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Pilot-Scale Ozone/Biological Activated Carbon Treatment of Reverse Osmosis Concentrate: Potential for Synergism Between Nitrate and Contaminant Removal and Potable Reuse

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ABSTRACT

With limited budgets, utilities may forego potable reuse of municipal wastewater to meet regulations requiring nitrate and contaminant removal from discharges. At 85% recovery, reverse osmosis (RO)-based potable reuse rejects contaminants into a concentrate flowrate that is 6.7-fold lower than wastewater discharges. This study evaluated the footprint and cost savings associated with treating nitrate and contaminants in RO concentrate vs. wastewater effluent. Pilot-scale ozone and biological activated carbon (BAC) treatment of RO concentrate provided design parameters needed for this comparison. Addition of 60 mg-C/L methanol as a carbon source was needed to achieve complete denitrification of 70 mg-N/L nitrate within a 30 min BAC empty bed contact time. Combined with pre-ozonation at 0.5 mg O_3/mg DOC, this treatment removed >74% of fipronil, imidacloprid, atenolol, DEET and sulfamethoxazole. Estimates indicated that applying ozone/BAC treatment to RO concentrate rather than conventional wastewater effluent for contaminant removal prior to discharge would offset 60% of the footprint and 25% of the cost required for the RO-based potable reuse train. Considering these savings, the reuse train cost could be recouped if the product water were sold at rates below those current in southern California. These results suggest synergy rather than competition between potable reuse and contaminant removal.

Keywords: RO concentrate; ozone; biological activated carbon; contaminants; cost

Water Impact Statement: Wastewater utilities are interested in potable reuse, but must also address limits on nitrate and contaminant discharges. Reverse osmosis (RO)-based potable reuse can facilitate contaminant treatment by concentrating them into smaller flowrate streams. Pilot-scale data on ozone/biological activated carbon treatment of RO concentrate were developed to inform cost and footprint estimates demonstrating synergy between RO-based reuse trains and contaminant removal.

1. Introduction

Among utilities in drought-prone areas, there is growing interest in the reuse of municipal wastewater effluents to expand water supplies.[1] However, utilities also may need to address regulatory drivers to remove nitrogen or contaminants that could contribute to poor water quality in receiving waters. Non-potable reuse (e.g., golf course irrigation) diverts nitrogen and contaminants from surface water discharge, but requires the installation of expensive separate distribution systems, and there may be only seasonal demand for this lower-value product water.

Interest in potable reuse is growing, because it produces a higher value product that can use existing distribution systems. However, faced with limited budgets, utilities may perceive the need to target funds towards addressing regulatory drivers on limiting nitrogen and contaminant discharges, and forego potable water production. Advanced treatment trains for potable reuse frequently treat nitrified municipal effluents by microfiltration (MF), reverse osmosis (RO) and a UV-based advanced oxidation process (AOP).[1,2] RO provides broad-screen physical removal of dissolved organic carbon (DOC), organic contaminants, nitrate and inorganic salts to a concentrate stream,[2-4] while AOP treatment provides broad-screen chemical oxidation of organic contaminants in the RO permeate.[5] For typical RO system operation at 85% water recovery,[2] the RO concentrate would feature 6.7-fold higher concentrations of DOC, organic contaminants, nitrate and inorganic salts than in the conventional municipal wastewater effluent supplying the reuse train. The mass loadings of contaminants discharged to receiving waters would be the same for direct discharge of conventional wastewater effluents or for discharge of the RO concentrate. However, the RO concentrate flowrate would be 15% of that of the conventional wastewater effluent. Switching the focus of treatment technologies for the removal of nitrate and organic contaminants prior to surface water discharge from conventional effluents to the 6.7-fold lower flowrate RO concentrates has the potential to reduce the costs and footprints of these treatments, all while producing a potable water supply.

While RO treatment would not change the mass loading of contaminants to surface waters, it reduces the dilution factor. The high salinity of RO concentrate (~4,000 mg/L total dissolved solids (TDS)) relative to freshwater (TDS <500 mg/L) has been a driving factor hindering RO concentrate disposal to inland waters, necessitating expensive zero liquid discharge systems.[6,7] However, salinity is less important for discharge to marine coastal waters (~35,000 mg/L TDS), where the majority of large-scale potable reuse projects are located.[8] Particularly for discharges to poorly-flushed estuaries, an emerging concern is the potential for the high concentrations of nitrate and contaminants (e.g., pesticides and pharmaceuticals) in RO concentrate to contribute to eutrophication and toxicity to organisms in receiving waters.[9-16] If treatment techniques were capable of removing nitrate and contaminants from RO concentrate efficiently, RO treatment for potable water production could facilitate the removal of these contaminants prior to discharge to coastal waters by concentrating these contaminants in a RO concentrate and reducing the size of the nitrate and contaminant treatment system.

Regarding RO concentrate treatment processes, coagulation/flocculation[17] and activated carbon adsorption[18] can remove up to 50% and 90% of DOC, but would be ineffective for nitrate removal and the activated carbon would be rapidly exhausted. AOPs, including those producing hydroxyl radical ($^{\bullet}$OH) by UV photolysis of hydrogen peroxide (UV/H_2O_2)[19-21] or by TiO_2 photocatalysis[17,18,22] and electrochemical oxidation,[23,24] have been applied to treat RO concentrates at laboratory-scale. While many of these studies focused on DOC removal,[17,18,20-22,24] several studies demonstrated the potential to degrade pharmaceuticals during AOP treatment of RO concentrate.[19,22,25] However, the high DOC concentrations in RO concentrates reduce the efficiency of the UV-based AOPs by limiting the UV transmittance[19] and scavenging $^{\bullet}$OH,[19,25] thereby necessitating high UV fluence (e.g., 16,000 mJ/cm^2)[20,21]. Electrochemical oxidation processes can generate undesirable transformation products, particularly by oxidizing chloride to form chlorate and chlorinated organic byproducts.[23,24,26]

Ozone and biological activated carbon (O_3/BAC) is a promising alternative for treatment of RO concentrate. O_3/BAC has been shown to efficiently remove organic contaminants, including pharmaceuticals and pesticides,[27-30] and disinfection byproduct precursors[31,32] from drinking waters wastewaters, and potable reuse waters.[33-35] Ozone itself can selectively target reactive organic contaminants in preference to DOC, but still achieve partial removal of less reactive contaminants by generating $^{\bullet}$OH, a non-selective oxidant. Ozone doses of 0.5-1.0 mg O_3/mg DOC have previously been shown to achieve significant removal of a range of organic contaminants from conventional wastewater effluents.[27] BAC treatment could further contribute to the removal of contaminants and ozone transformation products.[28-30]

However, evaluation of O_3/BAC treatment of RO concentrates has been more limited. While the ability of O_3/BAC to remove a range of organic contaminants from conventional wastewater effluents is encouraging, the impact of the more concentrated matrix in RO concentrate is unclear. For example, higher DOC concentrations could limit contaminant degradation by direct O_3 reactions by promoting the conversion of O_3 to $^{\bullet}OH$, and reduce overall contaminant degradation by scavenging $^{\bullet}OH$. Previous laboratory-scale research has demonstrated >80% degradation of two β-blocker pharmaceuticals in authentic RO concentrate at O_3 doses as low as 0.25 mg O_3/mg DOC.[36] A separate laboratory-scale study found >70% removal of 8 other pharmaceuticals at 0.25 mg O_3/mg DOC, but that 0.8-1.4 mg O_3/mg DOC was needed to reach 80% removal of atenolol, diclofenac and carbamazepine.[37] Neither study evaluated BAC treatment or the removal of nitrate from RO concentrate. A separate study involving laboratory-scale treatment of a RO concentrate with ~0.5 mg O_3/mg DOC followed by BAC with a 60 min Empty Bed Contact time (EBCT) demonstrated ~70% DOC removal, but did not evaluate contaminant removal and employed post-treatment with capacitive deionization to address nitrate removal.[38] Other laboratory-scale studies treating a high salinity (14 g/L TDS) RO concentrate with the UV/H_2O_2 AOP (16,000 mJ/cm^2 fluence) followed by BAC (60 min EBCT) observed 40-60% removal of DOC and 30-65% removal of nitrate; the limited denitrification was attributed to the high dissolved oxygen (DO) concentrations in the BAC effluent.[20,21]

Given the high bromide concentrations in RO concentrates (>1 mg/L), ozonation is expected to produce bromate.[36] Previous research involving laboratory-scale O_3/BAC treatment of conventional municipal wastewater effluents demonstrated that reduction of bromate was possible using the biodegradable DOC as the electron donor under the anaerobic conditions achieved with higher BAC EBCTs,[31] but whether BAC treatment could achieve bromate reduction under the higher DOC and salinity conditions of RO concentrate is unclear.

In contrast to current perceptions that utilities must choose between pursuing potable reuse and meeting regulatory limits on contaminant discharges from wastewater effluents, the overall goal of this study was to evaluate whether the use of a RO-based potable reuse train to produce a potable water supply could facilitate the removal of contaminants and nitrate by concentrating these compounds into a lower flowrate RO concentrate. Using a pilot-scale O_3/BAC system to treat RO concentrate from a potable reuse facility, the first objective was to characterize the O_3 doses and BAC EBCTs needed to remove pesticides, pesticide transformation products, pharmaceuticals, nitrate and bromate. The study evaluated whether nitrate and bromate reduction in the BAC unit could be achieved using the biodegradable DOC in RO concentrate or whether addition of methanol as an external electron donor was necessary. The second objective was to use these design parameters to provide an initial evaluation of the potential savings in footprint and costs associated with targeting nitrate and contaminant removal from RO concentrate rather than from conventional municipal wastewater effluents. Where discharge to coastal waters is possible, this evaluation would indicate the potential for synergy between the application of RO to generate a potable water supply and the removal of nitrate and contaminants.

2. Materials and methods

2.1. Pilot-scale O_3/BAC unit

The pilot study was conducted at Valley Water's (San Jose, CA) demonstration-scale potable reuse train consisting of microfiltration, RO and in the future, a UV-based AOP. The nitrified municipal wastewater effluent serving as the influent to the potable reuse train typically features ~6 mg/L DOC and 8-11 mg-N/L nitrate. The RO concentrate had 40 mg/L DOC, 3,800 mg/L TDS, 70 mg-N/L nitrate, and 660 mg/L as $CaCO_3$ alkalinity at pH 7.7 (Table 1). Ozone produced by a pilot-scale ozone generator (MiPRO^{TM} Advanced Oxidation Pilot System, Xylem, Inc., USA) was applied to 13.2 L/min of the RO concentrate. Since typical O_3 doses for application to RO concentrate treatment have not yet been defined, we applied two O_3 doses (20 mg/L and 40 mg/L), resulting in DOC-normalized O_3 doses within the range (0.5-1.0 mg O_3/mg DOC) being considered for ozonation of conventional municipal wastewater.[27,32] Ozone doses were determined using the flowrates of the RO concentrate and the gas from the O_3 generator, and the difference between the gas-phase O_3 concentrations measured upstream and downstream of a mixing chamber; a liquid-phase sensor verified that the O_3 residual in the RO concentrate was depleted within the 5 min residence time of the RO concentrate in the first O_3 contact chamber. The O_3-treated RO concentrate was routed to a pilot-scale BAC column at 75 mL/min with a peristaltic pump. The BAC unit was constructed by packing three 5.1 cm diameter × 0.9 m columns connected in series with virgin Calgon Carbon Filtrasorb 300M (Vacaville, CA) granular activated carbon (GAC; 0.8-1.0 mm particle diameters; Fig. S1). At the 75 mL/min flowrate, the total BAC EBCT was 45 min, although sample ports located after each column permitted collection of samples representing 15, 30 and 45 min EBCTs. While the lower BAC EBCTs are similar to those employed for BAC treatment of drinking waters or reuse waters,[39] the higher BAC EBCTs permitted the development of anaerobic conditions (see Section 3.1). The BAC columns were operated in the upflow mode to minimize the potential for air bubble accumulation in the columns; columns were backwashed when the column flowrate dropped by 10%. The BAC unit was covered to prevent algal growth.

Table 1

General water quality data for RO concentrate

Parameters	Pre-O_3	Post-O_3 (0.5 mg O_3/mg DOC)	Post-O_3 (1.0 mg O_3/mg DOC)
DOC (mg-C/L)	40	35	33
UVA_{254} (cm^{-1})	0.71	0.46	0.39
BOD_5 (mg/L)	2.3 ± 0.4[a]	5.4 ± 1.7	6.3 ± 1.4
BOD_5/DOC ratio	0.06	0.16	0.19
pH	7.7	7.6	7.6
Conductivity (µS/cm)	6400	6300	6300
Alkalinity (mg/L as $CaCO_3$)	660	670	670
Cl^- (mg/L)	950	950	1000
Br^- (mg/L)	2.7	2.6	2.5
BrO_3^- (µg/L)	<2	17	107
NO_2^- (mg-N/L)	<0.5	<0.5	<0.5
NO_3^- (mg-N/L)	70	70	70
SO_4^{2-} (mg/L)	640	670	700

[a] average ± standard deviation of analytical triplicates

To establish an active biofilm, the BAC column was fed with ozonated RO concentrate (20 mg/L O_3 or 0.5 mg O_3/mg DOC) for 7 months. Between 1-7 months, the DOC removal rate across the O_3/BAC unit was nearly constant at ~40% (Fig. S2); the constant DOC removal rate indicated exhaustion towards DOC of the GAC sorption sites and stable BAC biodegradation as the primary removal pathway. Although the BAC columns were not thermally insulated, the seasonal temperature changes in San Jose (CA) are moderate.

After acclimatization, RO concentrate was subjected to four experimental conditions in the following sequence: 1) 0.5 mg O_3/mg DOC and BAC, 2) 1.0 mg O_3/mg DOC and BAC, 3) 0.5 mg O_3/mg DOC, injection with methanol, and then BAC, and 4) no O_3, injection with methanol and then BAC. After operating under each condition for at least one month to stabilize system operation, samples were collected on two different sampling events over the course of a week from the raw RO concentrate, ozone effluent, and effluents of each BAC column (representing 15 min, 30 min, and 45 min total EBCT).

2.2. Sampling and analytical methods

Dissolved oxygen (DO) was measured on-site using a YSI ProODO optical probe (Xylem, Inc., NY) after collecting samples in vials previously purged with N_2 gas. Grab samples were collected in glass bottles and stored at 4 °C until analysis. DOC was measured using a Shimadzu TOC-L analyzer after filtration through 0.7-μm glass fiber filters that had been heated at 400 °C for 3 h. Nitrite and nitrate were measured using a Dionex DX-500 ion chromatography system. Bromate was analyzed by a certified laboratory following USEPA Method 317.1. BOD_5 was determined by Standard Methods 5210B.[40] Two pharmaceuticals (atenolol and sulfamethoxazole (SMX)), one insect repellent (DEET), two pesticides (imidacloprid and fipronil), and three fipronil transformation products (fipronil sulfone, fipronil sulfide and fipronil desulfinyl)[41,42] were extracted by solid phase extraction (SPE) and analyzed by liquid chromatography−mass spectrometry (LC−MS; Agilent 1260 HPLC system coupled to a 6460 triple quadrupole mass spectrometer) in the multiple reaction monitoring mode (MRM) with 1-10 ng/L reporting limits. Additional analytical details are provided in Text S1. The rationale for the selection of these contaminants is discussed in Section 3.2.

2.3. Initial footprint and cost savings estimates

Using the treatment parameters determined during the pilot tests, initial estimates were developed of the potential for savings in both plant footprint and costs associated with switching from treating conventional nitrified effluents to treating RO concentrate for nitrate and organic contaminant removal. The estimates considered treatment of a 265 million liter per day (ML/day) design flow conventional wastewater effluent vs. treatment of the 40 ML/day design flow RO concentrate stream that would be generated by RO treatment of the 265 ML/day conventional nitrified effluent for potable reuse at 85% water recovery. Operating costs were estimated assuming the average flow was 50% of the design flow; treatment plants are typically operated at 50% of the design flow and this assumption has been applied in previous cost estimating studies for potable reuse facilities.[43]

For treating both the conventional nitrified effluent or the RO concentrate, the estimates considered application of ozone at ~0.5 mg O_3/mg DOC followed by BAC with a 30 min EBCT and addition of methanol to facilitate denitrification, based upon the results of the RO concentrate pilot-testing (Sections 3.2 and 3.3). There are many technologies available for denitrification of conventional nitrified effluents. BAC units functioning as denitrifying biofilters were considered for removal of nitrate from the conventional wastewater stream, since this technology is capable of removing nearly all of the nitrate, and unlike separate-stage suspended growth biological denitrification processes, it can avoid the costs and footprint associated with clarifiers. No pilot testing was conducted for ozone and BAC treatment of the conventional nitrified effluent. However, the 0.5 mg O_3/mg DOC ozone dose achieved significant removal of a range of organic contaminants when applied to conventional wastewater effluents,[27] and O_3/BAC has been applied for contaminant removal in RO-free potable reuse trains.[28-30, 32, 39] While the BAC EBCTs typically are ≤ 15 min in such trains, we assumed that a 30 min EBCT would achieve the anaerobic conditions needed to promote denitrification after ozonation; this EBCT achieved denitrification when treating RO concentrate (see Section 3.3). When treating either conventional wastewater or RO concentrate by O_3/BAC, placing a degasser upstream of BAC could facilitate anaerobic conditions, by enhancing oxygen removal.

The capital costs (including labor, materials and contingencies), O+M costs and footprint associated with ozone and BAC treatment were obtained from Plumlee et al.,[43] which provides these values as a function of facility design flow, and assumes the average flow is 50% of the design flow for calculating O+M costs. For ozonation, the baseline capital and O+M costs provided by Plumlee et al. assume a 3 mg/L O_3 dose, but provide scaling factors to account for higher O_3 doses. The 3 mg/L O_3 baseline concentration would be sufficient to provide a 0.5 mg

O_3/mg DOC dose when treating the 6 mg-C/L DOC of the conventional nitrified effluent (i.e., 6.7-fold lower DOC than the 40 mg-C/L in the RO concentrate (Table 1)). However, for treatment of RO concentrate, the costs were corrected to provide a 20 mg/L O_3 concentration (0.5 mg O_3/mg DOC for the 40 mg-C/L DOC). To estimate the footprint, we assumed a 10 min hydraulic residence time in the ozone unit, and a 3 m height limit.

For the BAC units, Plumlee et al.[43] provides footprint and cost equations separately for BAC units with 10 min and 20 min EBCTs. Since cost values were not provided for a 30 min EBCT, we estimated the costs associated with a 30 min EBCT BAC unit assuming 20 min and 10 min EBCTs in series; these costs would be conservative since some features would be redundant. Plumlee et al.[43] indicates that the 10 min and 20 min EBCT units differ in height, but not footprint, so we assumed that a 30 min EBCT unit would have the same footprint. Since the costs associated with ozone and BAC provided by Plumlee et al.[43] were in 2011 dollars, these values were adjusted to July, 2019 dollars using the RSMeans® Construction Cost Indices.[44] The methanol costs associated with denitrifying biofilter treatment of municipal wastewater in a previous study[45] were scaled to the 70 mg-N/L nitrate concentration in the RO concentrate (Table 1) and the 10.4 mg-N-L nitrate concentration in the conventional wastewater (i.e., 6.7-fold lower than in RO concentrate) and converted to July, 2019 dollars using the RSMeans® Construction Cost Indices.[44]

Capital, O+M and footprint estimates were also developed for a potable reuse train consisting of microfiltration (265 ML/day), RO (265 ML/day) and a UV/hydrogen peroxide AOP (225 ML/day based on RO treatment at 85% recovery). These calculations served to indicate whether any savings in plant footprint and costs obtained by switching the treatment of organic contaminants and nitrate from the conventional wastewater effluent to RO concentrate could significantly contribute to the footprint and costs needed for the potable reuse train. Capital and O+M costs and footprint requirements for each process unit were provided as functions of facility size in Plumlee et al.,[43] and were corrected to July, 2019 dollars in the same fashion as discussed above. The capital costs and annual O+M costs for all of the process trains were converted to Equivalent Annual Costs (EACs) using a 40-year lifetime for the treatment train and a 4% discount rate. The spreadsheets for calculating costs and footprint are provided as Supporting Data.

It is important to emphasize that these estimates serve as only rough initial cost and footprint estimates. While the capital and O+M cost functions provided in Plumlee et al.[43] are intended to be comprehensive (i.e., include the costs of all equipment such as instrumentation), they encompass rough (Class 4) scoping costs. Cost and footprint requirements can vary substantially based upon site-specific differences. The goal here is to provide initial, rough indications of the potential for cost and footprint savings associated with treating nitrate and contaminants in RO concentrate, rather than conventional wastewater effluents.

3. Results and discussion

3.1. DOC removal and dissolved oxygen

While DOC removal is not a regulatory target for RO concentrate treatment, we evaluated DOC removal for comparison to previous evaluations. BAC treatment of RO concentrate without O_3 pre-treatment achieved 22% DOC removal after a 45 min EBCT (Fig. 1), concurring with previous bench-scale results for BAC treatment of RO concentrate.[20, 27, 38] Ozonation at

0.5 mg O_3/mg DOC and 1.0 mg O_3/mg DOC provided 13% and 19% DOC removal, respectively. However, subsequent BAC treatment achieved 36% and 42% additional DOC removal, respectively, for overall DOC removals of 49% and 61%, respectively; previous laboratory-scale research found 70% DOC removal after O_3/BAC treatment of RO concentrate,[38] potentially reflecting a higher fraction of biodegradable carbon in that RO concentrate. The majority of the removal (>75%) observed in the current study happened during the first 15 min EBCT. The enhanced DOC removal could reflect both the increase in biodegradability of the DOC provided by O_3 oxidation (note the increase in the BOD_5/DOC ratio with ozonation in Table 1),[38] but also the higher dissolved oxygen (DO) concentrations in the BAC influent, which increased from 7.4 mg/L to ~35 mg/L due to ozonation. Over 85% of the DO was consumed within 15 min of BAC EBCT and DO was not measurable after 45 min EBCT.

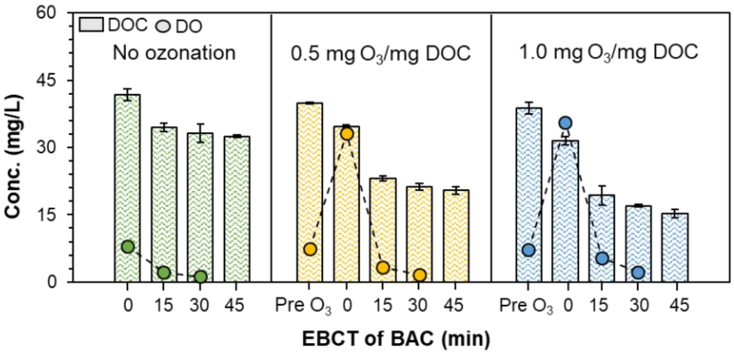

Fig. 1. Concentrations of DOC and DO at different BAC EBCT with different ozone doses. Error bars represent the range of duplicate samples collected on separate occasions.

3.2. Contaminant removal

Similar to the discharge of conventional municipal wastewater effluents, discharges of RO concentrates to coastal waters must meet regulatory guidelines on effluent toxicity based on *in* *vivo* assays. Regulatory limits for individual contaminants typically have not been established. There can be a wide range of contaminants in RO concentrate, and the drivers for toxicity are unclear. We focused on fipronil, imidacloprid, sulfamethoxazole, atenolol and DEET, because these contaminants were routinely detected in the RO concentrate, and because these compounds either are of known toxicological concern or exhibit a range of reactivity with ozone. The pesticides fipronil and imidacloprid are potentially important contributors to toxicity, since the U.S. EPA has indicated that 10 ng/L imidacloprid and 11 ng/L fipronil are benchmark concentrations that should not be exceeded to protect aquatic invertebrates during long-term exposure.[46] The concentrations of fipronil (165-217 ng/L) and imidacloprid (427-573 ng/L) measured in the RO concentrate over four months of sampling (Table S3) would need to be reduced by ~80% and ~95%, respectively, to meet these benchmark concentrations; to our knowledge, fipronil and imidacloprid concentrations have not been reported previously in RO concentrates. Similarly, sulfamethoxazole (SMX) was detected at 1,273-2,495 ng/L, which is higher than the 118 ng/L considered to be of toxicological concern in San Francisco Bay.[47] While there would be dilution in the receiving water, partial removal by treating RO concentrate would facilitate meeting these benchmarks, particularly for discharge to poorly-flushed estuaries. The concentrations of the other two contaminants measured over the four months of sampling ranged from 1,277-2,446 ng/L for atenolol and 100-661 ng/L for DEET (Table S3), and were similar to those previously reported in RO concentrates.[16] While the concentrations of atenolol and DEET were below those of concern for San Francisco Bay,[47] SMX (5.7×10^5 M^{-1} s^{-1})[48], atenolol (1.7×10^3 M^{-1} s^{-1})[36], and DEET (<10 M^{-1} s^{-1})[49] exhibited a wide range of reaction rate constants with ozone.

Except for SMX (7% removal), the removal achieved by BAC without O_3 pre-treatment ranged from 59% for DEET to 88% for imidacloprid and 89% for fipronil (Fig. 2). Thus, BAC treatment alone was able to remove a significant fraction of the contaminants. Contaminant degradation by O_3 treatment alone ranged from 19% for DEET to 81% for SMX at 0.5 mg O_3/mg DOC, and increased to 52% for DEET and imidacloprid to 93% for SMX at 1.0 mg O_3/mg DOC. At 45 min EBCT, the combined O_3/BAC treatment removed 74-100% removal of all five compounds at 0.5 mg O_3/mg DOC and 84-100% removal at 1.0 mg O_3/mg DOC. DEET was the most difficult of the five compounds to remove. The 52% removal of DEET by ozonation alone at 1.0 mg O_3/mg DOC was lower than the ~80% removal of DEET observed for the same ozone dose applied to conventional wastewater effluents.[27] The BAC treatment was also able to eliminate the O_3 transformation products of fipronil. For example, while ozonation increased the concentration of fipronil sulfone from 31 ng/L to 41 ng/L for 1.0 mg O_3/mg DOC, the subsequent BAC treatment (45 min EBCT) reduced its concentration to <1 ng/L (Fig. S3).

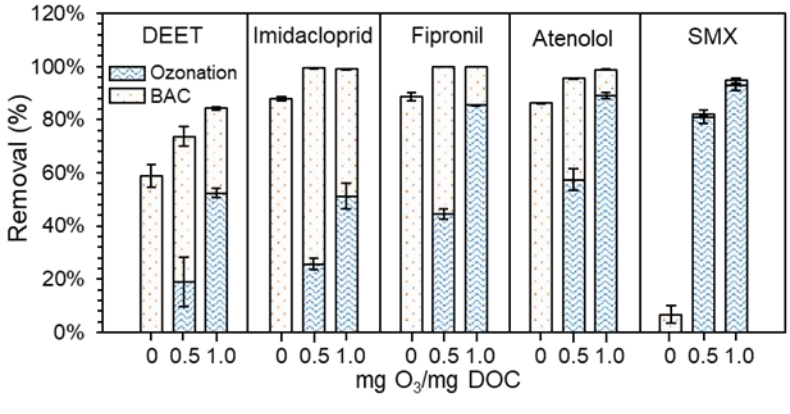

Fig. 2. Removal of contaminants from RO concentrate by O_3/BAC at different ozone doses corresponding to 0, 20 and 40 mg/L O_3. Error bars represent the range of duplicate samples collected on separate occasions.

3.3. Nitrate and bromate

The nitrate concentration in the RO concentrate was ~70 mg-N/L (Table 1). Even though oxygen was not measurable after 45 min BAC EBCT (Fig. 1), no nitrate removal was observed in the absence of O_3 pre-treatment (Fig. 3). Only ~10 mg/L DOC was removed, suggesting insufficient biodegradable carbon to drive nitrate reduction after depletion of dissolved oxygen. After treatment with 0.5 mg O_3/mg DOC and BAC, only 7% nitrate removal was observed, despite the 36% removal of DOC during BAC treatment (Fig. 3). While O_3 enhances the biodegradability of DOC, most of the biodegradable DOC removal occurred within the first 15 min of BAC EBCT concurrent with the consumption of DO (Fig. 1). DO served as the electron acceptor for the removal of most of the biodegradable DOC, leaving little biodegradable carbon to drive nitrate removal by biological denitrification. Thus, without ozonation, the biodegradable fraction of DOC was insufficient to drive denitrification, despite the low oxygen conditions. While ozonation increased the fraction of biodegradable carbon, this biodegradable carbon was consumed by the increased DO resulting from ozonation. Even after this DO was consumed and the anaerobic conditions needed for denitrification were achieved, the residual biodegradable carbon was insufficient to fuel significant denitrification.

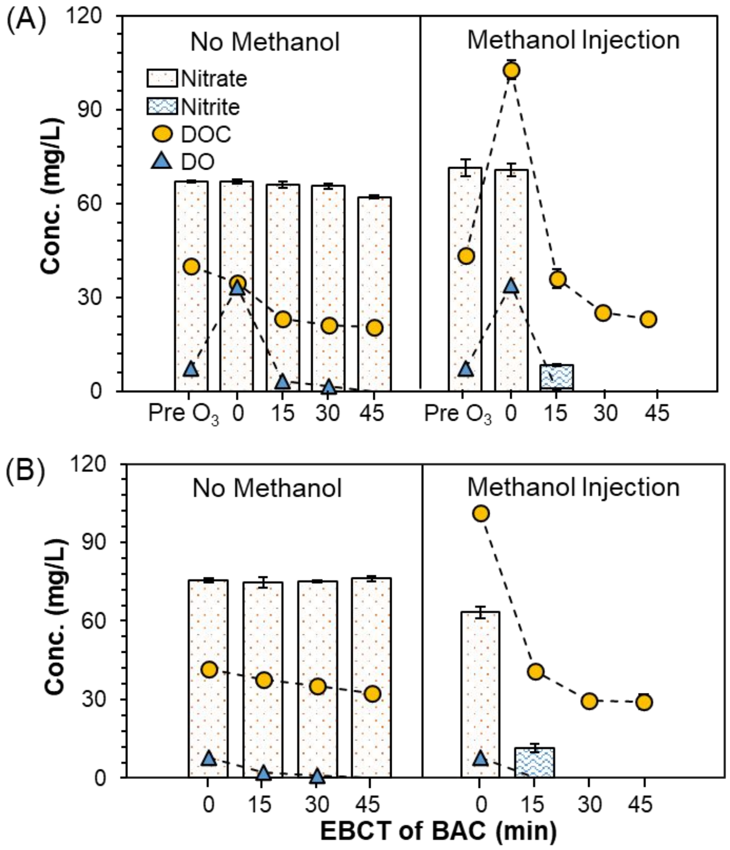

Fig. 3. Concentrations of DOC (mg-C/L), DO (mg/L), nitrite (mg-N/L) and nitrate (mg-N/L) at different BAC EBCTs without and with addition of 60 mg-C/L methanol A) after ozonation at 0.5 mg O_3/mg DOC and B) without ozone pre-treatment. For DO, symbols are not shown when the concentration was below the 0.5 mg/L detection limit. Samples were taken after acclimatization of the BAC for 7 months. Error bars represent the range of duplicate samples collected on separate occasions.

These results suggested the need to provide an additional bioavailable carbon source to achieve anaerobic conditions and drive denitrification. While addition of methanol as a bioavailable carbon source to drive denitrification has not been tested in RO concentrate, we expected methanol addition would accomplish nitrate reduction, based upon the known efficacy of methanol addition for denitrification in conventional wastewater effluents. However, methanol addition at pilot-scale was evaluated to determine the methanol concentration and the BAC EBCT required to achieve complete denitrification; these parameters are important for characterizing the costs associated with treating RO concentrate.

Initial tests involving pre-treatment with 0.5 mg O_3/mg DOC and addition of 40, 60 or 70 mg-C/L methanol indicated complete removal of nitrate for ≥ 60 mg-C/L methanol (Fig. S4). When 60 mg-C/L methanol was injected into the BAC influent as a bioavailable carbon source, the DO with or without ozone pre-treatment was not measurable after 15 min BAC EBCT. Significant denitrification was observed, concurring with expectations that denitrification requires anoxic conditions (Fig. 3). Nitrate removal was complete within a 30 min BAC EBCT and the DOC had returned to levels measured in the absence of methanol spiking. These results suggest that nearly all of the methanol added had been consumed, corresponding to a 1:1 molar ratio of methanol to nitrate. This molar ratio agrees fairly well with the stoichiometry for denitrification to produce nitrogen gas in equation 1, although denitrification can also produce N_2O. Addition of methanol after the first column could have reduced the methanol demand by avoiding partial methanol oxidation by aerobic biodegradation in the first column.

$$5\ CH_3OH + 6\ NO_3^- + 6\ H^+ \rightarrow 5\ CO_2 + 3\ N_2 + 13\ H_2O \qquad [1]$$

Ozonation of bromide-containing waters can form bromate (BrO_3^-);[50,51] although a potential human carcinogen with a 10 μg/L drinking water Maximum Contaminant Level in the U.S.,[52] much higher BrO_3^- concentrations are associated with aquatic toxicity (e.g., at 13.6 mg/L lowest observed effects level for cell division in marine phytoplankton)[53]. Ozonation of the RO concentrate, which featured 2.7 mg/L Br^-, formed 17 μg/L and 107 μg/L BrO_3^- at 0.5 mg O_3/mg DOC and 1.0 mg O_3/mg DOC, respectively (Table 1). In the absence of methanol injection, no significant BrO_3^- removal was observed by BAC treatment after ozonation at 0.5 mg O_3/mg DOC (Fig. 4). However, after 1.0 mg O_3/mg DOC treatment, BAC treatment reduced the BrO_3^- concentration from 107 μg/L to 24 μg/L. After ozonation at 0.5 or 1.0 mg O_3/mg DOC and injection of 60 mg-C/L methanol as an electron donor to promote biological bromate reduction, BAC treatment resulted in complete BrO_3^- removal (Fig. 4), similar to the results for nitrate removal. Although bromate may not be a toxicity driver for RO concentrate discharge, future research could evaluate anoxic BAC treatment to remove bromate when O_3/BAC is applied to conventional wastewater in RO-free potable reuse trains.

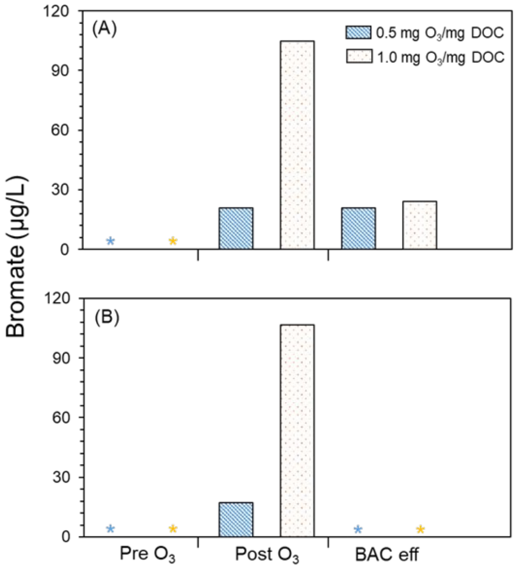

Fig. 4. Concentrations of bromate (μg/L) during O_3/BAC treatment (A) without and (B) with injection of 60 mg-C/L methanol prior to BAC treatment. Ozonation was conducted at 20 mg/L (0.5 mg O_3/mg DOC) and 40 mg/L (1.0 mg O_3/mg DOC). BAC eff = after 45 min BAC EBCT. * = below the detection limit (< 5 μg/L).

3.4. Initial estimates of footprint and cost savings

We developed rough, initial estimates of the potential magnitude of cost and footprint savings associated with addressing nitrate and contaminant removal in RO concentrate as opposed to conventional wastewater effluent to characterize whether the pursuit of RO-based potable reuse could facilitate other treatment goals. These initial estimates of the plant footprint and capital and O+M costs compared ozone (0.5 mg O_3/mg DOC) and BAC (30 min EBCT) treatment for nitrate and organic contaminant removal from a 265 ML/day nitrified conventional effluent vs. a 40 ML/day RO concentrate. If regulations require only nitrate removal, its removal could be achieved without ozonation by BAC treatment with methanol addition (Fig. 3). The pilot results indicate that complete removal of ~70 mg-N/L nitrate from the RO concentrate could be achieved by injecting ~60 mg-C/L methanol as an external carbon source followed by BAC treatment within a 30 min EBCT without or with ozone pretreatment. Since the stoichiometric requirement for methanol for denitrification (equation 1) and mass of nitrate in RO concentrate are the same as in conventional wastewater effluents, the cost of methanol supply would be similar. Switching from nitrate removal by BAC treatment of 265 ML/day of conventional nitrified wastewater effluent to BAC treatment of 40 ML/day RO concentrate decreased the footprint requirement by 968 m^2 from 1130 m^2 to 162 m^2 (Table 2). The capital and O+M costs also decreased, resulting in a decrease in the Equivalent Annual Cost (EAC) over the 40-year lifetime of the facilities of \$12.3 million/year, from \$16 million/year to \$3.7 million/year (Table 2).

Regarding organic contaminants, regulatory targets for other specific chemicals associated with potential toxicity to aquatic life in coastal receiving waters have not been developed. BAC treatment alone achieved 59-89% removal of 4 of 5 organic contaminants, including >80% removal of fipronil and imidacloprid. Combined with dilution by the receiving water, this level of treatment could help ensure that these pesticides do not exceed chronic toxicity thresholds in receiving waters. However, BAC achieved only 7% removal of sulfamethoxazole. The combination of ozone and BAC was able to remove >74% of all 5 organic contaminants. The ability of O_3/BAC treatment to address removal of both nitrate and organic contaminants may be attractive. Treatment by O_3/BAC of RO concentrate rather than the conventional nitrified effluent provided footprint savings of 1481 m^2 and \$13 million/year in EAC (Table 2).

These costs only compare treatment of conventional wastewater and RO concentrate for removal of nitrate and contaminants. The costs and footprint associated with the microfiltration, RO and the UV/hydrogen peroxide AOP (MF/RO/AOP) based treatment train needed to provide the RO concentrate must also be considered. We estimated the cost and footprint requirements for a MF/RO/AOP-based potable reuse train treating 265 ML/day of conventional municipal effluent to understand whether the cost and footprint savings associated with removing nitrate and organic contaminants from RO concentrate would make a meaningful contribution towards the potable reuse train. The MF/RO/AOP-based train would require 2,434 m^2 of footprint and an EAC of \$53 million/year (Table 2). Thus, if only nitrate removal were a concern, only methanol addition and BAC treatment of either conventional wastewater or RO concentrate would be needed prior to discharge; switching to BAC treatment of RO concentrate rather than BAC treatment of conventional wastewater discharge would liberate 40% of the footprint needed for the MF/RO/AOP-based potable reuse train, and the cost savings would contribute 23% of the EAC needed for the potable reuse train. If organic contaminant and nitrate removal were of concern, O_3/BAC of conventional wastewater or RO concentrate would be needed prior to discharge; switching to O_3/BAC treatment of RO concentrate rather than O_3/BAC treatment of conventional discharge would liberate 60% of the footprint needed for the potable reuse train and the cost savings would contribute 25% of the EAC needed for the reuse train.

In both cases, the cost savings would offset only ~25% of the costs associated with the potable reuse train. However, it is important to note that the potable reuse train produces a drinking water supply that can serve as a revenue stream. The 225 ML/day of potable water produced by the potable reuse train (i.e., for RO treatment at 85% recovery) would yield 82,180 ML/year of a potable water supply. Potable reuse water supplies typically are treated within a drinking water treatment plant before consumption. If the water could be sold as a raw water supply to a drinking water facility for \$644/ML, this revenue, by itself, would completely offset the EAC of the potable reuse train. If the ~25% contribution of the savings in EAC associated with treating nitrate and organic contaminants in the RO concentrate were considered, selling the water for \$487/ML would offset the EAC of the potable reuse train. For comparison, these prices are comparable to the \$594/ML price for untreated drinking water supplies proposed for 2019 by the Metropolitan Water District of Southern California.[54]

Table 2

Footprint and cost estimates for different treatment options

	Unit	Conventional Effluent			RO Concentrate			Savings	Potable Reuse
		Ozone [a]	BAC [b]	Ozone/BAC	Ozone	BAC [b]	Ozone/BAC	Ozone/BAC	MF/RO/AOP [d]
Footprint	m^2	604	1130	1734	91	162	253	1481	2434
Capital costs	$ million [e]	19	129	148	9.3	26	35	113	380
O+M costs	$ million/year	0.5	9.0	9.5	0.3	1.5	1.9	7.6	33
Methanol	$ million/year	0	0.9	0.90	0	0.9	0.90	0	0
EAC [f]	$ million/year	1.4	16	18	0.9	3.7	4.6	13	53

[a] O_3 based on treating 265 ML/day at 3 mg/L O_3, a 10 min residence time and a 3 m height limit

[b] Based on 30 min EBCT total treating 265 ML/day using 20 min EBCT units in series with 10 min EBCT units to limit the biofilter height

[c] O_3 based on treating 40 ML/day at 20 mg/L O_3, a 10 min residence time and a 3 m height limit

[d] Based on 30 min EBCT total treating 40 ML/day using 20 min EBCT units in series with 10 min EBCT units to limit the biofilter height

[d] Estimates for a 265 ML/day facility with footprint based on proportion to the 450 ML/day MF/RO/AOP facility at the Orange County Water District facility.

[e] July, 2019 dollars

[f] Equivalent Annual Cost using a 40 year lifetime and 4% discount rate

4. Conclusions

This study evaluated whether RO treatment for potable reuse facilitates addressing regulatory limits on the discharges of nitrate and contaminants to coastal receiving waters by enabling the treatment to be conducted on the 6.7-fold lower flowrate of RO concentrate. Pilot-testing of O_3/BAC treatment was conducted on RO concentrate to provide design parameters, which in turn informed an initial comparison of footprint and cost requirements between treating nitrate and organic contaminants in RO concentrate vs. in the conventional wastewater effluent. While BAC treatment alone removed 22% of DOC at a 45 min EBCT, pre-treatment with 0.5 mg O_3/mg DOC increased DOC removal to 49%. While the specific contaminants of highest toxicological concern in RO concentrates have not been identified, the concentrations of the pesticides imidacloprid and fipronil in RO concentrate exceeded benchmark concentrations for aquatic toxicity by ~4-17-fold. BAC treatment alone removed 88-89% of imidacloprid and fipronil, but only 7% of sulfamethoxazole. Pre-treatment with 0.5 mg O_3/mg DOC increased the removal of all 5 organic contaminants tested to 74-100%. It is important to note that O_3/BAC treatment would not remove all potential contaminants. For example, O_3/BAC treatment provides only partial removal of perfluorinated compounds in potable reuse trains;[55] however, the significant removal of a range of contaminants from the complex contaminant mixtures in RO concentrate should enhance effluent quality prior to discharge. Addition of 60 mg-C/L methanol prior to BAC treatment promoted the complete denitrification of the 70 mg-N/L nitrate within a 30 min EBCT. Estimates comparing application of 0.5 mg O_3/mg DOC, addition of methanol and BAC treatment with a 30 min EBCT between treatment of conventional wastewater effluent or its associated RO concentrate at a 6.7-fold lower flowrate indicated that switching to treatment of RO concentrate could save 60% of the footprint and 25% of the Equivalent Annual Cost associated with the RO-based potable reuse train. Instead of having to choose how to target limited budgets between compliance with regulatory limits on nitrate and contaminant discharges and the production of a potable water supply, our results suggest the potential for synergy between these goals.

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Supporting Information Available: Basic water quality parameters; additional materials and methods; pharmaceutical, pesticide, fipronil transformation product and bromate concentrations.

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Graphical Abstract