>-1</sup>),  $\Delta V_{DS}$  is the change in DS volume (L) during  
207 operation,  $A_m$  refers to the membrane area (m<sup>2</sup>), and  $t$  refers to the operation time (h). After the  
208 experiments, the concentrated FS was sampled and analyzed to obtain RSF using **Eq. (2)**,

$$209 \quad J_s = \frac{\Delta m_{DS}}{A_m t}, \quad (2)$$

210 where  $J_s$  refers to RSF (mol m<sup>-2</sup> h<sup>-1</sup>) and  $\Delta m_{DS}$  is the change in the mass of the draw solutes in the  
211 FS during operation (mol). The detailed experimental procedures are described in our previous  
212 studies (Kim et al., 2017c; Kim et al., 2017d).

213

### 214 2.4. Analytical methods for OMPs

215 The OMPs concentrations were obtained based on methods used in our earlier study (Kim et al.,  
216 2017c). After the experiments, 100 mL samples were collected, to which 10  $\mu$ L isotopes were

217 added (Cambridge Isotope Laboratories, Inc., USA). The OMPs were removed from the samples  
 218 using solid-phase extraction (Dione Autotrace 280 and Oasis cartridges). Then, the evaporation  
 219 for extrated samples was conducted at temperature of 60 °C for 1 hour and LC/MS grade methaol  
 220 was added in evaporated samples to make 1 mL samples. Finally, the OMPs concentrations were  
 221 measured using liquid chromatography (Agilent Technology 1260 Infinity LC unit, USA) and  
 222 mass spectrometry (AB SCIEX QTRAP 5500 mass spectrometer, Applied Biosystems, USA). The  
 223 recovery ratio (i.e., the ratio of the peak areas before and after extraction) was considered to  
 224 evaluate the loss of OMPs during the extraction and evaporation processes and to calculate the  
 225 final concentration of OMPs by multiplying the measured concentrations by the obtained recovery  
 226 ratio. Then, the OMPs forward flux (toward DS) was derived based on the mass balance for OMPs  
 227 species (Kim et al., 2012; Kim et al., 2017c) using **Eq. (3)**,

$$228 \quad J_{OMPs} = \frac{C_{OMPs}(V_{Di} + J_w A_m t)}{A_m t} = \frac{C_{OMPs} V_{Df}}{A_m t} \quad , \quad (3)$$

229 where  $C_{OMPs}$  refers to the concentration of OMPs in the DS ( $\mu\text{g L}^{-1}$ ),  $V_{di}$  and  $V_{df}$  are the initial and  
 230 final DS volumes (L), respectively, and  $J_{OMPs}$  refers to the forward flux of the OMPs from the FS  
 231 toward the DS ( $\mu\text{g m}^{-2} \text{h}^{-1}$ ).

232

## 233 2.5. Models for OMPs transport behaviors

### 234 2.5.1. Pore-hindrance transport model

235 It can be assumed that the FO membrane consisted of several cylindrical capillary tubes with the  
 236 same radius, where the spherical solute particles can penetrate through these FO membrane pores  
 237 (Xie et al., 2014b). The pore-hindrance transport model was originally developed to simulate blood  
 238 flow through individual capillaries (Bungay and Brenner, 1973), but it has also been utilized to  
 239 estimate rejections by size exclusion in porous membranes for microfiltration and ultrafiltration  
 240 (Rodgers and Miller, 1993), and the NF [27], RO [43], and FO processes (Nghiem et al., 2004; Xie  
 241 et al., 2014b; Yoon and Lueptow, 2005). So, the real OMPs rejection was determined using **Eq.**  
 242 **(4)** (Nghiem et al., 2004; Xie et al., 2014b),

$$243 \quad R_r = 1 - \frac{C_p}{C_m} = 1 - \frac{\varphi K_c}{1 - \exp(-P_e(1 - \varphi K_c))} \quad , \quad (4)$$

244 where  $R_r$  refers to the real rejection of the FO membrane,  $C_p$  is the permeate OMPs concentration  
 245 ( $\mu\text{g L}^{-1}$ ),  $C_m$  is the OMPs concentration at the membrane surface ( $\mu\text{g L}^{-1}$ ),  $K_c$  is the hydrodynamic

246 hindrance coefficient for convection,  $\varphi$  is the distribution coefficient, and  $Pe$  is the membrane  
 247 peplet number. The distribution coefficient (**Eq. (5)**) is related to the ratio of the OMPs radius to  
 248 the membrane pore radius (**Eq. (6)**):

$$249 \quad \varphi = (1 - \lambda)^2, \quad (5)$$

$$250 \quad \lambda = \frac{r_s}{r_p}. \quad (6)$$

251 The peplet number is defined as the ratio of the convective transport rate to the diffusive transport  
 252 rate, and can be obtained from **Eq. (7)**,

$$253 \quad Pe = \frac{K_c J_w l}{K_d D \varepsilon}, \quad (7)$$

254 where  $K_d$  refers to the hydrodynamic hindrance coefficient for diffusion,  $D$  refers to the Stokes-  
 255 Einstein diffusion coefficient ( $m^2 s^{-1}$ ),  $l$  is the active layer thickness (m), and  $\varepsilon$  refers to the active  
 256 layer effective porosity. The hydrodynamic hindrance coefficients for convection and diffusion  
 257 can be determined via **Eq. (8) and (9)**, respectively, which were proposed by Bungay and Brenner  
 258 (Bungay and Brenner, 1973):

$$259 \quad K_c = \frac{(2-\varphi)K_s}{2K_t}, \quad (8)$$

$$260 \quad K_d = \frac{6\pi}{K_t}. \quad (9)$$

261 Diffusion may be more dominant than convection in determining the solute transports when  $\lambda$  is  
 262 close to 1. Details on the calculations of the hydrodynamic hindrance coefficients can be found  
 263 elsewhere (Bungay and Brenner, 1973; Nghiem et al., 2004; Wang et al., 2014).

264

### 265 *2.5.2. Relationship between real rejection and observed rejection*

266 Since the real rejection is relative to the permeate and the active layer concentrations, as suggested  
 267 by **Eq. (4)**, the observed rejection ( $R_o = 1 - c_p/c_f$ ) must be calculated to obtain the OMPs  
 268 forward flux. The observed rejection can be obtained from the relationship between the real  
 269 rejection and the observed rejection, which is readily derived from concentration polarization in  
 270 film theory (Nghiem et al., 2004) and given by **Eq. (10)**:

$$271 \quad \ln \frac{(1-R_r)}{R_r} = \ln \frac{(1-R_o)}{R_o} - \frac{J_w}{k}, \quad (10)$$

272 where  $R_o$  refers to the observed rejection of the FO membrane and  $k$  refers to the mass transfer  
 273 coefficient related to the concentration polarization effects near the membrane active layer ( $\text{m s}^{-1}$ ).  
 274 Details on calculations of mass transfer coefficients are given elsewhere (Kim et al., 2017c).

275  
 276 *2.5.3. Simulation of OMPs forward flux*

277 To simulate the OMPs forward flux, the OMPs concentrations in the FS and the permeate should  
 278 be determined first. The change in the volume and OMPs concentration of the FS is calculated  
 279 using a mass balance based on **Eq. (11)**:

280 
$$\frac{dC_f(t)}{dt} = -\frac{J_w(t)A_m C_p(t)}{V_f(t)} - \frac{C_f(t)}{V_f(t)} \frac{dV_f(t)}{dt}, \quad (11)$$

281 where  $C_f(t)$  refers to the OMPs concentration in the FS ( $\mu\text{g L}^{-1}$ ),  $J_w(t)$  refers to the water flux ( $\text{L m}^{-2}$   
 282  $\text{h}^{-1}$ ),  $C_p(t)$  is the permeate OMPs concentration ( $\mu\text{g L}^{-1}$ ), and  $V_f(t)$  refers to the FS volume (L).  
 283 The water fluxes were obtained from the experimental data (**Eq. (1)**) and the permeate  
 284 concentrations were obtained from **Eq. (4)**. All parameters varied with respect to operation time.  
 285 The OMPs concentration in the DS should also be determined to obtain the average OMPs forward  
 286 flux. Similarly, the change in the volume and OMPs concentration of the DS is calculated from  
 287 the mass balance using **Eq. (12)**:

288 
$$\frac{dC_d(t)}{dt} = \frac{J_w(t)A_m C_p(t)}{V_d(t)} - \frac{C_d(t)}{V_d(t)} \frac{dV_d(t)}{dt}. \quad (12)$$

289 Then, average OMPs forward flux can be obtained via

290 
$$J_{s,OMPs}(t) = \frac{C_d(t)V_d(t)}{A_m}, \quad (13)$$

291 where  $C_d(t)$  refers to the concentration of OMPs in the DS ( $\mu\text{g L}^{-1}$ ),  $V_d(t)$  is the DS volume (L),  
 292 and  $J_{s,OMPs}(t)$  refers to the average forward OMPs flux ( $\mu\text{g m}^{-2}\text{L}^{-1}$ ).

293

294 **3. Results and discussion**

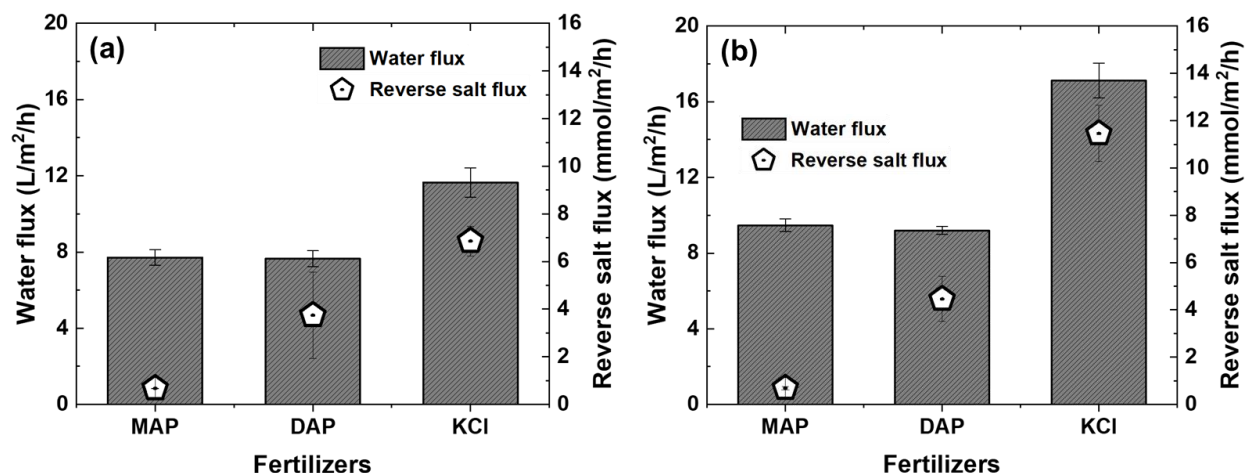
295 *3.1. FDFO membrane performance*

296 In the present study, we investigated the effects of employing three different fertilizer chemicals  
 297 (MAP, DAP, and KCl) as the DS in FDFO on the transport mechanisms of OMPs. Our previous  
 298 study showed that MAP and DAP have similar water fluxes but different RSF, while KCl has a  
 299 higher water flux and RSF than either MAP or DAP (Kim et al., 2017c). Here, we first conducted  
 300 FO experiments with each of these fertilizers as the DS. The results shown in **Fig. 1** confirm that

301 KCl exhibited the highest water flux, while MAP and DAP showed similar water fluxes regardless  
302 of the DS concentration, consistent with other studies (Kim et al., 2017c; Phuntsho et al., 2011).  
303 As presented in **Table S3**, DAP had the highest osmotic pressure. Therefore, since water flux is  
304 governed by the effective osmotic pressure gradient across the active layer, DAP might be  
305 expected to have the highest water flux. However, DAP with the lowest diffusion coefficient is  
306 expected to create higher ICP effect likely resulting in lower water flux than KCl. Besides the  
307 membrane structural parameter (support layer porosity and tortuosity), the diffusion coefficient of  
308 the solutes has a significant influence on the severity of ICP effects (McCutcheon and Elimelech,  
309 2006). On the other hand, MAP had a lower water flux than KCl despite their similar osmotic  
310 pressures (i.e., 49.85 atm and 43.3 atm for MAP 1 M and KCl 1 M, respectively). This was due to  
311 the high diffusivity and low viscosity of KCl compared to the other fertilizers tested as the DS. It  
312 has been shown in the past that high diffusivity and low viscosity of the DS reduce ICP in the  
313 support layer, thereby increasing the effective concentration gradient and improving the water flux  
314 (Kim et al., 2015).

315 We also investigated RSF for the three DS, as shown in **Fig. 1**. KCl showed the highest RSF,  
316 followed by DAP and MAP, at both 1 M and 2 M DS concentrations. This high RSF of KCl could  
317 be due to the low ICP discussed above. In addition, KCl has a lower hydrated diameter than either  
318 MAP or DAP, which possibly results in high salt permeability (Achilli et al., 2010). Despite the  
319 lower diffusivity of DAP (**Table S3**), DAP showed higher RSF than MAP. We attribute this to  
320 DAP containing more ions, and particularly ammonium ions ( $\text{NH}_4^+$ ), than MAP. Therefore, even  
321 though DAP had a lower effective concentration gradient, more ions existed on the active layer,  
322 which induced the high RSF. Furthermore, due to the reverse diffusion of these ammonium ions,  
323 the pH of the FS increased during the FDFO operation, consistent with our previous study (Kim  
324 et al., 2017c). RSF for the 2 M concentration was proportionately higher than for the 1 M  
325 concentration.

326



327  
 328 **Figure 1.** Water flux (columns, left axis) and reverse salt flux (open symbols, right axis) with three  
 329 fertilizers (MAP, DAP, and KCl) as the DS in FDFO at (a) 1 M DS concentration and (b) 2 M DS  
 330 concentration.

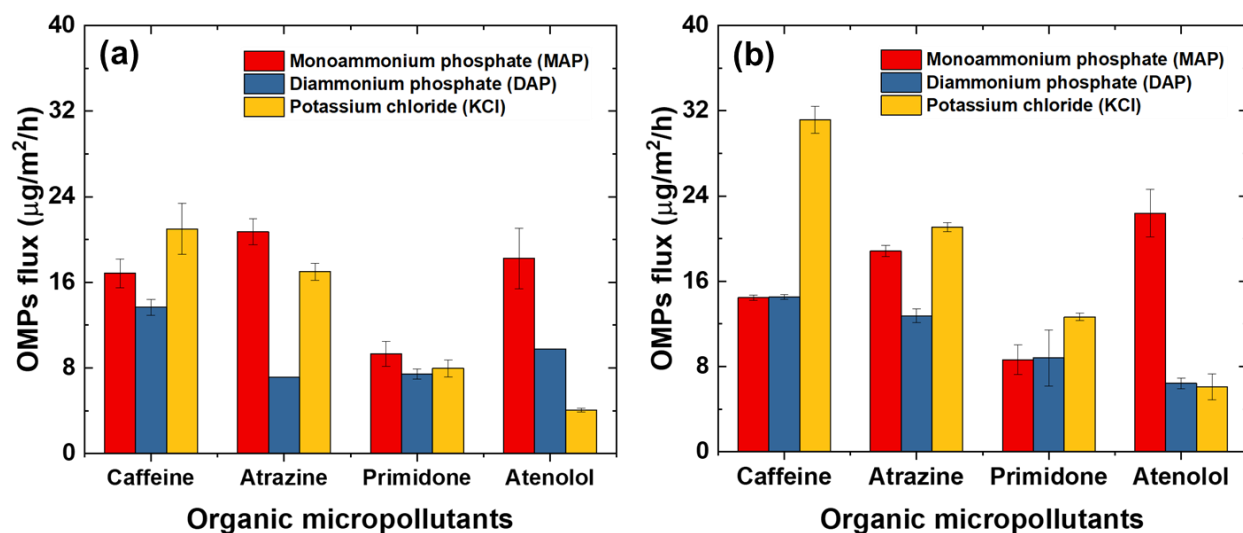
331  
 332 *3.2. OMPs transport behaviors in FDFO*

333 In order to investigate the effects of the physicochemical properties of the OMPs surfaces on their  
 334 transport behaviors during the FDFO process, we chose to use MAP as the DS. Since MAP had a  
 335 lower specific RSF (0.1 mmol L<sup>-1</sup>) compared to the other fertilizers (i.e., 0.3 mmol L<sup>-1</sup> for DAP  
 336 and 0.6 mmol L<sup>-1</sup> for KCl) at 1 M DS concentrations, we expected it to have a smaller impact on  
 337 the OMPs transport behavior. To evaluate the OMPs transport behaviors, we measured the OMPs  
 338 forward flux (see **Fig. 2**). Primidone showed the lowest OMPs flux (**Fig. 2a**), followed by caffeine,  
 339 atenolol, and atrazine. It is well known that OMPs transports in membrane-based processes are  
 340 dominantly influenced by their molecular weights (Kimura et al., 2004; Kiso et al., 2001; Xie et  
 341 al., 2014b). However, it was difficult to ascertain a good correlation between the forward OMPs  
 342 flux and the molecular weight, as shown in **Fig. S1a**. Even though atrazine and atenolol have  
 343 higher (or similar) molecular weights than caffeine and primidone, the OMPs fluxes of atrazine  
 344 and atenolol were higher than those of caffeine and primidone. Atrazine in particular exhibited a  
 345 much higher OMPs flux than primidone despite having a similar molecular weight (i.e., 216 g mol<sup>-1</sup>  
 346 and 218 g mol<sup>-1</sup> for atrazine and primidone, respectively).

347 When the DS concentration was increased from 1 M to 2 M, as shown in **Fig. 2b**, the OMPs  
 348 flux slightly decreased (i.e., reduction of 14.2%, 9.2%, and 7.1% for caffeine, atrazine, and  
 349 primidone, respectively), while the trends among the OMPs did not change significantly. **However,**

350 atenolol exhibited a different behavior, as its flux increased by 23.1%, from  $18.2 \mu\text{g m}^{-2} \text{h}^{-1}$  to  $22.4$   
 351  $\mu\text{g m}^{-2} \text{h}^{-1}$  which is possibly due to its positive charge. When FO process is operated at higher  
 352 water fluxes using higher DS concentrations, it also proportionately increases the atenolol  
 353 concentration at the membrane surface due to enhanced ECP effects. This likely enhanced OMP  
 354 flux of the positively charged atenolol aided by the increased electrostatic attraction with a  
 355 negatively charged FO membrane surface. Similar to the results at 1 M DS concentration, there  
 356 was no clear correlation between the molecular weight and the OMPs flux (**Fig. S1b**). These  
 357 phenomena are likely due to the different physicochemical characteristics (i.e., hydrophobicity and  
 358 surface charges) of the OMPs.

359



360  
 361 **Figure 2.** OMPs flux with three fertilizers as the DS (i.e., MAP, DAP, and KCl) during FDFO at  
 362 (a) 1 M DS concentration and (b) 2 M DS concentration.

363

364 To further investigate the effects of the DS properties on the OMPs transport behaviors, we  
 365 also tested DAP and KCl. As discussed in **Section 3.1**, DAP exhibited a similar water flux but  
 366 higher RSF than MAP, and KCl showed both a higher water flux and a higher RSF. When using  
 367 1 M DAP DS, atrazine exhibited the lowest OMPs flux (**Fig. 2a**) and the highest rejection rate  
 368 (**Table S4**, Supplementary Data), followed by primidone, atenolol, and caffeine. Compared with  
 369 1 M MAP DS, the OMPs fluxes were reduced overall (i.e., reduction ratio: 18.8%, 65.7%, 20.1%,  
 370 and 46.4% for caffeine, atrazine, primidone, and atenolol, respectively). This might be due to the

371 combined effects of the enhanced RSF and the increased FS pH on the OMPs transport behaviors,  
372 as suggested in **Section 3.1**.

373 When increasing the DS concentration from 1 M to 2 M, the OMPs fluxes increased by 6.1%,  
374 79.3%, and 18.3% for caffeine, atrazine, and primidone, respectively and while of atenolol, it  
375 decreased by 34.3%. This might be due to the enhanced water flux of  $9.2 \text{ L m}^{-2} \text{ h}^{-1}$  at 2 M DAP  
376 from  $7.6 \text{ L m}^{-2} \text{ h}^{-1}$  at 1 M DAP. Increasing the permeation drag force, i.e., water flux, could  
377 deteriorate the external concentration polarization, thereby increasing the OMPs forward flux. An  
378 increase of the atenolol forward flux can be due to slightly higher increase in the feed pH when  
379 2M DAP is used as DS (pH 9.73) compared to 1 M DAP as DS (pH 9.17) due to higher reverse  
380 diffusion of  $\text{NH}_4^+$  towards the FS at higher DS concentrations. Comparing the DAP DS with the  
381 MAP DS, only atrazine and atenolol exhibited noticeable changes in the OMPs forward flux. This  
382 result supports the theory that increases in RSF and FS pH have a more significant effect on the  
383 transports of hydrophobic and positively charged OMPs.

384 We conducted FDFO experiments using 1 M KCl as the DS to investigate the effect of RSF  
385 on the OMPs transport behaviors. Results show that atenolol exhibited the lowest OMPs flux ( $4.1$   
386  $\mu\text{g}^{-1} \text{ m}^{-2} \text{ h}^{-1}$ ), followed by primidone, atrazine, and caffeine. The OMPs fluxes of atrazine,  
387 primidone, and atenolol were reduced by 18%, 14.4%, and 77.8%, respectively, with 1 M KCl DS  
388 compared to 1 M MAP DS, despite the enhanced permeation drag force (50.9%). In contrast, the  
389 OMPs flux of caffeine was higher by 24.6% with 1 M KCl DS than with 1 M MAP DS. This may  
390 be because the OMPs flux can be dominantly influenced by operational factors, such as water flux,  
391 RSF, and physicochemical properties such as molecular size of the OMPs themselves. When the  
392 concentration of the KCl DS was increased to 2 M, atenolol had the lowest OMPs flux, followed  
393 by primidone, atrazine, and caffeine, similar to the trend seen with 1 M KCl DS (**Fig. 2b**).  
394 Therefore, it is interesting to note that the DS with the highest RSF showed a better linear  
395 correlation between the OMPs flux and the molecular weight (**Fig. S1**, Supplementary Data).

396

397 *3.3. Modeling OMPs transports using the pore-hindrance model: Transport mechanisms in FDFO*

398 *3.3.1. Effect of OMPs physicochemical properties on OMPs transport behaviors*

399 For a more detailed investigation of the OMPs transport behaviors during the FDFO process, we  
400 simulated the OMPs forward fluxes via the pore-hindrance model and the mass balance, and



401 compared the simulation results with the experimental data. To elucidate the effect of  
 402 physicochemical properties on the OMPs transports, we modeled the OMPs forward flux with 1  
 403 M MAP DS (**Fig. 3a**). Interestingly, the forward fluxes of all the OMPs were increased in the  
 404 simulations compared to the experiments because the pore-hindrance model considers only the  
 405 steric hindrance between the OMPs and the FO membrane; their chemical properties were not  
 406 taken into account. The results presented in the table in **Fig. 3a** show that atrazine and atenolol  
 407 exhibited more significant differences between their modeled and experimental OMPs fluxes than  
 408 caffeine and primidone, possibly because of their different physicochemical properties (i.e.,  
 409 hydrophobicity and surface charges) (**Fig. 4a**). The surfaces of caffeine, atrazine, and primidone  
 410 have similar neutral charges but different hydrophobicities (**Table 1**). *Atrazine has a hydrophobic*  
 411 *property and this could possibly cause adsorption of atrazine onto the membrane surface, thus,*  
 412 *enhancing OMPs transport through the moderately hydrophilic FO membrane (the contact angle*  
 413 *of the FO membrane's active layer was 79.5° as shown in Table 2).*To further confirm this  
 414 hypothesis, we calculated the adsorbed amounts of OMPs based on their mass balance; the results  
 415 are presented in **Table 3**. Atrazine, which has a neutrally charged surface, exhibited the second  
 416 highest adsorbed amount (i.e., 2.79 mg m<sup>-2</sup>, 0.17 mg m<sup>-2</sup>, 1.27 mg m<sup>-2</sup>, and 3.31 mg m<sup>-2</sup> for atrazine,  
 417 caffeine, primidone, and atenolol, respectively), which resulted in a higher concentration of OMPs  
 418 in the AL. Therefore, it held true that the hydrophobic interaction could be the dominant  
 419 mechanism for the transport behavior of atrazine. When the surface hydrophobicity was similar  
 420 (i.e., caffeine and primidone), caffeine showed a higher OMPs flux than primidone, implying that  
 421 the molecular weight was the dominant factor determining the forward flux of the OMPs.

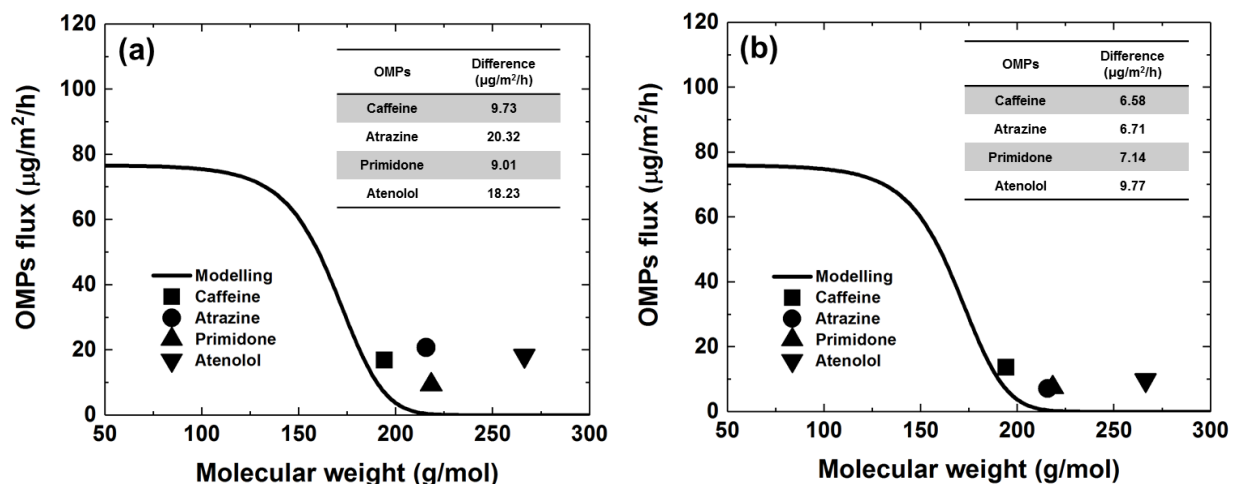
422  
 423 **Table 3.** Adsorbed amounts of OMPs on the membrane surface. Adsorbed amounts of OMPs were  
 424 estimated via simple mass balance.

|                                       | Caffeine | Atrazine | Primidone | Atenolol |
|---------------------------------------|----------|----------|-----------|----------|
| Adsorbed amount (mg m <sup>-2</sup> ) | 0.17     | 2.79     | 1.27      | 3.31     |

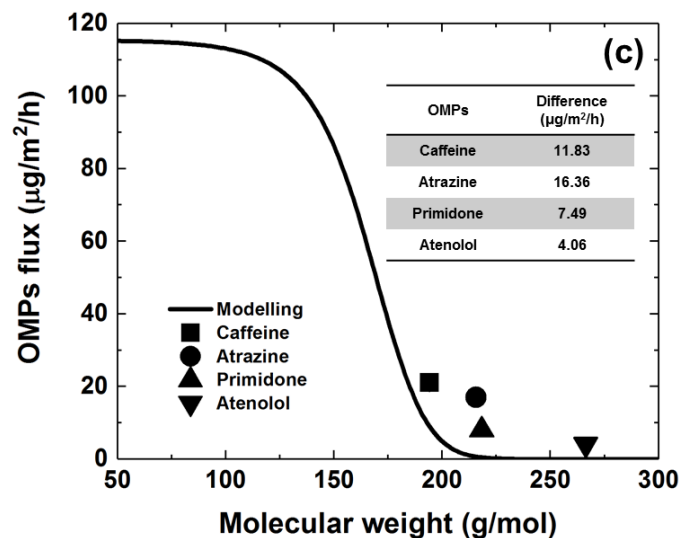
425  
 426 In addition to hydrophobicity, the surface charges of OMPs can seriously influence their  
 427 transport behavior via electrostatic repulsion or electrostatic attraction with electrically charged  
 428 membranes (Xie et al., 2012b). *Fig. 2a shows a higher forward flus for atenolol despite its high*

429 molecular weight and this might be due to the electrostatic attraction caused by the positively  
 430 charged atenolol OMP and the negatively charged surface of the FO membrane, as shown in **Table**  
 431 **1** and **Table 2**. In **Table 3**, we see that atenolol had the highest amount of OMPs ( $3.31 \text{ mg m}^{-2}$ )  
 432 adsorbed on the membrane surface. This could have induced a high OMPs concentration gradient  
 433 across the active layer, thereby enhancing the forward flux of atrazine. When the MAP DS  
 434 concentration was increased to 2 M from 1 M, the forward flux of atenolol was enhanced, which  
 435 can be explained due to enhanced ECP when FO is operated at higher water fluxes. This enhanced  
 436 atenolol concentration at the membrane surface increases its forward flux further aided by the  
 437 electrostatic attraction between the positively charged atenolol and negatively charged membrane  
 438 surface. Although the concentrations of the other OMPs also increases at the membrane surface  
 439 when the FO is operated at higher flux (higher ECP) however, their forward flux decreased which  
 440 is a rather unexpected behavior since forward solute fluxes are generally a function of its  
 441 concentration at the membrane surface. Hence, a further studies is required to gain better  
 442 understanding of why the forward fluxes of other OMPs behave differently when MAP DS is  
 443 operated at higher concentrations.

444



445



446  
 447 **Figure 3.** Model predictions (solid line) for OMPs flux with the varying solute molecular weight  
 448 simulated by the pore-hindrance transport model for (a) MAP DS, (b) DAP DS, and (c) KCl DS  
 449 at 1 M DS concentration. Also included are the measured solute forward fluxes of the OMPs:  
 450 caffeine, atrazine, primidone, and atenolol. Tables in each panel indicate the difference between  
 451 the modeled OMPs flux and the experimental data. The relevant parameters from **Table 1** and  
 452 **Table S2** were employed for the model calculation; other parameters were adopted from the  
 453 experimental data presented in **Fig. 1a**.

454  
 455 *3.3.2. Effect of alkaline fertilizer (DAP) DS on OMPs transport behaviors*  
 456 We also investigated the effect of an alkaline fertilizer DS (in this case, we used DAP) on the  
 457 transport behavior of OMPs during FDFO. An OMPs flux with 1 M DAP DS was simulated using  
 458 the experimental average water flux, presented in **Fig. 3b**. The differences between the modeled  
 459 OMPs flux and the experimental data were reduced for all the OMPs, but the forward fluxes of  
 460 atrazine and atenolol decreased compared to 1 M MAP DS. This could be due to the enhanced  
 461 RSF combined with a similar water flux (Xie et al., 2012a). The DAP DS had a higher RSF (i.e.,  
 462  $2.5 \text{ mmol m}^{-2} \text{ h}^{-1}$  and  $0.7 \text{ mmol m}^{-2} \text{ h}^{-1}$ , respectively) than the MAP DS, while the water flux was  
 463 very similar (i.e.,  $7.6 \text{ L m}^{-2} \text{ h}^{-1}$  and  $7.7 \text{ L m}^{-2} \text{ h}^{-1}$ , respectively) as shown in **Fig. 1a**. A high RSF  
 464 might hinder the transport of feed solutes through the FO membrane, resulting in a lower OMPs  
 465 forward flux. **In addition, the FS pH of the DAP DS increased from 7.05 to 9.17 during 10 h of**  
 466 **operation; this could potentially change the membrane surface properties (e.g., by decreasing the**

467 contact angle and slightly increasing the zeta potential) of the FO membrane due to hydrophilic  
468 surface functional groups (Xie et al., 2012b) as well as the surface charge of atenolol because of  
469 its pKa value of 9.6. Particularly, a reduced contact angle would suggest hydration swelling of the  
470 active layer (Ahmad et al., 2008). In this case, atrazine would not reach the FO membrane due to  
471 steric hindrance by the water molecules on the membrane surface, making hydrophobic interaction  
472 negligible (**Fig. 4b**). As a result, OMPs (i.e., atrazine and primidone) with similar molecular  
473 weights but different surface properties exhibited a similar OMPs flux.

474 For atenolol, we hypothesized that the increase in FS pH from 7.05 to 9.17, resulting in a pKa  
475 value of 9.6, changed the surface charge from positive to neutral while other OMPs maintained  
476 their surface charge properties. Therefore, atenolol was less adsorbed on the active layer and less  
477 likely to be transported into the DS (**Fig. 4b**). To verify this hypothesis, we calculated the adsorbed  
478 amounts of atenolol via the mass balance as  $3.31 \text{ mg m}^{-2}$  and  $2.27 \text{ mg m}^{-2}$  for MAP 1 M and DAP  
479 1 M, respectively. These amounts were similar to those of another study that found atenolol  
480 adsorption (the retardation factor) on a sandy aquifer material was reduced from 23.3 to 15.8 when  
481 pH was increased from 4 to 8 (Schaffer et al., 2012).

482 By simulating the OMPs flux with 2 M DAP DS using the experimental average water flux  
483 (**Fig. S2b**), we found that the OMPs transport behavior was dominantly influenced by enhanced  
484 steric hindrance. Besides, FS pH became 9.73 higher than that of DAP 1 M DS (pH 9.17), which  
485 further reduced the forward flux of atenolol by 34.3%. At higher pH, the atenolol loses its positive  
486 charge to become neutral thereby reducing the electrostatic attraction between the atenolol and  
487 charged membrane surface and hence lowering its forward flux. This is evident from the consistent  
488 trends shown in **Fig. S2b** and **Fig. 3b**, which implicate the increased RSF and a change in the  
489 surface properties of both the FO membrane and the OMPs resulting from the increased pH of the  
490 FS.

491

### 492 3.3.3. Effect of DS with high RSF (KCl) on OMPs transport behaviors

493 Lastly, we simulated the OMPs flux with 1 M KCl DS using experimental data and found a high  
494 water flux and high RSF. The modeled OMPs flux was noticeably increased with the KCl DS  
495 compared to the MAP DS and DAP DS. This was due to the high water flux of the KCl DS  
496 compared to the MAP and DAP DS. When comparing the modeled OMPs flux with the

497 experimental OMPs flux, atenolol exhibited the smallest difference, followed by primidone,  
498 caffeine, and atrazine (**Fig. 3c**), indicating that the OMPs with high molecular weights were more  
499 easily influenced by a high RSF. Therefore, we hypothesized that the forward fluxes of the OMPs  
500 were dominantly determined by the interplay among the water flux, RSF, and molecular size of  
501 the OMPs. **A high water flux causes enhanced external concentration polarization, potentially**  
502 **leading to an increased OMPs flux (Kim et al., 2017b)**. Hence, caffeine, which has a low molecular  
503 weight, may be more easily transferred to the DS than OMPs of higher weight. In addition, the  
504 transport of the OMPs was significantly influenced by their molecular weights due to the hindrance  
505 effect of a high RSF, as shown in **Fig. 4c**. Consequently, the forward flux of OMPs with high  
506 molecular weights became lower in 1 M KCl DS than in 1 M MAP DS. **Fig. S1e indicates that the**  
507 **forward OMPs flux was a function of molecular weight when using 1 M KCl DS.**

508 To validate this hypothesis, we compared the OMPs forward fluxes of 2 M KCl DS (**Fig. S1f**)  
509 and 2 M MAP DS (**Fig. S1b**). The results show that the forward fluxes of all the OMPs except  
510 atenolol were increased, supporting the hypothesis that the transport of OMPs with a high  
511 molecular weight is more affected by RSF than a high water flux. The removal rates of all the  
512 OMPs were increased with the KCl DS compared to the MAP DS (**Table S4**). This result agrees  
513 well with the results from other studies that a high water flux leads to a decrease in removal rates  
514 due to the dilution effect (Lee et al., 2004; Xie et al., 2013). Interestingly, the trends of the three  
515 OMPs with neutral surfaces (caffeine, atrazine, and primidone) with the KCl DS were similar to  
516 the trends with the MAP DS, but not the DAP DS. The reverse diffusion of the KCl DS did not  
517 influence the FS pH and, therefore, the surface chemical properties of the FO membrane were a  
518 governing factor in the transport of OMPs with a relatively low molecular weight.

519 The findings from the present study have significant implications for optimizing the FDFO  
520 process for treating wastewater that contains OMPs. When using MAP or KCl as the DS, the  
521 rejection of the OMPs was governed by the physicochemical properties of their surfaces. However,  
522 the DAP DS effectively rejected most of the OMPs due to the increased pH of the FS, which was  
523 caused by the backward diffusion of  $\text{NH}_4^+$  in the DS. This implies that an alkaline DS is  
524 recommended for the effective removal of OMPs from wastewater. We found that the  
525 experimental OMPs fluxes were higher than the theoretical OMPs fluxes obtained from the pore-  
526 hindrance model. This discrepancy is due to the solution-diffusion model being dominant for non-

527 porous membranes such as NF, RO, and FO membranes. Nevertheless, because the pore-hindrance  
528 model considers only the steric hindrance effect by size exclusion, it still helps us to understand  
529 how the surface properties of the OMPs and the FO membrane influenced the OMPs transport  
530 behaviors.

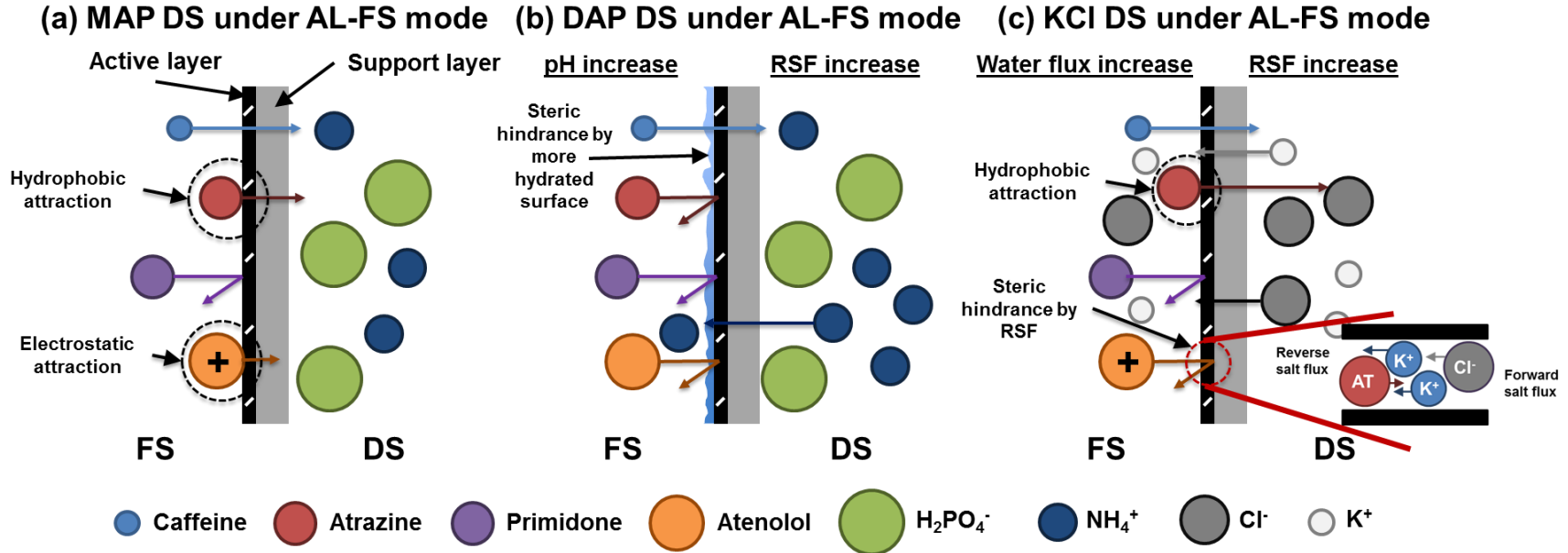
531

#### 532 **4. Conclusion**

533 We systematically investigated the OMPs transport mechanisms in FDFO using four different  
534 OMPs with different molecular weights and surface physicochemical characteristics and three  
535 different fertilizers as the DS. The transport behaviors of the OMPs were simulated using the pore-  
536 hindrance transport model in order to identify the effect of the physicochemical properties of the  
537 OMPs surfaces on their transport. The main findings drawn from the present study can be  
538 summarized briefly as follows:

- 539 • KCl showed the highest water flux and RSF; MAP and DAP exhibited similar water fluxes but  
540 different RSF.
- 541 • When using either the MAP or KCl DS (which had a moderate water flux and low RSF), the  
542 physicochemical properties (i.e., hydrophobicity and surface charge) of the OMPs determined  
543 their transport behavior. However, the remarkably increased RSF caused by using KCl as the  
544 DS could hamper the transport of OMPs with high molecular weights.
- 545 • With the DAP DS, the FO membrane was more hydrated because of the increased pH. RSF  
546 was also enhanced, which may have helped prevent the transport of OMPs through the FO  
547 membrane. Thus, rejection of all the tested OMPs was enhanced.
- 548 • The pore-hindrance model was instrumental in understanding the effects of the hydrodynamic  
549 properties and the physicochemical properties on OMPs transports.

550



**Figure 4.** Schematic descriptions of OMPs transport mechanisms in FO. RSF plays an important role in determining the OMPs transports. With MAP DS, which has low RSF, the OMPs transports are dominantly influenced by their properties (i.e., molecular weights, surface charges, and surface hydrophobicity). With DAP DS, which has an intermediate RSF, an increase in FS pH alters the surface physicochemical properties of both the FO membrane and the OMPs; hence, the OMPs transport was significantly influenced. With KCl DS, which has a high RSF, the transport behavior of the OMPs was affected by both the high RSF and the surface properties of OMPs.

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