

Demonstrating process robustness of potable reuse trains during challenge testing with elevated levels of acetone, formaldehyde, NDMA, and 1,4-dioxane

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ABSTRACT

Robustness of a demonstration potable reuse facility was evaluated through a series of system-wide chemical challenge tests spiking neutral low-molecular weight compounds (acetone, formaldehyde, *N*-nitrosodimethylamine (NDMA), and 1,4-dioxane) which are known to be challenging for removal through advanced treatment. Two advanced treatment train arrangements were compared: O₃/BAC-MF/UF-RO-AOP and RO-AOP. Ozone and biological activated carbon (O₃/BAC) offered significant attenuation of the smallest and most biologically degradable compounds tested: acetone and formaldehyde. These two compounds had limited reduction across the reverse osmosis (RO) membrane barrier and the different advanced oxidation process (AOP) setups used. 1,4-Dioxane was partially reduced across the oxidation barriers: 62% across ozonation and up to 95% across AOP depending on oxidant used and oxidant dose. Both a hydrogen peroxide (H₂O₂) based AOP (UV/H₂O₂) and a sodium hypochlorite (as HOCl) based AOP (UV/HOCl) demonstrated sufficient oxidation, providing no less than 0.5-log (68%) 1,4-dioxane attenuation required by regulators in the USA. NDMA was reduced across both UV/H₂O₂ and UV/HOCl from 157 to 267 ng/L to below the 10 ng/L established notification level for drinking water in California. Overall, addition of O₃/BAC enhanced cumulative removal of all the spiked trace organic chemicals, providing greater protection against the spiked contaminants than RO-AOP alone. In addition, online total organic carbon (TOC) monitoring successfully captured the presence of the spiked chemicals.

Key words | 1,4-dioxane, BAC, challenge testing, NDMA, ozone, potable reuse

INTRODUCTION

Climate change, population increase, and drought intensification are all factors that inevitably threaten the availability of reliable potable water supplies (NRC 2012). Thus, the practice of potable water reuse, defined as the use of highly treated municipal wastewater to augment drinking water supplies, is receiving increasing attention to help secure future potable water demands (Drewes & Khan 2015). Given that potable reuse challenges the traditional practice

of maximizing separation between sanitary waste streams and drinking water supply, it is of utmost importance to incorporate treatment that adequately protects public health and complies with existing regulations. The concept of robustness, or the ability for a system to address a broad variety of contaminants, has been influential in the design of potable reuse treatment trains (Pecson *et al.* 2015). This concept is rooted in the fact that there are potentially

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80,000 known chemical compounds in municipal wastewater effluents, such that no single process can adequately address all concerns (Drewes *et al.* 2013). Robustness is accomplished when multiple unit processes are combined to provide a range of removal mechanisms including biodegradation, adsorption, photolysis, oxidation, and physical separation. The goal of these combinations is to approach *fail-safe* systems that can reliably and continuously provide protection of public health. Although robustness is highly important to achieve potable reuse reliability, other concepts, such as redundancy (i.e., use multiple units for each process as well as power back-up) and treatment train resilience (i.e., adaptation to failures through high-frequency data and use of artificial intelligence) also build on the framework to protect public health (Pecson *et al.* 2015).

The use of an integrated membrane system followed by advanced oxidation is commonly used for the practice of potable reuse. One example of such trains is the full advanced treatment (FAT) train recognized by California's Division of Drinking Water (DDW). This treatment train couples reverse osmosis (RO) membranes (achieving a minimum sodium chloride rejection of 99.0%) and an oxidation process that demonstrates sufficient oxidation either by: adequate attenuation (50–68%) of nine indicator compounds representing different functional groups, or at least 0.5-log (68%) 1,4-dioxane attenuation validated through challenge testing (22 CCR § 60320.201). FAT is commonly implemented using an integrated membrane system (e.g., microfiltration (MF) or ultrafiltration (UF) followed by reverse osmosis) followed by an advanced oxidation process (AOP), commonly employed by coupling an ultraviolet (UV) irradiation system with hydrogen peroxide (H₂O₂). This treatment train (MF-RO-UV/H₂O₂) is used at the 4.4 m³/s (100 MGD) Orange County Water District Groundwater Replenishment System (OCWD GWRS), located in California, USA and is currently the largest potable reuse facility in the world.

The GWRS is an exceptionally well-managed facility with an excellent record of performance, achieving total organic carbon (TOC) concentrations in the final product water of less than 0.2 mg/L (OCWD 2018). Nevertheless, online TOC monitoring of the final product water revealed several short-term events of elevated RO permeate TOC concentrations exceeding 1 mg/L. Later, these incidences were

associated with unauthorized releases of acetone into the sewershed that were not captured by the existing industrial source control program or attenuated by the biological wastewater treatment plant or reverse osmosis treatment (Olivieri *et al.* 2016). There is currently no drinking water regulatory limit for acetone in the United States and experts concluded regarding these incidences that 'acetone features low acute and chronic toxicity and is not considered a carcinogen' (OCWD 2018), yet noted its passage through the most advanced full-scale treatment train raises a concern. This concern is particularly relevant for direct potable reuse schemes, which do not utilize an environmental buffer (e.g., surface water reservoir or groundwater aquifer) and, therefore, are characterized by shorter response time to address potential treatment failures and little opportunity, if any, for water quality equalization (Drewes & Khan 2015).

This study examines whether the integration of additional treatment processes might enhance mitigation of a broader spectrum of chemicals, enhancing the overall robustness of a treatment train. Specifically, ozone and biological activated carbon (O₃/BAC) is proposed as pre-treatment to an integrated membrane system followed by an AOP. The combination of O₃/BAC has been widely reported to offer a number of synergistic benefits, including significant transformation and removal of effluent organic matter (EfOM), effective oxidation of trace organic chemicals (TOrcs), biodegradation of bulk organic matter including oxidation byproducts, improved water quality for downstream treatment, reduction of TOrc mass load in the RO brine, and added pathogen inactivation (Gerrity *et al.* 2011, 2014; Trussell *et al.* 2015).

This study evaluated treatment train robustness of the 3,785 m³/d (1 MGD) North City Pure Water Demonstration Facility configured with O₃/BAC as pre-treatment to UF/MF-RO-AOP compared to RO-AOP alone in a series of system-wide chemical challenge tests. In addition, an alternative AOP using sodium hypochlorite (UV/HOCl) was tested to evaluate abatement of spiked 1,4-dioxane in comparison to UV/H₂O₂. Four low molecular weight, highly miscible compounds (acetone, formaldehyde, *N*-nitrosodimethylamine (NDMA), and 1,4-dioxane) were chosen for these spiking events. Additionally, online water quality analyzers (e.g., TOC) were used to assess their ability to detect chemical pulses throughout the treatment train.

MATERIALS AND METHODS

North City Pure Water Demonstration Facility

The North City Pure Water Demonstration Facility (PWDF) is located at the North City Water Reclamation Plant (NCWRP) in San Diego, USA and uses filtered secondary effluent (i.e., fully nitrified, partially denitrified secondary effluent followed by filtration with anthracite media) from the NCWRP as feed water. The PWDF was constructed in 2011 and has a production capacity of 3,785 m³/d (1 MGD) using an advanced treatment train consisting of parallel trains of MF and UF, two parallel RO trains, and UV/H₂O₂ as an AOP. In addition to this core treatment train, O₃/BAC was added as pre-treatment prior to the UF/MF trains in 2014. A summary of unit process characteristics and design criteria are provided in the Supplementary material (Table A1), available with the online version of this paper.

The containerized ozone system (WEDECO, Herford, Germany) contained a pressure swing adsorption (PSA) oxygen generator (AirSep AS-L, Chart Industries, Buffalo, NY, USA), ozone generator, dissolution systems, alarms, cooling water system, applicable instrumentation, and controls. The ozone generator had a capacity of 86.2 kg/day at 10% ozone gas concentration. During this study, the ozone system was operated to generate 61 kg/day of ozone at the design flow of 4,164 L/min (1,100 gpm). The applied ozone dose ranged from 10.2 to 10.8 mg/L, due to slight fluctuations in the oxygen flow produced by the PSA oxygen generator system. This equates to a typical O₃/TOC ratio of 1.3 to 1.4 at a median historical ozone influent TOC of 7.6 mg/L. Upon dissolution, the ozonated effluent passed through a custom-built ozone contactor that provided approximately 7 minutes of contact time at the design flow, which was sufficient for ozone to fully decay under normal conditions. Sodium bisulfite was proactively dosed at the end of the ozone contactor, in instances when ozone residual was still measurable (≥ 0.05 mg/L).

The BAC filtration system (Leopold, Zelienople, USA) consisted of two gravity-fed filters in parallel, each with 2 m of agglomerated coal-based granular activated carbon (GAC) CMR MUNIF300 (Calgon Carbon Corporation, Pittsburgh, USA) and a bed surface area of 16.7 m². At a design feed flow, the empty bed contact time was

approximately 15–16 minutes. Stabilization of TOC removal approximately eight months from commissioning indicated exhaustion of the GAC and conversion to BAC. Backwashes were typically performed 1–2 times a week to restore head loss. NCWRP filtered secondary effluent was used for backwashing the filters. PWDF BAC filter backwash water is conveyed to a local wastewater treatment plant and sent to ocean outfall once treated. A dual-stream Sievers M5310 C TOC analyzer (GE, Boulder, CO, USA) provided online TOC readings from the ozone influent and BAC effluent. This TOC analyzer oxidized organic compounds using UV radiation and ammonium persulfate.

BAC effluent was then treated through parallel trains of UF and MF, both using polyvinylidene difluoride (PVDF) hollow fibers. The UF system (H₂O Innovation, Québec, Canada) consisted of Toray (Poway, USA) HFU-2020 modules with a nominal pore size of 0.015 μ m that operated at >95% recovery. The MF system (Pall Corporation, Port Washington, USA) consisted of Pall Corporation UNA-620A modules with nominal pore size of 0.1 μ m that operate at >95% recovery. Flux for both systems was greater than or equal to 85 LMH (50 gfd) during testing. Automated backwashes were triggered approximately every 30 minutes for both systems and used MF/UF combined filtrate as backwash water. PWDF MF/UF backwash water is also conveyed to a local wastewater treatment plant and sent to ocean outfall once treated.

The RO system (EnAqua, Vista, USA) consisted of two trains. Train A was a two-stage system fitted with ESPA2 LD RO membranes (Hydranautics, Oceanside, CA, USA), whereas Train B was a three-stage system fitted with Toray TML20-400 RO membranes. Combined MF/UF filtrate was split among the RO trains that operated at 75–80% recovery. There was no acid pre-treatment at the time of the testing, and a proprietary anti-scalant AWC A-110 (American Water Chemicals, Plant City, FL, USA) was injected to the RO feed to control membrane scaling.

The AOP at PWDF was achieved by coupling low-pressure ultraviolet light with an oxidant to form hydroxyl (\cdot OH) radicals. The TrojanUVPhox (TrojanUV, Ontario, Canada) UV-based system supplied a total power of 18.0 kW. The reactor power was throttled between the minimum power level of 60% to 100%, based on the influent water UV transmittance (UVT) to target 1.2-log NDMA

destruction through photolysis alone. Typically, power use was maintained to achieve an electrical energy for destruction (EED) of 0.079 kWh/m³ for 1.2-log target NDMA removal at an average UV intensity of 50 mW/cm². As for the oxidants, a hydrogen peroxide (30%) delivery system supplied 3 mg/L, although a higher dose of 6 mg/L was also evaluated. The use of sodium hypochlorite (12.5%) was examined as an alternative AOP (UV/HOCl). For UV/HOCl testing, sodium hypochlorite was dosed at either 1 or 3 mg/L as Cl₂.

Spiked chemicals

Four low molecular weight, highly water miscible TOxCs were chosen for the spiking events: 1,4-dioxane, NDMA, acetone, and formaldehyde. The properties of the spiked compounds are provided in the Supplementary material (Table A2, available online). These compounds, which are commonly detected in wastewater effluents, represent a class of compounds known to be challenging for removal through advanced treatment which offers various treatment mechanisms. 1,4-dioxane, which has a drinking water notification level of 1 µg/L in the State of California, and has been used as a stabilizer for solvents. The presence of 1,4-dioxane in wastewater became problematic for groundwater recharge project in southern California, prompting a need for additional water treatment, namely, UV/H₂O₂ (California

Water Boards 2018). The presence of acetone, as discussed, was associated with elevated RO permeate TOC levels at an advanced full-scale treatment train (Olivieri *et al.* 2016). NDMA is a known carcinogen with a drinking water notification level of 10 ng/L in the State of California. NDMA has been detected in both drinking water wells and wastewater effluents and is a known chloramination by-product (Mitch *et al.* 2003). Formaldehyde is a known oxidation by-product and has a drinking water notification level of 0.1 mg/L in the State of California (Wert *et al.* 2007).

Spiking events

A batch chemical spike solution was prepared using City of San Diego potable water and Sigma-Aldrich or Ricca Company chemicals of grade ACS or higher. The spiking solution was fed to the process flow using a diaphragm pump either before ozone injection for the O₃/BAC-MF/UF-RO-AOP configuration or prior to the RO-AOP train, as shown in Figure 1. It was assumed that removal of the spiked compounds by MF/UF would not occur, since these membranes typically have orders of magnitude higher molecular weight cut-off. Target feed concentrations were chosen to ensure samples were detected throughout the treatment train. A total of four spiking events were conducted. Mix 1 was spiked at a targeted feed concentration of 1 µg/L, 2,700 µg/L, 370 µg/L, 200 µg/L, and

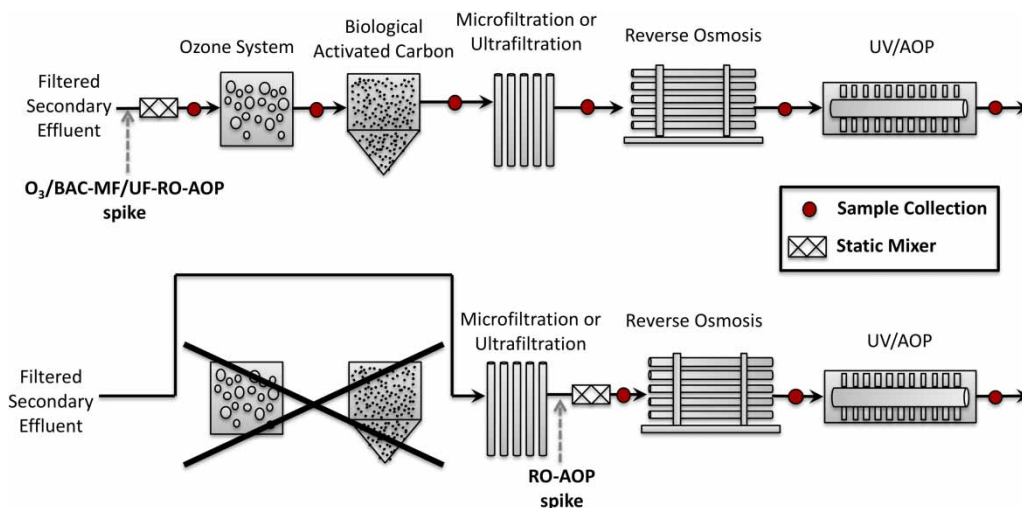


Figure 1 | Treatment train arrangements investigated during spiking events.

860 µg/L of NDMA, acetone, formaldehyde, methanol, and 1,4-dioxane, respectively. Methanol was present in the 10% (v/v) formaldehyde stock at a concentration of 1.59%. Mix 2 was spiked at targeted feed concentration of 330 µg/L and 1,700 µg/L of acetone and 1,4-dioxane, respectively. Acetone was spiked alone at a targeted feed concentration of 1,300 µg/L during the third spike event. Lastly, 1,4-dioxane was spiked alone at a targeted feed concentration of 1,700 µg/L during a fourth spike event. For each event, the spike was injected and the facility was operated for a period equal to three system-wide hydraulic retention times (HRTs) prior to sample collection to ensure steady-state conditions had been reached. The system-wide HRT was approximately 53 minutes at design flow. In addition, the online TOC analyzers located on the ozone influent and RO permeate were used to indicate steady-state concentrations of the spike. Once steady-state conditions were reached, triplicate samples were collected throughout the spike to account for any variations in spike delivery of the diaphragm pump. Samples were collected before and after each treatment process. Cumulative removals were calculated using feed concentrations from each treatment configuration.

On-site measurements

pH and temperature were measured using a Hach Multi-Parameter meter. UV transmittance (UVT) was measured using a Hach DR 4000 benchtop spectrophotometer. Total and free chlorine were measured using the Hach Chlorine Pocket Colorimeter II, while peroxide was measured using the Hach Peroxide Test Kit Model HYP-1.

Analysis of spiked constituents and water quality parameters

Eurofins Eaton Analytical (Monrovia, USA) performed analysis for the spiked constituents as well as general water quality. Analysis of NDMA, 1,4-dioxane, acetone, and formaldehyde was performed using standard methods (EPA 521, EPA 522, EPA 524.2, EPA 556, respectively). Other analyzed water quality parameters, including methods and instrumentation, and method reporting limit are provided in the Supplementary material (Table A3, available online).

OH-radical exposure for ozone treatment

OH-radical exposure ($\cdot\text{OH}$ exposure, M s) (Equation (1)) was calculated based on 1,4-dioxane removal during the ozonation using the 1,4-dioxane OH-radical rate constant (k_{OH}) $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Anbar et al. 1966).

$$\cdot\text{OH} \text{ exposure} = \frac{\ln\left(\frac{[1,4 - \text{dioxane}]_t}{[1,4 - \text{dioxane}]_0}\right)}{-2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}} \quad (1)$$

Estimated scavenging rate OH-radical steady-state concentration for AOP treatment

The estimated scavenging rate ($\sum_i k_{\text{Si}}[\text{Si}]$, s^{-1}) was calculated to compare AOP treatment efficacy for the different challenge tests and treatment arrangements and to compare against baseline conditions (i.e., without spiking). The first order scavenging rate constant (s^{-1}) has been defined by Lee et al. (2016) as a function of the water matrix components (such as dissolved organic carbon (DOC), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), nitrite (NO_2^-), and bromide (Br^-)). This present study has applied a modified approach from Lee et al. (2016) that also accounts for scavenging of spiked compounds of known concentration (Equation (2)). The spiked chemical (C_i) k_{OH} constants used were as follows – formaldehyde: $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Marron et al. 2019), acetone: $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Stefan et al. 1996), NDMA: $4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Lee et al. 2007), and 1,4-dioxane: $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Anbar et al. 1966). A k_{OH} of $2.1 \times 10^4 (\text{mg C/L})^{-1} \text{ s}^{-1}$ was applied for the baseline organic matter ($\text{TOC}_{\text{baseline}}$) measured in the RO permeate. The k_{OH} applied for baseline TOC has been reported elsewhere as the average rate constant for the reaction of OH-radical of varying wastewater matrices (Lee et al. 2013). The k_{OH} for HCO_3^- , CO_3^{2-} , NO_2^- , Br^- are provided elsewhere (Lee et al. 2016).

$$\begin{aligned} \sum_i k_{\text{Si}}[\text{Si}] = & \sum k_{\text{OH},C_i}[C_i] + k_{\text{OH},\text{TOC}_{\text{baseline}}}[\text{TOC}_{\text{baseline}}] \\ & + k_{\text{OH},\text{HCO}_3^-}[\text{HCO}_3^-] + k_{\text{OH},\text{CO}_3^{2-}}[\text{CO}_3^{2-}] \\ & + k_{\text{OH},\text{NO}_2^-}[\text{NO}_2^-] + k_{\text{OH},\text{Br}^-}[\text{Br}^-] \end{aligned} \quad (2)$$

Furthermore, the OH-radical steady-state concentration ($(\cdot\text{OH})_{\text{ss}}$, M) was calculated similarly as in Lee et al. (2016):

ratio of $\cdot\text{OH}$ formation rate from oxidant photolysis (ν_{OH} , M s^{-1}) divided by the estimated scavenging rate (s^{-1}). The ν_{OH} term was calculated based on oxidant molar absorption coefficient (ϵ) and quantum yield (Φ), as well as average photon fluence rate ($E'_{\text{p,ave}}$) as described in Lee *et al.* (2016), where $\epsilon_{\text{H}_2\text{O}_2} = 19 \text{ M}^{-1} \text{ cm}^{-1}$ and $\Phi_{\text{H}_2\text{O}_2} = 1.0 \text{ mol einstein}^{-1}$ (Baxendale & Wilson 1957), $\epsilon_{\text{HOCl}} = 59 \text{ M}^{-1} \text{ cm}^{-1}$ and $\Phi_{\text{HOCl}} = 1.0 \text{ mol einstein}^{-1}$ (Feng *et al.* 2007). UV fluence (H'), UV irradiation time (t), and molar photon energy at 254 nm was used to calculate $E'_{\text{p,ave}}$ as described in Lee *et al.* (2016). H' was calculated based on unpublished work at the facility using collimated beam to experimentally determine NDMA's photolysis coefficient, k_p , of $764 \text{ L} \cdot \text{einstein}^{-1} \cdot \text{cm}^{-1}$ following a previously published method (Hokanson *et al.* 2016).

RESULTS AND DISCUSSION

Water quality and TOC monitoring during challenge testing

Feed water quality from tertiary effluent and other sampling locations is provided in the Supplementary material (Tables A4 and A5), available with the online version of this paper. Online TOC monitoring was employed in order to detect pulses of organic contaminants in the feed water. Online TOC monitoring during the Mix 1 spiking event is provided in Figure 2. TOC monitoring indicated that the spiked chemicals were captured by the TOC analyzers at the monitored locations (i.e., ozone influent, BAC effluent, and RO permeate). An increase from a baseline average of 8.0 mg/L to approximately 8.5 mg/L was observed in the ozone influent. Nonetheless, a typical 40–50% TOC removal across BAC was observed during the spiking event, indicating that effective transformation of bulk organic matter was maintained even under conditions of elevated chemical loading.

In terms of RO permeate TOC, an increase from a baseline average of 33 $\mu\text{g/L}$ and 45 $\mu\text{g/L}$ to approximately 850 $\mu\text{g/L}$ and 1,700 $\mu\text{g/L}$ was observed for the $\text{O}_3/\text{BAC}/\text{MF}/\text{UF}/\text{RO}/\text{AOP}$ and RO/AOP treatment only, respectively. The lower RO permeate TOC was achieved when O_3/BAC pre-treatment was in place.

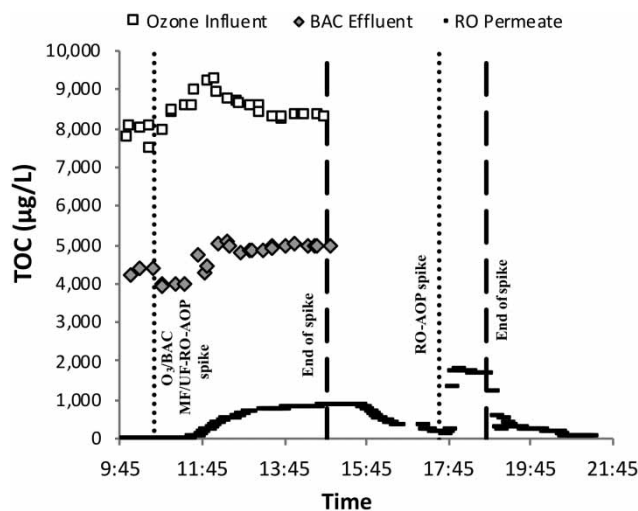


Figure 2 | Online TOC monitoring during challenge test Mix 1.

Effectiveness of RO-AOP treatment during chemical challenge tests

Graphical results for the RO-AOP treatment process configuration during the Mix 1 event are presented in the Supplementary material (Figure A1, available online) as cumulative removal of the spiked chemicals. Near complete NDMA removal was achieved across this treatment process, reaching a 98.5% overall reduction and a product concentration of 5 ng/L which is below the California notification level of 10 ng/L. The NDMA notification level was established in 1998 by California's DDW as a health-based advisory level since this chemical lacked a maximum contaminant level (MCL) (DDW 2018). DDW can impose certain requirements and recommendations when the NDMA is found at a concentration greater than the notification level. The $\text{UV}/\text{H}_2\text{O}_2$ process (at 3 mg/L H_2O_2) provided 98% NDMA attenuation, most likely due to its susceptibility to direct UV-photolysis, as discussed elsewhere (Sharpless & Linden 2003). $\text{UV}/\text{H}_2\text{O}_2$ provided NDMA destruction beyond the design criterion of 1.2-log (94% removal) suggesting effective photolysis even during this challenge condition. RO alone provided an additional NDMA removal of 22%.

RO alone provided 69% and 9% removal for 1,4-dioxane and formaldehyde, respectively. Attenuation for 1,4-dioxane was expected to occur across the $\text{UV}/\text{H}_2\text{O}_2$ treatment

process based on its relatively high k_{OH} . However, during this event, the UV/H₂O₂ process achieved 45% 1,4-dioxane reduction and negligible formaldehyde reduction. During this round of testing, the AOP system (UV with 3 mg/L H₂O₂) was short of the 0.5-log (68%) removal requirement for 1,4-dioxane. OH-radical scavenging from unintentional reactions of spiked methanol and/or from acetone intermediates were suspected to affect the removal of 1,4-dioxane (challenge test OH-radical scavenging rate: $6.11 \times 10^5 \text{ s}^{-1}$; baseline OH-radical scavenging rate: $5.96 \times 10^5 \text{ s}^{-1}$, Supplementary material, Table A6, available online). The UV/H₂O₂ process influent acetone concentration was 2,367 µg/L; methanol was not measured. Past work at this facility showed that the UV/H₂O₂ process at 3 mg/L H₂O₂ did provide the minimum 0.5-log (68%) reduction of 1,4-dioxane when spiked without the simultaneous presence of organic solvents (Trussell et al. 2015). In addition, the UV reactor shut down during this spiking event which would have influenced 1,4-dioxane removal across the AOP system. Therefore, the results of this test did not properly represent the performance of the AOP system. The shutdown of the UV reactor was exclusive to this demonstration facility. In the case of a full-scale facility, a sudden UV reactor shutdown would trigger alarms and divert the product water as *off-spec*. With respect to formaldehyde, other studies (Guimarães et al. 2012) reported considerable attenuation using an EED greater than 20 kWh/m³ and high oxidant dose (~900 mg/L H₂O₂). The exposure time of the PWDF AOP system is less than a minute at design flow, which is a comparable exposure time of full-scale systems. The removal of acetone by RO was limited to 16% and no removal occurred during the UV/H₂O₂ process, which is consistent with findings from Stefan et al. (1996) who reported significant competition between acetone intermediates and OH-radicals as well as mechanistic acetone recycling.

In summary, the uncharged, low molecular weight, highly water miscible and OH-radical recalcitrant compounds (here tested as formaldehyde and acetone) were not well removed by the advanced treatment trains employing physical separation (i.e., MF/UF, RO), photolysis (i.e., UV/H₂O₂), and OH-radical chemical oxidation (i.e., UV/H₂O₂) as treatment mechanisms. Due to the elevated presence of acetone and formaldehyde in the UV/H₂O₂ influent, it is suspected that

considerable scavenging may have occurred, hindering the attenuation of 1,4-dioxane, which is designed for at least 0.5-log (68%) reduction, yet only 45% reduction was measured. As such, the upfront attenuation of compounds that would otherwise hinder downstream processes is a noteworthy benefit of enhancing treatment robustness of potable reuse treatment trains. AOP performance and OH-radicals scavenging rates are discussed in the section 'Alternative AOP (UV/HOCl) for 1,4-dioxane attenuation'.

Enhancing robustness with O₃/BAC as pre-treatment to UF/MF-RO-AOP

In order to investigate whether treatment robustness against challenge conditions could be enhanced, O₃/BAC served as pre-treatment to MF/UF-RO-AOP. Results reported as cumulative log removal for Mix 1 spiked compounds are presented in Figure 3. The ozone process alone provided 62% of 1,4-dioxane attenuation. This reduction most likely occurred via OH-radical exposure since 1,4-dioxane is recalcitrant to ozone, though susceptible to OH-radicals. The formation of OH-radicals during wastewater ozonation has been shown to proceed via the effluent organic matter

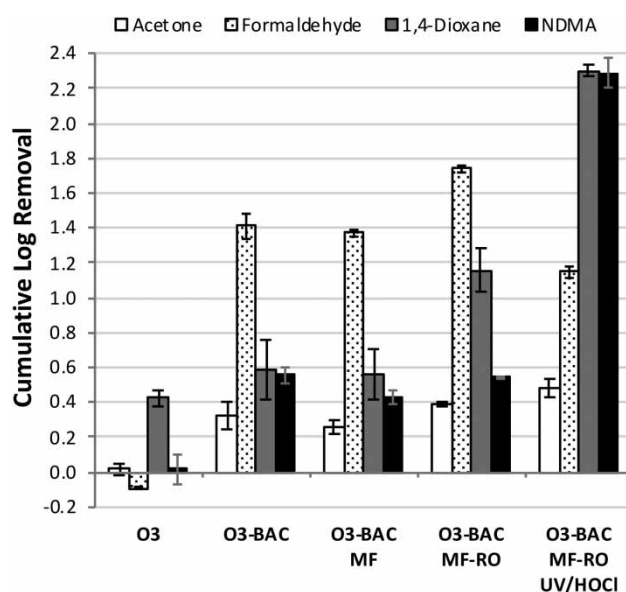


Figure 3 | Cumulative removal of spiked chemicals during Mix 1 spiking event for O₃/BAC-MF/UF-RO-AOP treatment train. 3 mg/L as Cl₂ was used for the UV/HOCl. Tertiary effluent concentrations: acetone 2,667 µg/L; formaldehyde 307 µg/L; 1,4-dioxane 907; NDMA 550 ng/L. Error bars indicate log removal standard deviation measured for the triplicate samples.

pathway due to the presence of electron-rich moieties (Nöthe *et al.* 2009). Indeed, the calculated OH-radical exposure based on 1,4-dioxane removal was 4.0×10^{-10} M s, which agrees with a previous study that evaluated similar O_3 :TOC ratios as were applied at the PWDF (Lee *et al.* 2013). An additional 28% removal of 1,4-dioxane was measured across BAC. Additional removal of 75% 1,4-dioxane occurred during RO treatment, similar to when RO-AOP was employed without pre-treatment by O_3 /BAC. In addition, an alternative AOP employing UV/HOCl was investigated for the O_3 /BAC-MF/UF-RO-AOP configuration resulting in a reduction of 1,4-dioxane of 93%, and surpassed the 0.5-log (68%) criterion (22 CCR § 60320.201).

The large standard deviation of NDMA concentrations after ozonation makes it difficult to confirm whether NDMA formation occurred during this process as reported by others (Gerrity *et al.* 2015). Removal of NDMA during BAC treatment was 71%, likely from biodegradation. Although NDMA has been characterized as biodegradable (Sedlak & Kavanaugh 2006), the responsible organisms and mechanisms are not well understood (Sharp *et al.* 2005), but controlled studies revealed that both oxic and anoxic conditions during biofiltration result in efficient NDMA degradation (Drewes *et al.* 2006). Similar to testing with RO-AOP only, NDMA removal of 24% was observed by the RO membranes. The 98% attenuation across UV/HOCl represents a removal beyond the 1.2 log (94%) AOP design criteria. The product water quality exhibited NDMA concentration of 3 ng/L, which is below the California drinking water notification level of 10 ng/L (DDW 2018).

As for formaldehyde, a formation of 73 µg/L was measured during ozonation. Formaldehyde is a known ozonation by-product resulting from the breakdown of large molecular weight organic compounds into smaller and more hydrophilic organic molecules (Urfer *et al.* 1997; Wert *et al.* 2007). These by-products are typically well biodegradable, as was confirmed by a 97% reduction of formaldehyde across BAC. All other processes, including RO, exhibited negligible removal of formaldehyde. A slight increase in formaldehyde concentration from 5 to 22 µg/L was observed during UV/HOCl treatment, likely due to oxidation reactions of the co-spiked contaminants and any remaining organic matter (Sarathy & Mohseni 2009). The efficient attenuation of formaldehyde across BAC underlines

the importance of biodegradation as an additional treatment barrier to safeguard against compounds that are not adequately removed by RO-AOP treatment.

Acetone, like formaldehyde, is a known biodegradable compound (IPCS 1998). Ozonation had little impact on acetone concentrations in the feed water, whereas BAC provided an acetone reduction of 50%. Acetone removal by the BAC was inferior to formaldehyde and even NDMA. One hypothesis for this could be the preference of the biological populations for other well biodegradable compounds, such as formaldehyde, in the presence of a higher acetone concentration. Reverse osmosis provided 25% acetone reduction during challenge testing, and the AOP process, configured as UV/HOCl, provided 20% acetone removal.

The use of a biologically active barrier (here implemented as BAC) provided significant removal of formaldehyde and acetone. In addition, ozone represents an additional barrier against non-biodegradable chemicals and provided considerable 1,4-dioxane attenuation implying OH-radical formation and direct ozone attack as important attenuation mechanisms. The alternative UV AOP, using 3 mg/L HOCl, surpassed the minimum requirement of 0.5-log (68%) removal of 1,4-dioxane even when other organic compounds were present (challenge test OH-radical scavenging rate: 4.99×10^5 s⁻¹; baseline OH-radical scavenging rate: 4.94×10^5 s⁻¹, Supplementary material, Table A6). Formation of formaldehyde during ozonation followed by a high removal by BAC demonstrates the strong synergy of the combined O_3 /BAC process. In summary, the addition of O_3 /BAC to MF/UF-RO-AOP provided higher overall removal for all the spiked constituents when compared to RO-AOP only; (cumulative removals – acetone: 66% versus 15%, formaldehyde: 93% versus 10%, 1,4-dioxane: 99.5% versus 83%, NDMA: 99.5% versus 98.5%). As such, the O_3 /BAC-MF/UF-RO-AOP treatment configuration can treat higher feed contaminant concentrations before product water limit concentrations are reached. Considering the measured removals from this study, the O_3 /BAC-MF/UF-RO-AOP can treat up to 1.4 mg/L of formaldehyde while meeting the 0.1 mg/L notification level, up to 2,000 ng/L of NDMA while meeting the 10 ng/L notification, up to 2.37 mg/L of acetone while meeting the 0.5 mg/L product water TOC limit, and up to 200 µg/L of 1,4-dioxane while meeting the 1 µg/L notification level. In contrast, the

RO-AOP can treat up to 0.11 mg/L acetone, 667 ng/L NDMA, 0.95 mg/L formaldehyde, and 5.9 µg/L 1,4-dioxane while meeting respective contaminant (or TOC) limits.

Effect of acetone concentration on BAC performance

Further challenge tests were performed to evaluate BAC performance on acetone removal at different acetone feed concentrations. BAC degradation of acetone appeared to be more effective at lower acetone feed concentrations, when 95% removal took place at 383 µg/L feed acetone (Mix 2). Only 50% removal was measured when acetone feed concentration was 2,555 µg/L and spiked with other compounds (Mix 1). When spiked alone, 64% removal was measured with acetone feed concentration of 1,161 µg/L. Previous studies have reported that acetone remained biodegradable in activated sludge treatment as long as the initial concentration of acetone was not above a toxic level identified as 500 mg/L (IPCS 1998). The concentrations tested in this study were far less than the claimed toxic concentration. Although acetone percentage removal decreased as initial concentrations increased, the amount of acetone degraded by BAC was greatest at highest feed acetone concentration tested. At the highest feed concentration tested, the BAC degraded 1,278 µg/L acetone (BAC feed: 2,555 µg/L, BAC effluent: 1,277 µg/L), compared to 366 µg/L degraded at the lowest feed concentration tested (BAC feed: 383 µg/L, BAC effluent: 17 µg/L). This indicates that the BAC process remained effective at attenuating acetone even under conditions of elevated chemical loading.

Alternative AOP (UV/HOCl) for 1,4-dioxane attenuation

While chlorine radicals (Cl^{\cdot}) generated during UV/HOCl treatment do influence degradation of certain compounds (Wang *et al.* 2016), current knowledge is that these radicals do not provide significant removal of 1,4-dioxane due to the relatively low rate constant (Patton *et al.* 2017). The use of UV/HOCl provides a number of benefits over UV/H₂O₂, including secondary residual disinfection, lower chemical cost, and reduced chemical management (Rosenfeldt *et al.* 2013). While UV/HOCl does provide its benefits, considerations in terms of pH must be taken into

account. The dissociation of free chlorine into either HOCl (hypochlorous acid) or OCl⁻ (hypochlorite ion) is pH dependent, where an acidic pH favors formation of HOCl. During these experiments, pH was maintained below 6 (Supplementary material, Table A5) where concentration of HOCl relative to OCl⁻ is expected to be greater than 95% (Feng *et al.* 2007). For AOP applications, HOCl is preferred over OCl⁻, since OCl⁻ is less efficient as an oxidant than HOCl for generation of OH-radicals.

Additional challenge tests evaluated UV/HOCl as an alternative AOP to UV/H₂O₂. For these tests, 1,4-dioxane was spiked alone (Singly) or spiked with acetone (Mix 2). Mix 2 UV/AOP influent acetone concentration was considerably lower than for Mix 1: 14 µg/L and 257 µg/L for the O₃/BAC-MF/UF-RO-AOP and RO-AOP, respectively. The percent removal for 1,4-dioxane in the two evaluated AOP configurations is compared in Figure 4. The alternative AOP (UV/HOCl) provided sufficient 1,4-dioxane oxidation to meet the 0.5-log (68%) oxidation criteria at both high (3 mg/L) and low (1 mg/L) oxidant dose. In general, a noticeable increase in 1,4-dioxane removal was measured when higher oxidant doses were used. The UV/H₂O₂ also provided 1,4-dioxane attenuation beyond 0.5 log (68%) at both high (6 mg/L) and low (3 mg/L) oxidant

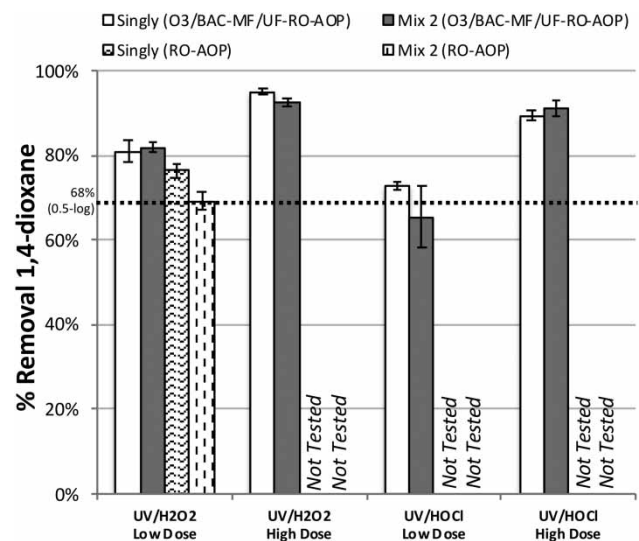


Figure 4 | AOP evaluation on 1,4-dioxane attenuation. Low UV/H₂O₂ dose: 3 mg/L, high UV/H₂O₂ dose: 6 mg/L, low UV/HOCl: 1 mg/L, high UV/HOCl dose: 3 mg/L. Dashed horizontal line represents 0.5-log (68%) 1,4-dioxane removal criterion. Error bars indicate log removal standard deviation measured for the triplicate samples.

doses in follow-up experiments, including when only the RO-AOP (FAT) treatment train was used. Although OH-radical scavenging from higher concentration of the co-contaminants and ambient TOC during Mix 1 RO-AOP was suspected, a correlation between calculated $[\text{OH}]_{\text{ss}}$ and 1,4-dioxane reduction was performed to better understand this single event with lower 1,4-dioxane reduction (Supplementary material, Figure A2, available online). Indeed, from the correlation shown in Figure A2, the Mix 1 RO-AOP result was an outlier as it made the correlation between these two variables no longer significant once included ($\alpha = 0.05$, $N = 13$) as compared to correlation between all other challenge tests performed during this study. As such, an external factor (i.e., sudden shutdown of the UV reactor) can be deduced to have caused lower 1,4-dioxane reduction for this event.

CONCLUSIONS

The objective of this study was to evaluate, through a series of challenge tests, if enhanced treatment would be provided when O_3/BAC was added as pre-treatment to RO-AOP. A series of challenge tests were carried out to quantify unit process and cumulative reduction of low molecular spiked compounds (acetone, formaldehyde, NDMA, and 1,4-dioxane).

- Cumulative removal of the four spiked chemicals was greater when O_3/BAC was added as pre-treatment to RO-AOP. During the spike, O_3/BAC also provided lower TOC levels in the RO permeate compared to RO-AOP only.
- The RO-AOP train provided significant protection against NDMA and 1,4-dioxane, particularly through the UV/ H_2O_2 process. The RO-AOP train provided limited removal of acetone (15%) and formaldehyde (10%).
- BAC adds a treatment barrier based on biodegradation mechanism that was effective at attenuating the spiked compounds not addressed by the RO-AOP treatment train. BAC provided 95% formaldehyde removal during the challenge test. Acetone removal appeared to be concentration dependent. At the highest acetone concentration investigated, a removal of 50% was observed,

while 96% removal was achieved at the lowest acetone concentration. RO-AOP cumulative removal for acetone and formaldehyde was 15% and 10%, respectively.

- 1,4-Dioxane reduction (62%) during ozonation suggested formation of OH-radicals, likely formed in the presence of organic matter, which augmented the attenuation of this compound during ozone treatment.
- The online TOC analyzer captured the spiked chemicals, making it a powerful tool for operators to detect and respond to chemical pulses.
- The alternative AOP (UV/ HOCl) provided comparable 1,4-dioxane attenuation as UV/ H_2O_2 . Additional testing showed that both AOP configurations provided at least 0.5-log (68%) 1,4-dioxane reduction. Higher 1,4-dioxane attenuation was achieved when a higher oxidant dose was used.

Ultimately, the results from this study reinforce the importance of implementing a robust potable reuse treatment train including redundant treatment processes to address the broad variety of chemicals that may be present in wastewater effluents. The addition of O_3/BAC as pre-treatment to RO-AOP provided additional protection against all the spiked contaminants, indicating that robust treatment trains are able to handle greater contaminant loading in events of chemical peaks (such as illicit chemical discharges). As such, the implementation of robust potable reuse treatment trains with redundant treatment processes in addition to enhanced monitoring is highly relevant for potable reuse projects, particularly those that do not utilize an environmental buffer.

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