

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

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ABSTRACT: Reverse osmosis (RO) treatment of municipal wastewater effluent is becoming more common as water reuse is implemented in water-stressed regions. Where RO concentrate is	Wastewater RO	
discharged with limited dilution, concentrations of trace organic contaminants could pose risks to aquatic ecosystems. To provide a		Open-water wetlands transform trace organics
concentrate, a pilot-scale treatment system comprising open-water unit-process wetlands with and without ozone pretreatment was studied over a 2-year period. A suite of ecotoxicologically relevant		

data from open-water wetlands that treated municipal wastewater effluent. Phototransformation rates were comparable to or as much as 60% slower than those predicted by models that accounted for light penetration and scavenging of reactive oxygen species. Several compounds were transformed during ozone pretreatment that were poorly removed in the open-water wetland. The combined treatment system resulted in a decrease in the risk quotients of trace organic contaminants in the RO concentrate, but still dilution may be required to protect sensitive species from urban-use pesticides with low environmental effect concentrations.

■ INTRODUCTION

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

organic contaminants was partially removed via photo- and biotransformations, including β -adrenergic blockers, antivirals, antibiotics, and pesticides. Biotransformation rates were as fast as or up to approximately 50% faster than model predictions based upon

> Chronic toxicity to sensitive aquatic species is a serious concern at the concentrations of trace organic contaminants in the RO concentrate produced from the treatment of municipal wastewater effluent. For instance, the β -adrenergic blocker propranolol, a compound that occurs in wastewater effluent at concentrations ranging from 19 to 290 $\mbox{ ng/L,}^{7-9}$ would be expected in RO concentrate at concentrations ranging from approximately 110 to 1700 ng/L. For reference, reproduction in Japanese medaka (Oryzias latipes) is affected at propranolol concentrations as low as 500 ng/L.¹⁰ Chronic exposure to the compound also reduces the heart rate of zebrafish (Danio rerio) at concentrations as low as 87 ng/L.¹¹ Because β -blockers often exhibit additive effects on aquatic organisms, the co-occurrence of propranolol and other β -blockers in RO concentrate could exacerbate these impacts.¹² Similarly, fipronil, a widely used phenylpyrazole pesticide that acts as a neurotoxin, occurs in municipal wastewater effluent at concentrations ranging from

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approximately 14 to 120 ng/L. $^{13-16}$ In response to findings related to the aquatic toxicity of fipronil, the USEPA has set a chronic aquatic life benchmark value of 11 ng/L for invertebrates. 17

RO concentrate treatment is a major challenge because most technologies are unable to remove trace organic contaminants and nitrate—one of the other contaminants of greatest concern when RO concentrate is discharged into estuaries-in a costeffective manner.^{18,19} Among the many different treatment technologies capable of removing trace organic contaminants from municipal wastewater effluent, ozonation, followed by biological treatment on sand or biological activated carbon (BAC) has proven to be one of the most cost-effective and practical methods.^{20–23} For example, when RO concentrate was treated with 10 mg/L ozone ($O_3/DOC \sim 0.2$), 80-90% removal of β -blockers was observed.²⁴ BAC treatment can provide further removal of trace organic contaminants and reduce concentrations of oxidation byproducts produced during ozonation.^{20,23} However, the O₃/BAC system does not remove nitrate from RO concentrate.²⁵

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

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

MATERIALS AND METHODS

Pilot Treatment System. The pilot-scale ozone/wetland system was operated between July 2017 and September 2019, as described elsewhere.³¹ The system consisted of two shallow (30 cm deep) parallel open-water treatment wetland cells lined with an impermeable liner. The surface area of each wetland was approximately 200 m². The inlet flow rate to each cell was approximately 13 L/min. Cell 1 received RO concentrate directly from an adjacent advanced water treatment facility. Cell 2 received RO concentrate from the same facility after ozone pretreatment. Ozone was produced in a pilot-scale ozone generator (MiPROTM Advanced Oxidation Pilot System, Xylem, Inc.) and was applied in a contact chamber with a 5 min residence time, within which the ozone residual in the RO

concentrate was depleted. Typical TDS, conductivity, DOC, and pH values for the RO concentrate entering both cells are presented in the Supporting Information (Section S1.1). The hydraulic residence time in the open-water wetland cell was approximately 3 days, as confirmed by lithium bromide tracer tests.³¹

Pharmaceuticals, pharmaceutical transformation products, and water quality parameters (including pH, chloride, dissolved organic carbon, dissolved inorganic carbon, nitrate, and nitrite) were monitored approximately every 2–4 weeks during the summers of 2018 and 2019 (i.e., June to August), and approximately every 1–2 months between September and May. Samples for pesticide analysis were collected quarterly throughout the study period, with additional samples collected every 2–4 weeks during the summer of 2018. The initial ozone concentration for cell 2 pretreatment was set to 20 mg O_3/L throughout the study period, with the exception of a 6-week period during the summer of 2018, when 40 mg O_3/L was applied; these ozone concentrations correspond to ~0.5 mg O_3/mg DOC and ~1.0 mg O_3/mg DOC, respectively.

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

Sampling and Analytical Methods. Dissolved oxygen, pH, temperature, and conductivity measurements were made in the pilot-scale system at approximately 10 AM, when samples were collected. Samples collected by autosamplers were mixed, then 40 mL aliquots for the analysis of trace organic contaminants other than pesticides were filtered into amber glass vials using 0.7 μ m glass fiber filters in the field and transported on ice to the laboratory. 500 mL sample aliquots for pesticide analysis (i.e., imidacloprid, fipronil, and fipronil transformation products) were filtered and held at 4 °C prior to solid-phase extraction and liquid chromatography with tandem mass spectrometry analysis, following previously described methods.³³ Trace organic contaminants were analyzed by isotope dilution within 48 h of collection on an Agilent 1260 series high-performance liquid chromatograph system and an Agilent 6460 Triple Quadrupole mass spectrometer using methods adapted from methods described previously (Section S1.2).^{26,28,29} Calibration standards were made in a matrix-matched solution containing dissolved ions at concentrations representative of the RO concentrate matrix (Section S1.2). The limit of quantification (LOQ) was designated as the lowest calibration standard level with a signal-to-noise ratio greater than 10. When concentrations were below the LOQ, a value equal to half of the LOQ was used for the calculation of summary statistics.³⁴ Concentrations of 11 trace organic contaminants (shown in Figure 3) exceeded the LOQ in >90% of samples collected from cell 1 (no ozone),



Figure 1. Average (\pm standard deviation) observed (measured) and modeled removal rates (via direct photolysis and reaction with reactive intermediates) of propranolol and carboxy-abacavir in open-water wetlands during summer (June to August) 2018 (n = 6) and 2019 (n = 3) and winter

(November 2018 to March 2019, n = 3) sampling events.

except for propranolol, which was present in the RO concentrate at concentrations above the LOQ on 14 of the 20 days when samples were collected. Concentrations of two additional antivirals (lamivudine and abacavir) were below the LOQ in >90% of samples. These compounds were also present below their limits of detection (i.e., they were not present at a signal-tonoise ratio of >3).

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

The full monitoring data set is available at https://doi.org/10. 25740/12qf-5243.

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

First-order removal rate constants for previously studied compounds were compared to predictions made with bio- and photo-transformation models developed for open-water wetlands. Predictions were not made for pesticides because the necessary parameters (i.e., quantum yield and reaction rate constants with photoproduced reactive intermediates) are not available in the literature. The biotransformation model estimates first-order removal rates in a well-established biomat as a function of water temperature.^{29,35} The phototransformation model uses the input values of pH, water column depth, and concentrations of relevant species (i.e., dissolved organic carbon, dissolved inorganic carbon, nitrate, and nitrite) as well as sunlight irradiance and absorbance spectra to estimate the rates of direct and indirect photolysis (i.e., DOM-, nitrate-, and nitrite-sensitized reactions via photoproduced reactive intermediates including ¹O₂, ³DOM*, [•]OH, [•]CO₃⁻, and [•]NO₂). Further details on the phototransformation model have been described previously and the relevant equations and parameters are provided in Section S1.4.^{28,36} The contribution of ${}^{1}O_{2}$ to phototransformation was updated from previous versions of the

model to account for recently published quantum yield data (Section S2.3). Water quality parameters measured in samples from each sampling event were used as inputs to the model (Section S2.3). The results for both photolysis and bio-transformation models were produced for each individual sampling event and are reported as the average values from the model with standard deviation of output across sampling events.

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RESULTS AND DISCUSSION

Photo- and Bio-transformation in RO Concentrate. β-Blockers and carboxy-abacavir, which have been studied previously in open-water wetlands that received municipal wastewater effluent and water from an effluent-dominated river,^{26,28–30} were used as indicator compounds to evaluate the effectiveness of open-water wetlands treating RO concentrate. In those previous studies, atenolol and metoprolol removal was mostly attributable to biotransformation, whereas propranolol and abacavir removal mainly involved phototransformation.²⁰ Carboxy-abacavir was used in this study as an indicator compound for phototransformation because abacavir was present below the LOQ (i.e., <20 ng/L), and the carboxylate transformation product was also removed mainly by photolysis.²⁶ The removal of these compounds from the RO concentrate in the pilot-scale treatment system exhibited firstorder kinetics, which have been established in laboratory microcosms and previous field studies of open-water wetlands (Figure S4).^{29,30,3}

Phototransformation. Propranolol removal rates were 30-60% lower than those predicted by a photolysis model developed for secondary wastewater effluent (Figure 1),²⁸ possibly due to inhibition of organic matter-sensitized reactions in the RO concentrate. The model predictions indicated that approximately 80% of the propranolol phototransformation was attributable to reactions with excited triplet states of organic matter (³DOM*) in open-water wetlands treating municipal wastewater effluent.²⁸ Electron-transfer reaction rates with ³DOM* decrease with increasing ionic strength and halide concentrations. For instance, the rate of disappearance of 17β estradiol by organic matter-sensitized phototransformation was approximately 40% lower at an ionic strength of 50 mM compared to that of freshwater (I = 10 mM) and was further inhibited due to halide ion-specific effects.³⁷ The RO concentrate in the pilot-scale system had an ionic strength of



Figure 2. Average (\pm standard deviation) observed and modeled removal rates of β -blockers in open-water wetland cells without (cell 1) and with (cell 2) ozone pretreatment during summer (June to August) 2018 (n = 6) and 2019 (n = 3) and winter (November 2018 to March 2019, n = 3) sampling events.

approximately 60 mM, indicating that the salinity of the RO concentrate was likely responsible for the lower-than-predicted rate of ³DOM*-sensitized photolysis of propranolol.

Average rates of the disappearance of carboxy-abacavir were consistent with model predictions in summer 2019 and about 40% lower than those predicted in summer 2018. Carboxyabacavir removal rate constants were compared with predicted rates for abacavir because quantum yields for direct photolysis and bimolecular rate constants for reactions with oxidants were not available for carboxy-abacavir (further details regarding the abacavir photolysis model are provided in Section S1.4). When the RO concentrate containing both abacavir and carboxyabacavir was irradiated in a sunlight simulator, the pseudo-firstorder carboxy-abacavir photolysis rate constant was approximately 25% lower than that of abacavir (Figure S1), whereas in the summer of 2019, the observed rate constant was 15% lower than the predicted removal rate constant for abacavir. Abacavir was removed via reaction with reactive oxygen species rather than direct reactions with ³DOM*. Therefore, the good agreement between the observed and modeled rate constants is consistent with the findings that energy-transfer reactions of ³DOM* (i.e., formation of ${}^{1}O_{2}$) are not affected by ionic strength or the presence of chloride.³⁸ Furthermore, the good agreement (i.e., within 10%) between model predictions and observed removal rate constants for carboxy-abacavir in the summer of 2019 is promising for predicting the summer performance of other compounds that are phototransformed via a combination of direct photolysis and reactions with photoproduced reactive intermediates.

The predicted and observed rate constants for both compounds were higher in summer 2019 than in summer 2018. The predicted rate constants for propranolol and carboxyabacavir photolysis were approximately 35 and 25% higher in 2019 than in 2018, respectively, because RO concentrate samples collected in 2019 exhibited lower light absorbance on average than samples collected in 2018 (Figure S2). The observed phototransformation rates were lower than those predicted in 2018, likely due to the greater cloud cover and the presence of floating algae during the summer of 2018. Daily sunlight irradiance data for model calculations were taken from the simple model of the atmospheric radiative-transfer of sunshine at 40 degrees North latitude,³⁹ which assumes clear, cloudless days. Historical weather data for San Jose, CA (https://darksky.net), indicated that there was greater cloud cover during daylight hours preceding sampling events in summer 2018 than in summer 2019 (i.e., clear sky was reported for 63% of daylight hours prior to sampling in 2018 and for 94%

of sunlight hours prior to sampling in 2019). In addition, more floating algae and duckweed partially covered the open-water wetland cells during some sampling events—in 2018, up to approximately 40% of cell 1 was covered in floating algae on sampling dates, whereas in 2019, <20% of the cell was covered during all sampling events.

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

Biotransformation. Biomat growth and activity were observed throughout the study period. Changes in microbial ecology and indicators of biological activity are discussed elsewhere.³¹ Notably, although pH and dissolved oxygen profiles indicated strong photosynthetic activity within 1 month of startup, the biomat microbial community evolved throughout the first 18 months of operation, and greater nitrate removal in the biomat was observed in summer 2019 compared to that in summer 2018.³¹

The removal of atenolol and metoprolol was consistent with predictions from biotransformation models developed for openwater wetlands treating wastewater effluent (Figure 2).²⁹ During the summer of 2018, the calculated rate constants in the cell without ozone pretreatment (cell 1) averaged 0.50 and 0.48 d^{-1} for atenolol and metoprolol, respectively, which were similar to the predicted rate constants of 0.57 and 0.43 d^{-1} , respectively. In 2019, atenolol and metoprolol removal rates exceeded the predicted rates in cell 1 ($0.87 d^{-1}$ observed vs $0.58 d^{-1}$ predicted for atenolol and 0.61 d⁻¹ observed vs 0.43 d⁻¹ predicted for metoprolol). The faster removal observed in 2019 was consistent with greater biomat activity in 2019 compared to that in 2018, which was supported by observations of greater biomat depth and nitrate removal capacity in 2019.31 As predicted, removal rates declined during the cooler, winter months.



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 and n = 3 for each ozone dose). Propranolol data for 20 ppm ozone is from 2019 due to non-detects for all three sampling rounds using 20 ppm ozone in 2018. SMX = sulfamethoxazole.



Figure 4. Average (\pm 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 to August).

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

Ozone pretreatment could increase biotransformation rates by increasing the fraction of labile organic matter available to support the growth of biomat organisms. In the pilot-scale treatment system, biodegradable organic carbon (BDOC) concentrations were 83% higher following treatment with 20 mg O_3/L .³¹ BDOC has been used by researchers as a measure of labile organic matter that can support microorganisms in effluent-impacted waters.⁴³ However, the rates of removal of atenolol and metoprolol were not significantly different in the two open-water cells in the summer (Wilcoxon signed-rank test for significance: atenolol *P* = 0.18, metoprolol *P* = 0.06) or in the winter (atenolol *P* = 0.4, metoprolol *P* = 0.2), indicating that the higher BDOC concentrations did not enhance the biotransformation rates of these compounds.

Pilot-Scale System Performance. The combination of photo- and bio-transformations in the open-water wetlands with ozone pretreatment resulted in the removal of a suite of compounds susceptible to different removal mechanisms. During ozonation, contaminant transformation occurred by direct reactions with O₃ and by reactions with hydroxyl radical ($^{\circ}$ OH) generated during O₃ decomposition.⁴⁴ Previous research has sorted organic contaminants into five categories based on their reaction rate constants with O₃ and $^{\circ}$ OH; this research has demonstrated that degradation of contaminants within each category is similar across municipal wastewater effluents as a function of ozone dose on a mg O₃/mg DOC basis.⁴⁵ Contaminants with high reaction rate constants with O₃ (k_{O_1})

~ 10⁵ M⁻¹ s⁻¹) are transformed rapidly at an O₃/DOC ratio of >0.25, whereas contaminants with intermediate rate constants with O₃ (e.g., $k_{O_3} \sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$) require higher O₃/DOC ratios for removal. Contaminants with low ozone reaction rate constants ($k_{O_3} < 10 \text{ M}^{-1} \text{ s}^{-1}$) are removed by a combination of reactions with ozone and hydroxyl radical, such that their removal rate depends on both k_{O_3} and k_{OH} . The same categorization scheme has recently been demonstrated to apply in RO concentrate.³³ In this study, contaminants with rate constants for direct reactions with O₃ greater than 10⁵ M⁻¹ s⁻¹ exhibited decreases in concentrations above 80% during pretreatment with ~0.5 mg O₃/mg-DOC. For compounds with lower rate constants, this ozone dose resulted in a transformation of less than 50% of the compound by a combination of ozone and hydroxyl radical reactions.

At an added O₃ concentration of 40 mg O₃/L (\sim 1 mg O₃/mg-DOC), followed by open-water wetland treatment, concentrations of all detected compounds except imidacloprid and tenofovir decreased by at least 85% during the summer of 2018 (Figure 3), indicating that the concentrations remaining after treatment were equivalent to or lower than those that would have been discharged in wastewater prior to the construction of a potable water reuse system. When 20 mg O₃/L was applied during the summer of 2018, concentrations of atenolol, propranolol, and trimethoprim decreased by more than 85%, whereas concentrations of the other eight compounds decreased by 60-84% following passage through the hybrid treatment system. The performance of the open-water wetland system improved in its second year of operation (Figure 4), such that concentrations of all compounds except fipronil, imidacloprid, and tenofovir decreased by at least 85% in the hybrid treatment when 20 mg O₃/L was applied. The efficacy of the wetland system declined considerably during wintertime (Figure S6).

Both ozone and open-water wetlands contributed substantially to the removal of the three β -blockers and fipronil. The concentrations of these four compounds decreased by over 50% in the open-water wetlands without ozone pretreatment. Ozone treatment reduced concentrations of atenolol, metoprolol, and fipronil by 34-47% with an applied dose of 20 mg O₃/L and by 76–96% with an applied dose of 40 mg O_3/L . In the open-water wetland cell downstream of ozone treatment, these three compounds were further transformed, leading to an overall removal of \geq 90% when 40 mg O₃/L was combined with openwater wetland treatment. Propranolol concentrations decreased below the LOQ at both 20 and 40 mg/L ozone doses. Propranolol has a bimolecular reaction rate constant for reactions with ozone that is approximately 2 orders of magnitude higher than the respective rate constants for metoprolol or atenolol (i.e., $\sim 10^5$ vs 2 $\times 10^3$ M⁻¹ s⁻¹), and has been previously observed to be more efficiently removed via ozonation of RO concentrate.²⁴ Therefore, propranolol was well-removed by either the open-water wetland or ozonation, and there was no benefit from combining both treatments during the summer months.

Emtricitabine, trimethoprim, carbamazepine, and sulfamethoxazole were primarily removed by ozonation, with a modest contribution from the open-water wetland in 2019 but not in 2018. Trimethoprim, sulfamethoxazole, and carbamazepine are known to undergo relatively fast reactions with ozone (bimolecular rate constants are above 10^{5} M⁻¹ s⁻¹ for all three compounds).⁴⁴ Despite their relatively high reactivity with ozone, a dose of 40 mg/L was required to achieve 85% removal of these compounds by ozone treatment in 2018, likely due to the presence of ozone scavengers, including nitrite (approximately 0.1 mM).^{31,33} Concentrations of these compounds increased on average by approximately 10% in the open-water wetlands in summer 2018 due to evaporation of water (Section S2.1). In 2019, concentrations of emtricitabine and trimethoprim decreased by up to 40% in the open-water wetlands (Figure 4), most likely due to biotransformation, whereas carbamazepine and sulfamethoxazole concentrations decreased by less than 10%. The partial removal of these compounds in the openwater wetlands in 2019 resulted in >85% overall removal with an ozone dose of 20 mg/L, indicating that the lower ozone dose may be sufficient for these compounds when paired with a wellestablished open-water wetland system.

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

Sulfamethoxazole was primarily removed by phototransformation in open-water wetlands treating municipal wastewater effluent²⁹ but was not removed in the pilot-scale system in 2018. The concentrations of sulfamethoxazole only decreased 8-21% in the open-water wetlands during the summer of 2019. Sulfamethoxazole concentrations increased more than chloride during all sampling events in 2018 (Figure S3), which may indicate that transformation products that were released by the wastewater treatment plant underwent back-transformation to the parent compound in the open-water wetlands. This hypothesis is supported by previous observations of backtransformation of metabolites of sulfamethoxazole in sunlit systems,^{46,47} and the observation that sulfamethoxazole phototransformation rates matched modeled rates when sulfamethoxazole was added to the RO concentrate and irradiated with a solar simulator.³⁰

Imidacloprid and tenofovir exhibited the slowest removal rates, with modest contributions to removal from both ozone and open-water wetland treatments. Without pretreatment, imidacloprid concentrations decreased by an average of 22% in the open-water wetland during the summer of 2018 and by 31% in the summer of 2019. Ozone pretreatment reduced imidacloprid concentrations by 24 and 55% at 20 and 40 mg O₃/L, respectively. The partial removal of imidacloprid was consistent with the slow reaction rate constant for the reaction of imidacloprid with ozone ($k_{O_3} = 10.9 \text{ M}^{-1} \text{ s}^{-1}$) and a moderate reaction rate constant with hydroxyl radical ($k_{OH} = 4.2 \times 10^9$ M⁻¹ s⁻¹).^{33,48} Further imidacloprid removal occurred in the open-water wetland, resulting in an overall removal of about 50-75%. Concentrations of tenofovir only decreased by 15 and 25% in the open-water wetland in the summers of 2018 and 2019, respectively. Tenofovir was partially removed by O₃ with concentrations decreasing by 14 and 57% at 20 and 40 mg O_3/L_2 respectively. Although the rate constant for the reaction between ozone and tenofovir has not been reported previously, the low removal of tenofovir in this system likely indicates a slow direct reaction rate with ozone for this compound, and its removal



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.

during ozonation was likely primarily due to reactions with hydroxyl radical. $^{\rm 49}$

Implications for Ecological Risk from RO Concentrate.

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

Imidacloprid, fipronil, and carbamazepine exhibited the highest risk quotients before and after treatment (Figure 5). Imidacloprid risk quotients ranged from 41 to 69 and from 29 to 51 in untreated and treated RO concentrate, respectively. Fipronil risk quotients ranged from 13 to 17 in the untreated RO concentrate. The risk quotient for fipronil ranged from 2.5 to 3.4 after passage of water through the hybrid treatment system, compared to 6.8–9.5 and 2.8–8.1 for ozone and wetlands alone, respectively. Carbamazepine risk quotients ranged from 13 to 19 in the untreated and wetland-treated RO concentrate and from 0.2 to 5.6 in the ozone-treated RO concentrate.

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

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Risk quotients also exceeded unity in the untreated RO concentrate for propranolol and sulfamethoxazole (Figure 5). Following ozone treatment, risk quotient values were approximately 1 or less for sulfamethoxazole. Following open-water wetland treatment, the risk quotient for propranolol ranged from less than 1 to 1.3. Ozone treatment lowered the propranolol risk quotient to less than 1 with or without the open-water wetland treatment. The removal of these pharmaceutical compounds to concentrations near or below their PNECs indicates that these contaminants are unlikely to pose a risk in the treated RO concentrate, whereas significant dilution would be necessary to achieve risk quotient values below unity in the untreated concentrate.

For the antibiotics trimethoprim and sulfamethoxazole, minimum selective concentrations can be used to derive PNECs indicative of antibiotic resistance risk.⁵⁵ The PNEC derived for sulfamethoxazole using this method is over 2 orders of magnitude higher than its PNEC for chronic aquatic toxicity, indicating that the aquatic toxicity PNEC used herein is more conservative than the PNEC for antibiotic resistance. For trimethoprim, the risk quotient obtained from the PNEC for aquatic toxicity was always <0.1 (Section S1.5). However, the PNEC derived for antibiotic resistance is lower (0.5 vs 10 μ g/L for chronic toxicity) and of the same order of magnitude as the concentration of trimethoprim in the RO concentrate (~0.6 μ g/L), indicating that antibiotic resistance risk from this compound may be important for future considerations of the compound's ecological impacts.

The risk quotients in excess of 1 for imidacloprid, fipronil, and carbamazepine in the treated RO concentrate indicate that

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

Although this risk quotient analysis was limited to a small set of compounds because of the availability of ecotoxicological data, the results highlighted contaminants of particular concern in RO concentrate (i.e., urban-use pesticides) and allowed us to assess the relevance of the monitored contaminants to ecotoxicity. It is worth noting that this analysis could not account for the toxicity contributions of unidentified transformation products or other compounds lacking chronic ecotoxicity data. Risk quotient analysis also cannot account for the poorly understood effects of complex mixtures. Despite these limitations, we found that the combination of ozone and open-water wetland treatment effectively removed several trace organic contaminants that would otherwise pose potential risks to aquatic ecosystems and substantially reduced the need for dilution of other compounds. Overall, ozone treatment was able to achieve risk quotients below 1 for some compounds with known environmental effect concentrations, while open-water wetlands contributed substantially to the removal of compounds with slow ozone reaction rate constants (e.g., fipronil required a hybrid treatment to achieve a risk quotient below 5). Finally, currently available data indicate that imidacloprid may cause chronic adverse effects on aquatic organisms even in treated RO concentrate, indicating the need to reduce the inputs of this compound into sewer systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04406.

Details on analytical and sampling methods, risk quotient analysis methods, details of photolysis model inputs, and formation of transformation products (PDF)

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Notes

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