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Transformation of Trace Organic Contaminants from Reverse Osmosis Concentrate by Open-Water Unit-Process Wetlands with and without Ozone Pretreatment

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1 Transformation of Trace Organic Contaminants from
2 Reverse Osmosis Concentrate by Open-Water Unit Process
3 Wetlands with and without Ozone Pre-Treatment
4
5

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43 **Abstract**

44 Reverse osmosis (RO) treatment of municipal wastewater effluent is becoming more
45 common as water reuse is implemented in water-stressed regions. Where RO concentrate
46 is discharged with limited dilution, concentrations of trace organic contaminants could
47 pose risks to aquatic ecosystems. To provide a low-cost option for removing trace organic
48 compounds from RO concentrate, a pilot-scale treatment system comprised of open-water
49 unit process wetlands with and without ozone pre-treatment was studied over a two-year
50 period. A suite of ecotoxicologically-relevant organic contaminants was partially removed
51 via photo- and bio-transformation, including β -adrenergic blockers, antivirals, an
52 antibiotic, and pesticides. Biotransformation rates were as fast or up to approximately 50%
53 faster than model predictions based upon data from open-water wetlands that treated
54 municipal wastewater effluent. Phototransformation rates were comparable to or as much
55 as 60% slower than predicted by models that accounted for light penetration and
56 scavenging of reactive oxygen species. Several compounds were transformed during ozone
57 pre-treatment that were poorly removed in the open-water wetland. The combined
58 treatment system resulted in a decrease in the risk quotients of trace organic contaminants
59 in RO concentrate, but dilution still may be required to protect sensitive species from
60 urban-use pesticides with low environmental effect concentrations.

61 **Introduction**

62 As potable water reuse becomes more popular, the volume of concentrate produced by
63 reverse osmosis (RO) treatment of municipal wastewater effluent will increase.^{1,2} Under
64 conditions typically employed in potable water reuse systems (e.g., 85% water recovery),
65 RO concentrate contains wastewater-derived trace organic contaminants, nutrients, salts,
66 and natural organic matter at concentrations that are approximately 5-7 times higher than
67 those measured in wastewater effluent.^{3,4} Potable water reuse projects often release RO
68 concentrate through deep ocean outfalls or release it to water bodies where dilution and
69 mixing reduce concentrations of trace organic contaminants to levels below aquatic toxicity
70 thresholds close to the discharge points.⁵ For instance, Orange County Water District
71 discharges approximately 60 million liters per day through a deep ocean outfall, and
72 potable reuse projects in Singapore and Perth, Australia follow a similar approach.
73 Although some RO concentrate is discharged to inland waters (e.g., Big Spring, Texas),
74 there is an increasing recognition that future projects may require treatment prior to
75 discharge. One example is San Jose, California, where the expansion of water reuse in an
76 area that discharges wastewater and RO concentrate to San Francisco Bay is driving the
77 local water utility to pursue RO concentrate treatment.⁶

78

79 Chronic toxicity to sensitive aquatic species is a serious concern at the concentrations of
80 trace organic contaminants in RO concentrate produced from treatment of municipal
81 wastewater effluent. For instance, the β -adrenergic blocker propranolol, a compound that
82 occurs in wastewater effluent at concentrations ranging from 19 to 290 ng/L,⁷⁻⁹ would be
83 expected in RO concentrate at concentrations ranging from approximately 110 to 1700

84 ng/L. For reference, reproduction in Japanese medaka (*Oryzias latipes*) is affected at
85 propranolol concentrations as low as 500 ng/L.¹⁰ Chronic exposure to the compound also
86 reduces the heart rate of zebrafish (*Danio rerio*) at concentrations as low as 87 ng/L.¹¹
87 Because β -blockers often exhibit additive effects on aquatic organisms, the co-occurrence
88 of propranolol and other β -blockers in RO concentrate could exacerbate these impacts.¹²
89 Similarly, fipronil, a widely used phenylpyrazole pesticide that acts as a neurotoxin, occurs
90 in municipal wastewater effluent at concentrations ranging from approximately 14 to 120
91 ng/L.¹³⁻¹⁶ In response to findings related to aquatic toxicity of fipronil, the USEPA has set
92 a chronic aquatic life benchmark value of 11 ng/L for invertebrates.¹⁷

93

94 RO concentrate treatment is a major challenge because most technologies are unable to
95 remove trace organic contaminants and nitrate—one of the other contaminants of greatest
96 concern when RO concentrate is discharged to estuaries—in a cost-effective manner.^{18,19}
97 Among the many different treatment technologies capable of removing trace organic
98 contaminants from municipal wastewater effluent, ozonation followed by biological
99 treatment on sand or biological activated carbon (BAC) has proven to be one of the most
100 cost-effective and practical methods.²⁰⁻²³ For example, when RO concentrate was treated
101 with 10 mg/L of ozone ($O_3:DOC \sim 0.2$), 80-90% removal of β -blockers was observed.²⁴
102 BAC treatment can provide further removal of trace organic contaminants and reduce
103 concentrations of oxidation byproducts produced during ozonation.^{20,23} However, the
104 O_3/BAC system does not remove nitrate from RO concentrate.²⁵

105

106 Open-water wetlands efficiently removed nitrate and trace organic contaminants from
107 secondary effluent and from an effluent-dominated river via a combination of
108 biotransformation and sunlight-induced phototransformation reactions.²⁶⁻³⁰ The challenges
109 associated with making predictions about application of this technology to the treatment of
110 RO concentrate include the impacts of organic matter and salinity on indirect
111 phototransformation and on the establishment of a microbial community capable of
112 removing contaminants in the open-water wetlands. In addition, the fate of some
113 contaminants of particular concern for aquatic toxicity, such as phenylpyrazole pesticides,
114 has not been evaluated previously.

115

116 To assess the potential for using open-water wetlands to remove trace organic contaminants
117 from RO concentrate, we studied a treatment system that combines ozone pre-treatment
118 and treatment in open-water unit process wetlands. We hypothesized that the combination
119 of removal mechanisms would provide a robust barrier for a broad suite of organic
120 contaminants in the wetland while simultaneously removing contaminants that are not
121 affected by ozonation (e.g., nitrate).³¹ Furthermore, we hypothesized that the biological
122 activity in open-water wetlands could serve as an effective alternative to biological
123 activated carbon or sand filtration for removing compounds that are susceptible to
124 biotransformation. We tested these hypotheses by combining the analysis of surrogate
125 compounds indicative of photo- and bio-transformation removal mechanisms with analysis
126 of urban-use pesticides that have been identified by experts as concerns for the San
127 Francisco Bay.³²

128

129 **Materials and Methods**

130 *Pilot Treatment System*

131 The pilot-scale ozone/wetland system was operated between July 2017 and September
132 2019, as described elsewhere.³¹ The system consisted of two shallow (30 cm deep)
133 parallel open-water treatment wetland cells lined with an impermeable liner. The surface
134 area of each wetland was approximately 200 m². The inlet flow rate to each cell was
135 approximately 13 L/min. Cell 1 received RO concentrate directly from an adjacent
136 advanced water treatment facility. Cell 2 received RO concentrate from the same facility
137 after ozone pre-treatment. Ozone was produced in a pilot-scale ozone generator
138 (*MiPROTM Advanced Oxidation Pilot System, Xylem, Inc.*) and was applied in a contact
139 chamber with a 5-minute residence time, within which the ozone residual in the RO
140 concentrate was depleted. Typical TDS, conductivity, DOC, and pH values for the ROC
141 entering both cells are presented in the SI (Section S1.1). The hydraulic residence time in
142 the open-water wetland cell was approximately 3 days, as confirmed by lithium bromide
143 tracer tests.³¹

144

145 Pharmaceuticals, pharmaceutical transformation products, and water quality parameters
146 (including pH, chloride, dissolved organic carbon, dissolved inorganic carbon, nitrate, and
147 nitrite) were monitored approximately every 2 to 4 weeks during the summers of 2018 and
148 2019 (i.e., June-August), and approximately every 1 to 2 months between September-May.
149 Samples for pesticide analysis were collected quarterly throughout the study period, with
150 additional samples collected every 2-4 weeks during the summer of 2018. The initial ozone
151 concentration for Cell 2 pre-treatment was set at 20 mg-O₃/L throughout the study period,
152 with the exception of a 6-week period during the summer of 2018, when 40 mg-O₃/L was

153 applied; these ozone concentrations correspond to ~0.5 mg O₃/mg DOC and ~1.0 mg
154 O₃/mg DOC, respectively.

155

156 Samples were collected at the inlet and outlet of the cells by either composite or grab
157 sampling methods. From July 2017 to April 2019, 9-L composite samples were collected
158 over a 24-hour period with an autosampler (Teledyne ISCO GLS) into a glass composite
159 sampling container that was kept on ice. From June to September 2019, 9-L grab samples
160 were collected by operating the autosamplers over a 5-minute period. The two sampling
161 techniques were both used for sampling on August 28, 2019. Concentrations of trace
162 organic contaminants measured with the two techniques on this date typically varied by
163 <15%, and differences in observed removal were not statistically significant (Wilcoxon
164 Signed Rank Test, P=0.060). Further details are provided in Section S1.3. Grab samples
165 were also collected throughout the study at two intermediate locations within the cells, after
166 hydraulic residence times of approximately 1 and 2 days along the flow path of each cell.

167

168 *Sampling and Analytical Methods*

169 Dissolved oxygen, pH, temperature, and conductivity measurements were made at the
170 pilot-scale system at approximately 10 AM, when samples were collected. Samples
171 collected by autosamplers were mixed, then 40-mL aliquots for analysis of trace organic
172 contaminants other than pesticides were filtered into amber glass vials using 0.7- μ m glass
173 fiber filters in the field and transported on ice to the laboratory. 500-mL sample aliquots
174 for pesticide analysis (i.e., imidacloprid, fipronil, and fipronil transformation products)
175 were filtered and held at 4°C prior to solid phase extraction and LC-MS/MS analysis

176 following previously described methods.³³ Trace organic contaminants were analyzed
177 with isotope dilution within 48 hours of collection on an Agilent 1260 series High
178 Performance Liquid Chromatograph and Agilent 6460 Triple Quadrupole Mass
179 Spectrometer using methods adapted from methods described previously (S1.2).^{26,28,29}
180 Calibration standards were made in a matrix-matched solution containing dissolved ions
181 at concentrations representative of the RO concentrate matrix (S1.2). The limit of
182 quantification (LOQ) was designated as the lowest calibration standard level with a
183 signal-to-noise ratio greater than 10. When concentrations were below the limit of
184 quantification, a value equal to half of the LOQ was used for the calculation of summary
185 statistics.³⁴ Concentrations of 11 trace organic contaminants (shown in Figure 3)
186 exceeded the LOQ in >90% of samples collected from Cell 1 (no ozone), except for
187 propranolol, which was present in the RO concentrate at concentrations above the LOQ
188 on fourteen of the twenty days when samples were collected. Concentrations of two
189 additional antivirals (lamivudine and abacavir) were below the LOQ in >90% of samples.
190 These compounds were also present below their limits of detection (i.e., were not present
191 at a signal-to-noise ratio of >3).

192

193 Dissolved organic and inorganic carbon were measured using a Shimadzu TOC-V/CSH
194 Analyzer. Nitrate and chloride were analyzed by ion chromatography (Dionex DX-120).
195 Nitrite was quantified using the Griess reagent method. UV/vis absorbance (200-700 nm)
196 in RO concentrate was measured in unfiltered samples with a UV-visible
197 spectrophotometer (Shimadzu UV-2600).

198

199 The full monitoring data set is available at <https://purl.stanford.edu/mp388hh4436>.

200

201 *Rate Constant Estimation*

202 Removal rate constants were calculated for individual sampling events using contaminant
203 concentrations measured in samples collected along the flow path of each wetland (i.e.,
204 samples representing a residence time of 0, 1, 2, and 3 days in the wetland cells), and were
205 corrected for evaporation, which averaged 10% between the inlet and outlet of the wetland
206 in summer (Section S2.1). Removal rate constants assumed a negligible contribution from
207 sorption to biomat solids, as observed previously.²⁹

208

209 First-order removal rate constants for previously-studied compounds were compared to
210 predictions made with bio- and photo-transformation models developed for open-water
211 wetlands. Predictions were not made for pesticides because the necessary parameters
212 (i.e., quantum yield and reaction rate constants with photoproduct reactive
213 intermediates) are not available in the literature. The biotransformation model estimates
214 first-order removal rates in a well-established biomat as a function of water
215 temperature.^{29,35} The phototransformation model uses input values of pH, water column
216 depth, and concentrations of relevant species (i.e., dissolved organic carbon, dissolved
217 inorganic carbon, nitrate, and nitrite) as well as sunlight irradiance and absorbance
218 spectra to estimate rates of direct and indirect photolysis (i.e., DOM-, nitrate-, and nitrite-
219 sensitized reactions via photoproduct reactive intermediates including $^1\text{O}_2$, $^3\text{DOM}^*$,
220 $\cdot\text{OH}$, $\cdot\text{CO}_3^-$, and $\cdot\text{NO}_2$). Further details on the phototransformation model have been
221 described previously and relevant equations and parameters are provided in Section
222 S1.4.^{28,36} The contribution of $^1\text{O}_2$ to phototransformation was updated from previous
223 versions of the model to account for recently published quantum yield data (Section

224 S2.3). Water quality parameters measured in samples from each sampling event were
225 used as inputs to the model (S2.3). Results for both photolysis and biotransformation
226 models were produced for each individual sampling event and are reported as the average
227 values from the model with standard deviation of output across sampling events.

228

229 **Results and Discussion**

230 *Photo- and Bio-Transformation in RO Concentrate*

231 The β -blockers and carboxy-abacavir, which have been studied previously in open-water
232 wetlands that received municipal wastewater effluent and water from an effluent-
233 dominated river,^{26,28-30} were used as indicator compounds to evaluate the effectiveness of
234 open-water wetlands treating RO concentrate. In those previous studies, atenolol and
235 metoprolol removal was mostly attributable to biotransformation, whereas propranolol and
236 abacavir removal mainly involved phototransformation.^{26,29} Carboxy-abacavir was used in
237 this study as an indicator compound for phototransformation because abacavir was present
238 below the LOQ (i.e., <20 ng/L), and the carboxylate transformation product also was
239 removed mainly by photolysis.²⁶ The removal of these compounds from RO concentrate in
240 the pilot-scale treatment system exhibited first-order kinetics, which have been established
241 in laboratory microcosms and previous field studies of open-water wetlands (Figure
242 S4).^{29,30,35}

243

244 *Phototransformation*

245 Propranolol removal rates were 30-60% lower than predicted by a photolysis model
246 developed for secondary wastewater effluent (Figure 1),²⁸ possibly due to inhibition of

247 organic matter-sensitized reactions in RO concentrate. The model predictions indicated
 248 that approximately 80% of the propranolol phototransformation was attributable to
 249 reactions with excited triplet states of organic matter ($^3\text{DOM}^*$) in open-water wetlands
 250 treating municipal wastewater effluent.²⁸ Electron transfer reaction rates with $^3\text{DOM}^*$
 251 decrease with increasing ionic strength and halide concentrations. For instance, the rate of
 252 disappearance of 17 β -estradiol by organic matter-sensitized phototransformation was
 253 approximately 40% lower at an ionic strength of 50 mM compared to freshwater (I=10
 254 mM), and was further inhibited due to halide ion-specific effects.³⁷ RO concentrate in the
 255 pilot-scale system had an ionic strength of approximately 60 mM, indicating that the
 256 salinity of the RO concentrate was likely responsible for the lower-than-predicted rate of
 257 $^3\text{DOM}^*$ -sensitized photolysis of propranolol.

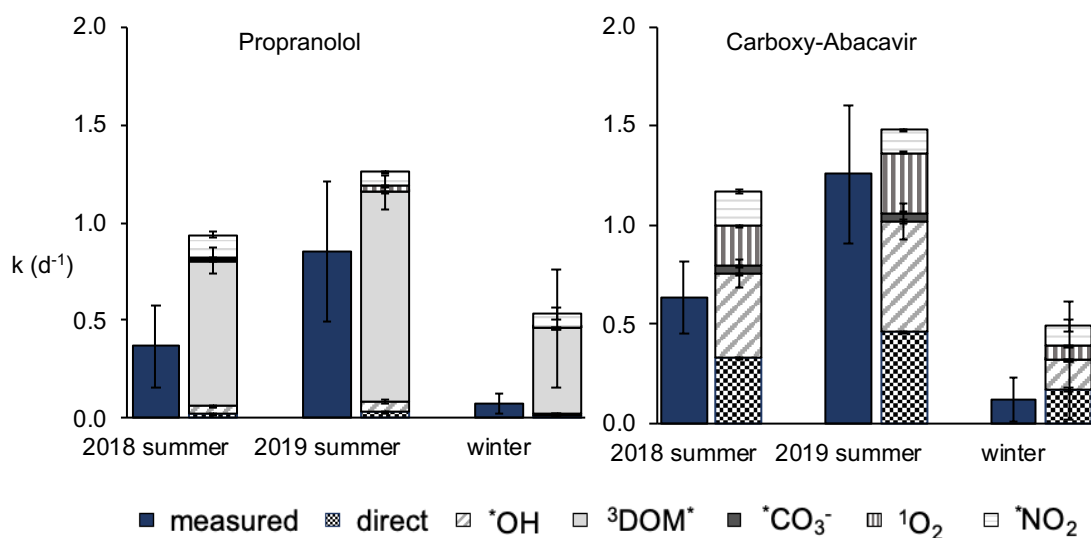


Figure 1. Average (+/- standard deviation) observed (measured) and modeled removal rates (via direct photolysis and reaction with reactive intermediate) of propranolol and carboxy-abacavir in open-water wetlands during summer (June-August) 2018 ($n=6$) and 2019 ($n=3$) and winter (November 2018-March 2019, $n=3$) sampling events.

258

259 Average rates of the disappearance of carboxy-abacavir were consistent with model
260 predictions in summer 2019 and about 40% lower than predicted in summer 2018.
261 Carboxy-abacavir removal rate constants were compared to predicted rates for abacavir
262 because quantum yields for direct photolysis and bimolecular rate constants for reactions
263 with oxidants were not available for carboxy-abacavir (further details regarding the
264 abacavir photolysis model are provided in Section S1.4). When RO concentrate containing
265 both abacavir and carboxy-abacavir was irradiated in a sunlight simulator, the pseudo-first
266 order carboxy-abacavir photolysis rate constant was approximately 25% lower than that of
267 abacavir (Figure S1), whereas in the summer of 2019 the observed rate constant was 15%
268 lower than the predicted removal rate constant for abacavir. Abacavir is removed via
269 reaction with reactive oxygen species rather than direct reactions with $^3\text{DOM}^*$. Therefore,
270 the good agreement between observed and modeled rate constants is consistent with
271 findings that energy transfer reactions of $^3\text{DOM}^*$ (i.e., the formation of $^1\text{O}_2$) are not affected
272 by ionic strength or the presence of chloride.³⁸ Furthermore, the good agreement (i.e.,
273 within 10%) between model predictions and observed removal rate constants for carboxy-
274 abacavir in the summer of 2019 is promising for predicting summer performance for other
275 compounds that are phototransformed via a combination of direct photolysis and reactions
276 with photoproducted reactive intermediates.

277

278 Predicted and observed rate constants for both compounds were higher in summer 2019
279 than in summer 2018. The predicted rate constants for propranolol and carboxy-abacavir
280 photolysis were approximately 35% and 25% higher in 2019 than in 2018, respectively,
281 because RO concentrate samples collected in 2019 exhibited lower light absorbance on
282 average than samples collected in 2018 (Figure S2). Observed phototransformation rates

283 were lower than predicted in 2018, likely due to greater cloud cover and the presence of
284 floating algae during the summer of 2018. Daily sunlight irradiance data for model
285 calculations were taken from the Simple Model of the Atmospheric Radiative Transfer of
286 Sunshine (SMARTS) at 40 degrees North latitude,³⁹ which assumes clear, cloudless days.
287 Historical weather data for San Jose, CA (<https://darksky.net>) indicated that there was
288 greater cloud cover during daylight hours preceding sampling events in summer 2018 than
289 in summer 2019 (i.e., clear sky was reported for 63% of daylight hours prior to sampling
290 in 2018, and for 94% of sunlight hours prior to sampling in 2019). In addition, more
291 floating algae and duckweed partially covered the open-water wetland cells during some
292 sampling events – in 2018, up to approximately 40% of Cell 1 was covered in floating
293 algae on sampling dates, whereas in 2019, <20% of the cell was covered during all
294 sampling events.

295

296 Predicted and observed removal in winter months decreased for both compounds due to
297 decreased sunlight irradiance, and observed removal rates were slower than predicted. The
298 average removal rate constants in winter were approximately 90% lower than those
299 measured in summer (i.e., the propranolol removal rate constant decreased from 0.85 to
300 0.08 d⁻¹ and the carboxy-abacavir removal rate constant decreased from 1.26 to 0.13 d⁻¹),
301 which was a larger difference than predicted (i.e., predicted winter rate constants were 58%
302 and 66% lower than predicted summer rate constants for propranolol and abacavir,
303 respectively). The greater-than-predicted effect of season may have been due to increased
304 cloud cover in the winter. In the summer of 2019, it was on average clear during 79% of
305 daylight hours preceding sampling, whereas in winter it was cloudy or raining
306 approximately 70% of the time between sunrise and sunset.

307

308 *Biotransformation*

309 Biomat growth and activity was observed throughout the study period. Changes in
310 microbial ecology and indicators of biological activity are discussed elsewhere.³¹ Notably,
311 although pH and dissolved oxygen profiles indicated strong photosynthetic activity within
312 one month of startup, the biomat microbial community evolved throughout the first 18
313 months of operation and greater nitrate removal in the biomat was observed in summer
314 2019 compared to summer 2018.³¹

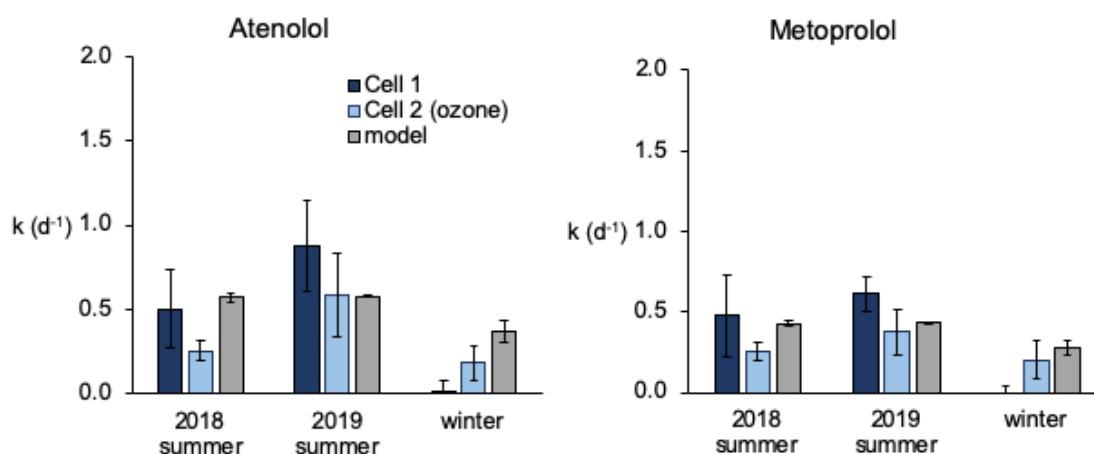


Figure 2. Average (+/- standard deviation) observed and modeled removal rates of β -blockers in open-water wetland cells without (Cell 1) and with (Cell 2) ozone pre-treatment during summer (June-August) 2018 ($n=6$) and 2019 ($n=3$) and winter (November 2018-March 2019, $n=3$) sampling events.

315

316 Removal of atenolol and metoprolol was consistent with predictions from
317 biotransformation models developed for open-water wetlands treating wastewater effluent
318 (Figure 2).²⁹ During the summer 2018, calculated rate constants in the cell without ozone
319 pre-treatment (Cell 1) averaged 0.50 d^{-1} and 0.48 d^{-1} for atenolol and metoprolol,
320 respectively, which were similar to the predicted rate constants of 0.57 d^{-1} and 0.43 d^{-1} . In

321 2019, atenolol and metoprolol removal rates exceeded predicted rates in Cell 1 (0.87 d⁻¹
322 observed vs. 0.58 d⁻¹ predicted for atenolol, 0.61 d⁻¹ observed vs. 0.43 d⁻¹ predicted for
323 metoprolol). The faster removal observed in 2019 was consistent with greater biomat
324 activity in 2019 compared to 2018, which was supported by observations of greater biomat
325 depth and nitrate removal capacity in 2019.³¹ As predicted, removal rates declined during
326 the cooler, winter months.

327

328 The formation of relatively high concentrations of the known biotransformation product of
329 both β -blockers, metoprolol acid, was observed in both cells (Figure S5). Metoprolol acid
330 concentrations increased on average from 4.7 nM (likely present due to formation in the
331 wastewater treatment plant)^{40,41} to 10.1 nM in the summer, while atenolol and metoprolol
332 decreased from 4.3 to 0.6 nM and 7.6 to 2.2 nM, respectively. The increase in metoprolol
333 acid accounted for approximately 78% of the atenolol and metoprolol removed (i.e., the
334 sum of the molar concentrations of the three compounds decreased 22% on average from
335 inlet to outlet). This decrease in the total concentration of the parent compounds and the
336 measured biotransformation product was likely due to the occurrence of other
337 transformation pathways. For instance, metoprolol acid produced by biotransformation of
338 metoprolol in activated sludge batch reactors accounted for only ~25% of metoprolol
339 removal.⁴² Results from previous studies of open-water wetland microcosms treating
340 wastewater effluent indicated that metoprolol acid did not undergo further
341 biotransformation.²⁹

342

343 Ozone pre-treatment could increase biotransformation rates by increasing the fraction of
344 labile organic matter available to support the growth of biomat organisms. In the pilot-scale
345 treatment system, biodegradable organic carbon (BDOC) concentrations were 83% higher
346 following treatment with 20 mg-O₃/L.³¹ BDOC has been used by researchers as a measure
347 of the labile organic matter that can support microorganisms in effluent-impacted waters.⁴³
348 However, the rates of removal of atenolol and metoprolol were not significantly different
349 in the two open-water cells in the summer (Wilcoxon signed-rank test for significance:
350 atenolol P=0.18, metoprolol P=0.06), or in the winter (atenolol P=0.4, metoprolol P=0.2)
351 indicating that the higher BDOC concentrations did not enhance biotransformation rates of
352 these compounds.

353

354 *Pilot-Scale System Performance*

355 The combination of photo- and bio-transformation in the open-water wetlands with ozone
356 pre-treatment resulted in removal of a suite of compounds susceptible to different removal
357 mechanisms. During ozonation, contaminant transformation occurred by direct reactions
358 with O₃ and by reactions with hydroxyl radical (\cdot OH) generated during O₃
359 decomposition.⁴⁴ Previous research has sorted organic contaminants into five categories
360 based on their reaction rate constants with O₃ and \cdot OH; this research has demonstrated that
361 degradation of contaminants within each category is similar across municipal wastewater
362 effluents as a function of ozone dose on a mg O₃/mg DOC basis.⁴⁵ Contaminants with high
363 reaction rate constants with O₃ ($k_{O_3} \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$) are transformed rapidly at an O₃/DOC ratio
364 of >0.25, whereas contaminants with intermediate rate constants with O₃ (e.g.,
365 $k_{O_3} \sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$) require higher O₃/DOC ratios for removal. Contaminants with low ozone

366 reaction rate constants ($k_{O_3} < 10 \text{ M}^{-1}\text{s}^{-1}$) are removed by a combination of reactions with
367 ozone and hydroxyl radical, such that their removal rate depends on both k_{O_3} and k_{OH} . The
368 same categorization scheme has recently been demonstrated to apply in ROC.³³ In this
369 study, contaminants with rate constants for direct reactions with O_3 greater than $10^5 \text{ M}^{-1}\text{s}^{-1}$
370 exhibited decreases in concentrations above 80% during pre-treatment with $\sim 0.5 \text{ mg-}$
371 $O_3/\text{mg-DOC}$. For compounds with lower rate constants, this ozone dose resulted in
372 transformation of less than 50% of the compound by a combination of ozone and hydroxyl
373 radical reactions.

374

375 At an added O_3 concentration of $40 \text{ mg-}O_3/\text{L}$ ($\sim 1 \text{ mg-}O_3/\text{mg-DOC}$) followed by open-water
376 wetland treatment, concentrations of all detected compounds except imidacloprid and
377 tenofovir decreased by at least 85% during the summer of 2018 (Figure 3), indicating that
378 the concentrations remaining after treatment were equivalent to or lower than those that
379 would have been discharged in wastewater prior to construction of a potable water reuse
380 system. When $20 \text{ mg-}O_3/\text{L}$ was applied during the summer of 2018, concentrations of
381 atenolol, propranolol, and trimethoprim decreased by more than 85% whereas
382 concentrations of the other eight compounds decreased by 60-84% following passage
383 through the hybrid treatment system. The performance of the open-water wetland system
384 improved in its second year of operation (Figure 4), such that concentrations of all
385 compounds except fipronil, imidacloprid, and tenofovir decreased by at least 85% in the

386 hybrid treatment when 20 mg-O₃/L was applied. The efficacy of the wetland system
 387 declined considerably during wintertime (Figure S6).

388

389 Both ozone and open-water wetlands contributed substantially to the removal of the three
 390 β-blockers and fipronil. The concentrations of these four compounds decreased by over

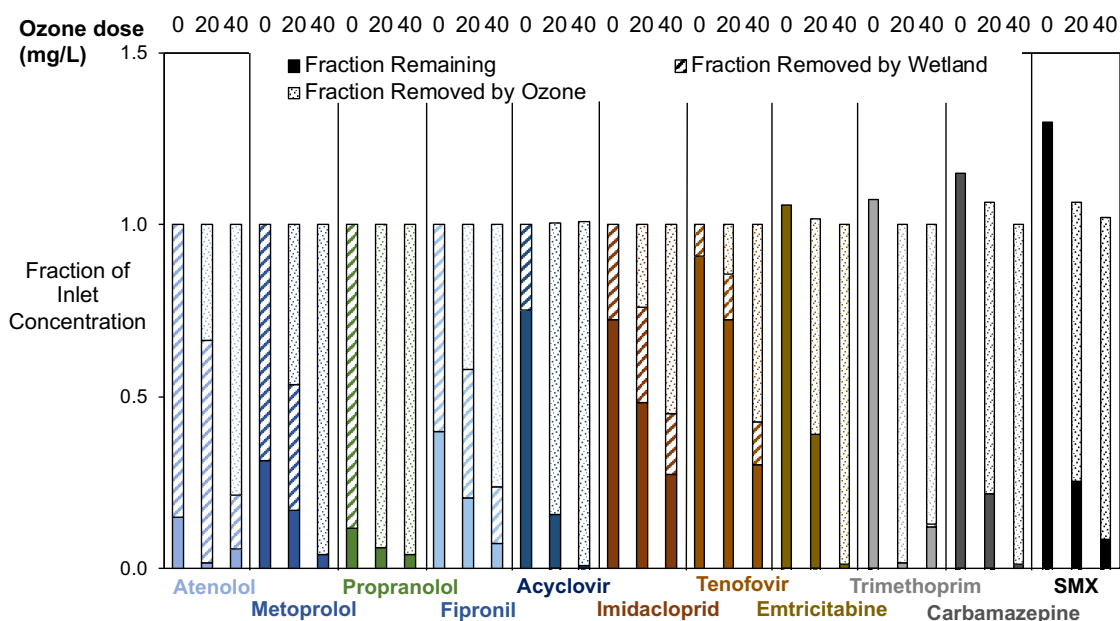


Figure 3. Average fraction of contaminant concentrations removed during and remaining after wetland and/or ozone (20 or 40 ppm) treatment during summer sampling in 2018 ($n=3$ for wetland alone, $n=3$ for each ozone dose). Propranolol data for 20 ppm ozone is from 2019 due to non-detects for all 3 sampling rounds using 20 ppm ozone in 2018. SMX = Sulfamethoxazole.

391 50% in the open-water wetlands without ozone pre-treatment. Ozone treatment reduced
 392 concentrations of atenolol, metoprolol and fipronil by 34%-47% with an applied dose of
 393 20 mg-O₃/L, and by 76%-96% with an applied dose of 40 mg-O₃/L. In the open-water
 394 wetland cell downstream of ozone treatment, these three compounds were further
 395 transformed, leading to overall removal of $\geq 90\%$ when 40 mg-O₃/L was combined with
 396 open-water wetland treatment. Propranolol concentrations decreased to below the limit of

397 quantification at both a 20-mg/L and 40-mg/L ozone dose. Propranolol has a bimolecular
 398 reaction rate constant for reactions with ozone that is approximately two orders of
 399 magnitude higher than the respective rate constants for metoprolol or atenolol (i.e., $\sim 10^5$
 400 $M^{-1}s^{-1}$ vs $2 \times 10^3 M^{-1}s^{-1}$), and has been previously observed to be more efficiently removed
 401 via ozonation of RO concentrate.²⁴ Therefore, propranolol was well-removed by either the
 402 open-water wetland or ozonation, and there was no benefit from combining both treatments
 403 during the summer months.

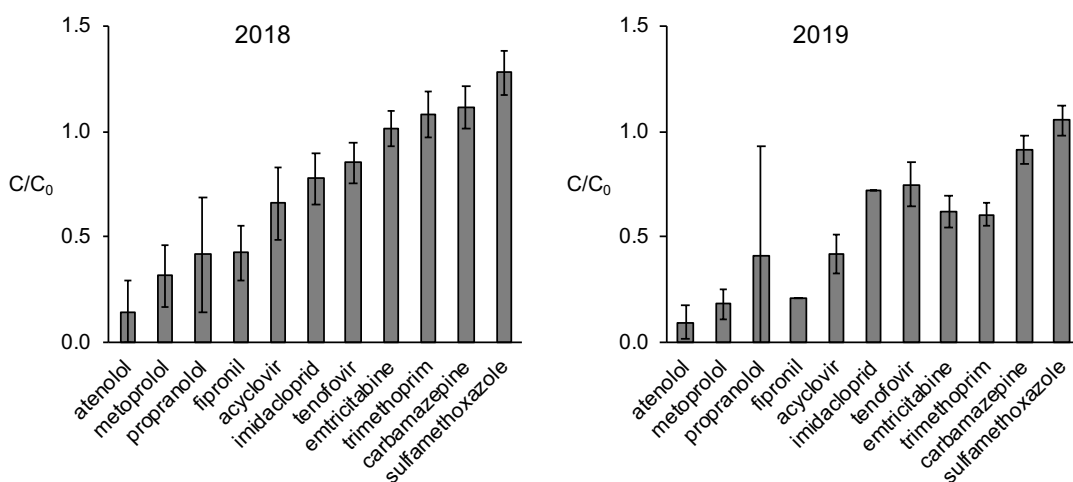


Figure 4. Average (+/- standard deviation) fraction of contaminants remaining after open-water wetland treatment during summer sampling events in 2018 ($n=6$) and 2019 ($n=3$) (Cell 1, June-August).

404
 405 Emtricitabine, trimethoprim, carbamazepine, and sulfamethoxazole were primarily
 406 removed by ozonation, with a modest contribution from the open-water wetland in 2019
 407 but not in 2018. Trimethoprim, sulfamethoxazole and carbamazepine are known to undergo
 408 relatively fast reactions with ozone (bimolecular rate constants are above $10^5 M^{-1}s^{-1}$ for all
 409 three compounds).⁴⁴ Despite their relatively high reactivity with ozone, a dose of 40 mg/L
 410 was required to achieve 85% removal of these compounds by ozone treatment in 2018,

411 likely due to the presence of ozone scavengers, including nitrite (approximately 0.1
412 mM).^{31,33} Concentrations of these compounds increased on average by approximately 10%
413 in the open-water wetlands in summer 2018 due to evaporation of water (Section S2.1). In
414 2019, concentrations of emtricitabine and trimethoprim decreased by up to 40% in the
415 open-water wetlands (Figure 4), most likely due to biotransformation, whereas
416 carbamazepine and sulfamethoxazole concentrations decreased by less than 10%. The
417 partial removal of these compounds in the open-water wetlands in 2019 resulted in >85%
418 overall removal with an ozone dose of 20 mg/L, indicating that the lower ozone dose may
419 be sufficient for these compounds when paired with a well-established open-water wetland
420 system.

421

422 The enhanced removal of trimethoprim in 2019 relative to 2018 was consistent with
423 biotransformation serving as the primary removal mechanism for this compound in the
424 open-water wetlands. Effluent trimethoprim concentrations were within 15% of modeled
425 concentrations based on biotransformation rates observed in the summer of 2019 (Figure
426 S7). In open-water wetlands treating wastewater effluent, trimethoprim primarily
427 underwent biotransformation with less than 40% of the removal due to photolysis.²⁹ In RO
428 concentrate, only 25% of the removal of trimethoprim was predicted to occur via
429 phototransformation.

430

431 Sulfamethoxazole was primarily removed by phototransformation in open-water wetlands
432 treating municipal wastewater effluent²⁹ but was not removed in the pilot-scale system in
433 2018. The concentrations of sulfamethoxazole only decreased 8-21% in the open-water
434 wetlands during the summer of 2019. Sulfamethoxazole concentrations increased more

435 than chloride during all sampling events in 2018 (Figure S3), which may indicate that
436 transformation products that were released by the wastewater treatment plant underwent
437 back-transformation to the parent compound in the open-water wetlands. This hypothesis
438 is supported by previous observations of back-transformation of metabolites of
439 sulfamethoxazole in sunlit systems,^{46,47} and the observation that sulfamethoxazole
440 phototransformation rates matched modeled rates when sulfamethoxazole was added to
441 RO concentrate and irradiated with a solar simulator.³⁶

442

443 Imidacloprid and tenofovir exhibited the slowest removal rates, with modest contributions
444 to removal from both ozone and open-water wetland treatment. Without pre-treatment,
445 imidacloprid concentrations decreased by an average of 22% in the open-water wetland
446 during the summer of 2018 and by 31% in the summer of 2019. Ozone pre-treatment
447 reduced imidacloprid concentrations by 24% and 55% at 20 mg-O₃/L and 40 mg-O₃/L,
448 respectively. The partial removal of imidacloprid was consistent with the slow reaction rate
449 constant for reaction of imidacloprid with ozone ($k_{O_3} = 10.9 \text{ M}^{-1} \text{ s}^{-1}$) and moderate reaction
450 rate constant with hydroxyl radical ($k_{OH} = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^{33,48} Further imidacloprid
451 removal occurred in the open-water wetland, resulting in overall removal of about 50-75%.
452 Concentrations of tenofovir only decreased by 15% and 25% in the open-water wetland in
453 the summers of 2018 and 2019, respectively. Tenofovir was partially removed by O₃ with
454 concentrations decreasing by 14% and 57% at 20 mg-O₃/L and 40 mg-O₃/L, respectively.
455 Although the rate constant for reaction between ozone and tenofovir has not been reported
456 previously, the low removal of tenofovir in this system likely indicates a slow direct
457 reaction rate with ozone for this compound, and its removal during ozonation was likely
458 primarily due to reactions with hydroxyl radical.⁴⁹

459

460 *Implications for ecological risk from RO concentrate*

461 Risk quotients were calculated to assess the contribution that hybrid treatment would make
462 towards reducing the effects of RO concentrate discharge on aquatic ecosystems. Risk
463 quotients (the ratio of environmental concentrations, ECs, to predicted no-effect
464 concentrations, PNECs) are often used as a screening tool to assess the potential impacts
465 associated with the discharge of contaminants to the aquatic environment.^{50,51} EC values
466 are estimated from typical concentrations discharged to the environment (in this case RO
467 concentrate, with and without treatment) multiplied by a dilution factor (we used a factor
468 of 1 to represent a worst-case scenario of no dilution, which may be relevant for effluent-
469 dominated rivers or estuaries with poor mixing at the point of dilution). In this approach,
470 predicted no-effect concentrations are derived from toxicity data for multiple species across
471 trophic levels,⁵¹ where the lowest no-observed effect concentration among all tested
472 species was divided by an assessment factor (usually 10 or 50 when chronic toxicity data
473 are available).⁵² We used freshwater PNEC values and established EPA benchmark values
474 (assigned an assessment factor of 1) from literature values. For some compounds (i.e.,
475 antivirals) a lack of chronic ecotoxicity data meant that no PNEC data could be calculated.
476 Further details regarding risk quotient analysis are provided in section S1.5.

477

478 Imidacloprid, fipronil, and carbamazepine exhibited the highest risk quotients before and
479 after treatment (Figure 5). Imidacloprid risk quotients ranged from 41 to 69 and 29 to 51
480 in untreated and treated RO concentrate, respectively. Fipronil risk quotients ranged from
481 13 to 17 in untreated RO concentrate. The risk quotient for fipronil ranged from 2.5 to 3.4
482 after passage of water through the hybrid treatment system, compared to 6.8-9.5 and 2.8-

483 8.1 for ozone and wetlands alone, respectively. Carbamazepine risk quotients ranged from
484 13 to 19 in untreated and wetland-treated RO concentrate, and from 0.2 to 5.6 in ozone-
485 treated RO concentrate.

486

487 Transformation products of fipronil can also contribute to aquatic toxicity, but yielded an
488 order of magnitude lower risk quotients than fipronil. Fipronil sulfone was present in the
489 highest concentration in untreated RO concentrate (Figure S8), consistent with its
490 formation during aerobic biological treatment of wastewater.¹⁵ Fipronil sulfone risk
491 quotients ranged from 0.6-1.3 in untreated and treated samples, with the highest risk
492 quotients observed following ozone treatment. Formation of fipronil desulfinyl, a
493 transformation product observed during sunlight or UV irradiation of fipronil, was observed
494 in the wetlands.^{53,54} However, the risk quotient for fipronil desulfinyl was always <0.1.
495 Fipronil sulfide had a risk quotient of approximately 0.1 in untreated RO concentrate and
496 <0.1 following treatment by open-water wetlands and/or ozone.

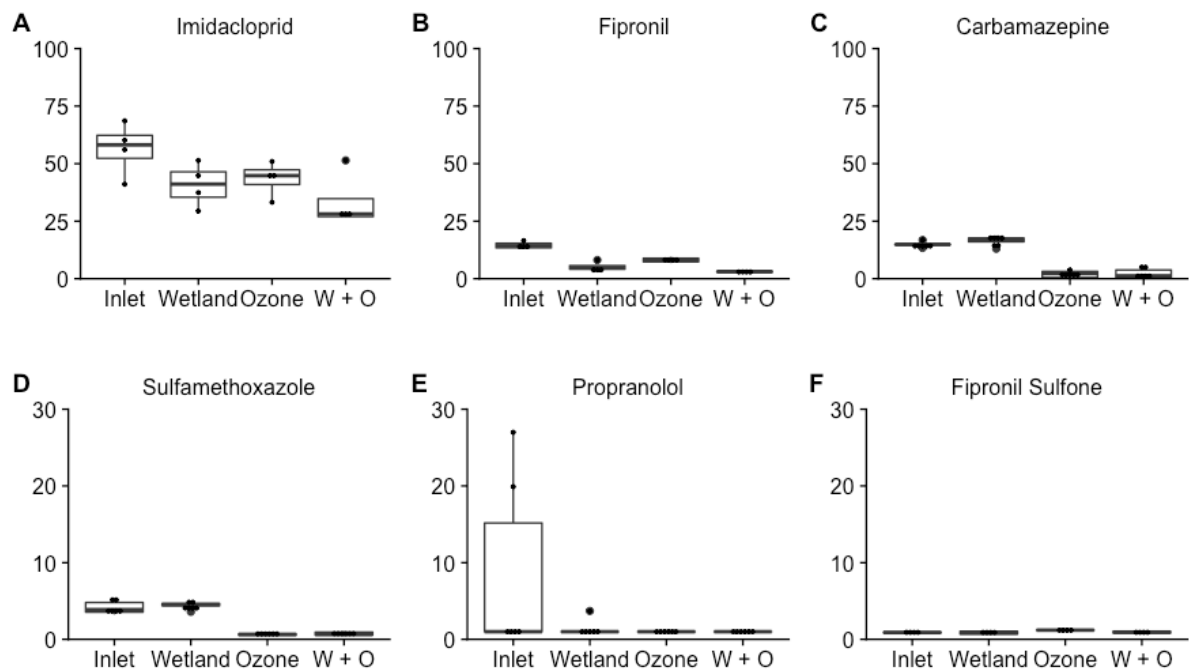


Figure 5. Risk quotients for untreated and treated RO concentrate. The middle line of each box is the median value. W+O = treated by ozone and wetland. Ozone-treated values are for a dose of 20 mg/L. Values were calculated for all summer sampling events in 2018 and 2019.

497

498 Risk quotients also exceeded unity in untreated RO concentrate for propranolol and
 499 sulfamethoxazole (Figure 5). Following ozone treatment, risk quotient values were
 500 approximately one or less for sulfamethoxazole. Following open-water wetland treatment,
 501 the risk quotient for propranolol ranged from less than 1 to 1.3. Ozone treatment lowered
 502 the propranolol risk quotient to less than one with or without the open-water wetland. The
 503 removal of these pharmaceutical compounds to concentrations near or below their
 504 predicted no-effect concentrations indicates that these contaminants are unlikely to pose a
 505 risk in treated RO concentrate, whereas significant dilution would be necessary to achieve
 506 risk quotient values below unity in untreated concentrate.

507

508 For the antibiotics trimethoprim and sulfamethoxazole, minimum selective concentrations
509 can be used to derive PNECs indicative of antibiotic resistance risk.⁵⁵ The PNEC derived
510 for sulfamethoxazole using this method is over two orders of magnitude higher than its
511 PNEC for chronic aquatic toxicity, indicating that the aquatic toxicity PNEC used herein
512 is more conservative than the PNEC for antibiotic resistance. For trimethoprim, the risk
513 quotient obtained from the PNEC for aquatic toxicity was always <0.1 (S1.5). However,
514 the PNEC derived for antibiotic resistance is lower (0.5 µg/L vs. 10 µg/L for chronic
515 toxicity), and the same order of magnitude as the concentration of trimethoprim in the RO
516 concentrate (~0.6 µg/L), indicating that antibiotic resistance risk from this compound may
517 be important for future considerations of the compound's ecological impacts.

518

519 The risk quotients in excess of one for imidacloprid, fipronil, and carbamazepine in treated
520 RO concentrate indicate that dilution or other approaches to reduce concentrations of these
521 contaminants may be necessary to avoid ecological effects from discharge of RO
522 concentrate. A dilution factor of 6, which may be achievable in many cases, combined with
523 hybrid treatment, would be sufficient to reduce fipronil and carbamazepine risk quotients
524 below unity. However, the approximately 25 times dilution that would be required for
525 imidacloprid after hybrid treatment will not be possible near many water reuse facilities. A
526 more feasible approach for this compound may be source control (i.e., limiting
527 imidacloprid use in communities where effluent discharges to treatment plants that are used
528 for water recycling).

529

530 Although this risk quotient analysis was limited to a small set of compounds due to the
531 availability of ecotoxicological data, the results highlighted contaminants of particular
532 concern in RO concentrate (i.e., urban-use pesticides) and allowed us to assess the
533 relevance of the monitored contaminants to ecotoxicity. It is worth noting that this analysis
534 could not account for the toxicity contributions of unidentified transformation products or
535 other compounds lacking chronic ecotoxicity data. Risk quotient analysis also cannot
536 account for the poorly-understood effects of complex mixtures. Despite these limitations,
537 we found that the combination of ozone and open-water wetland treatment effectively
538 removed several trace organic contaminants that would otherwise pose potential risks to
539 aquatic ecosystems and substantially reduced the need for dilution of other compounds.
540 Overall, ozone treatment was able to achieve risk quotients below one for some compounds
541 with known environmental effect concentrations, while open-water wetlands contributed
542 substantially to removal of compounds with slow ozone reaction rate constants (e.g.,
543 fipronil required hybrid treatment to achieve a risk quotient below 5). Finally, currently-
544 available data indicate that imidacloprid may cause chronic adverse effects on aquatic
545 organisms even in treated RO concentrate, indicating a need to reduce inputs of this
546 compound into sewer systems.

547

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560

561 **Supporting Information**

562 Details on analytical and sampling methods, risk quotient analysis methods, details of
563 photolysis model inputs, formation of transformation products. This information is
564 available free of charge via the Internet at <http://pubs.acs.org>.

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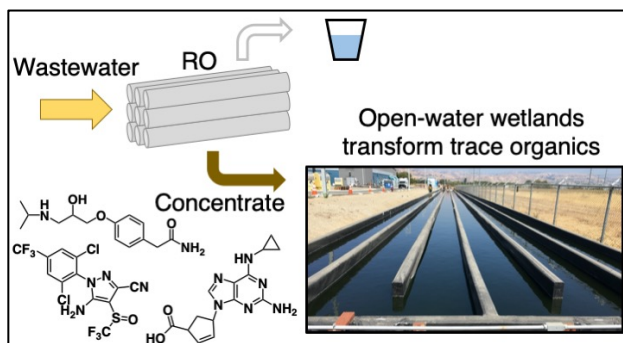
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Graphical Abstract