

# Demonstration-scale evaluation of ozone-biofiltrationgranular activated carbon advanced water treatment for managed aquifer recharge

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[Correction added on 10 January 2024, after first online publication: The copyright line was changed.]

#### Abstract

The Sustainable Water Initiative for Tomorrow (SWIFT) program is the effort of the Hampton Roads Sanitation District to implement indirect potable reuse to recharge the depleted Potomac Aquifer. This initiative is being demonstrated at the 1-MGD SWIFT Research Center with a treatment train including coagulation/flocculation/ sedimentation (floc/sed), ozonation, biofiltration (BAF), granular activated carbon (GAC) adsorption, and UV disinfection, followed by managed aquifer recharge. Bulk total organic carbon (TOC) removal occurred via multiple treatment barriers including, floc/sed (26% removal), ozone/BAF (30% removal), and adsorption by GAC. BAF acclimation was observed during the first months of plant operation which coincided with the establishment of biological nitrification and dissolved metal removal. Bromate formation during ozonation was efficiently controlled below 10 µg/L using preformed monochloramine and preoxidation with free chlorine. N-nitrosodimethylamine (NDMA) was formed at an average concentration of 53 ng/L post-ozonation and was removed >70% by the BAFs after several months of operation. Contaminants of emerging concern were removed by multiple treatment barriers including oxidation, biological degradation, and adsorption. The breakthrough of these contaminants and bulk TOC will likely determine the replacement interval of GAC. The ozone/BAC/GAC treatment process was shown to meet all defined treatment goals for managed aquifer recharge. © 2021 Water Environment Federation

## • Practitioner points

- Floc/sed, biofiltration, and GAC adsorption provide important barriers in carbonbased treatment trains for bulk TOC and trace organic contaminant removal.
- Biofilter acclimation was observed during the first three months of operation in each operating period as evidenced by the establishment of nitrification.
- Bromate was effectively controlled during ozonation of a high bromide water with monochloramine doses of 3–5 mg/L.
- NDMA was formed at an average concentration of 53 ng/L by ozonation and complete removal was achieved by BAFs after several months of biological acclimation.
- An average 25% removal of 1,4-dioxane was achieved via oxidation by hydroxyl radicals during ozonation.

#### Key words

1,4-dioxane; biofiltration; bromate; granular activated carbon; managed aquifer recharge; NDMA; ozone; total organic carbon

# INTRODUCTION

WATER reuse has been implemented in recent years to combat environmental challenges associated with overuse of water resources. Common drivers for these projects include combating water scarcity and augmenting existing ground/surface water resources (US EPA, 2017). While water reuse often relies on membrane-based technologies in conjunction with reverse osmosis (RO), especially at coastal locations with existing ocean disposal, ozone/biofiltration-based treatment has several advantages associated with lower operating cost and elimination of brine waste streams (Gerrity et al., 2014). This provides a major benefit to inland utilities with few options for brine disposal. Additionally, ozone/biofiltration treatment may produce water that is more suitable for groundwater recharge from a geochemical compatibility standpoint (Vaidya et al., 2019). While there have been numerous studies of ozone-biofiltration-based advanced water treatment, there have been few at a large scale. Several full-scale ozone-biofiltration reuse facilities that have been operated in the United States include Gwinnett County, Georgia (Funk et al., 2019), Rio Rancho, New Mexico (City of Rio Rancho, 2017), El Paso, Texas (Sheng, 2005), and Abilene, Texas (Enprotec/Hibbs & Todd Inc.) while many others are still in the pilot testing or planning phase. The primary drawback observed in these treatment schemes is the limited capacity for total organic carbon (TOC) and total dissolved solids removal (Hooper et al., 2020), and the need for reliable and efficient nitrogen removal in the upstream wastewater treatment facility. However, in many cases ozone-biofiltration treatment is able to meet nearly every other treatment goal, as well as efficient trace organic contaminant removal, at a lower cost when compared with other membrane/advanced oxidation-based treatments (Plumlee et al., 2014; Sundaram et al., 2014).

Ozone treatment provides many benefits in water reuse applications including oxidation of organics, dissolved metals, taste and odor-causing compounds, and pathogen inactivation. The treatment goals and operation of the ozone system vary widely depending on the application. For example, utilizing ozone for the purpose of disinfection can often require a higher dose and closer process control than other applications. Efficiently controlling the ozone system is integral to maintaining finished water quality. The primary drawback associated with the implementation of ozone oxidation/disinfection is the formation of disinfection by-products (DBPs). Bromate is a well-known DBP which forms by the ozonation of bromide containing waters. This compound is regulated with a maximum contaminant level (MCL) of 10 µg/L (US EPA, 1998). Bromate forms via multiple reaction pathways including direct reactions with ozone and indirect reactions with the secondary oxidant, hydroxyl radicals (Pinkernell & von Gunten, 2001). While there are many strategies that can be implemented to interrupt or modify these formation pathways, common bromate control methods applied in water and wastewater treatment include pH suppression, ammonia addition, hydrogen peroxide addition, and free chlorine or monochloramine addition (Buffle et al., 2004; Soltermann et al., 2017). These mechanisms for control are less understood in the context of wastewater ozonation

scavenging capacity of wastewater. Pilot testing has shown the benefits of using monochloramine to suppress hydroxyl radical exposure and form intermediate compounds, such as bromamines, thereby limiting bromate formation by the indirect pathway (Buehlmann et al., 2017). This study will highlight the use of monochloramine and peroxidation with free chlorine to control bromate formation at a demonstration-scale ozonebiofiltration plant. Ozone treatment is also a well-established treatment technology for the removal of contaminants of emerging concern (CECs), which includes a suite of pharmaceuticals, pes-

due to the high bromide concentrations and increased radical

cern (CECs), which includes a suite of pharmaceuticals, pesticides, personal care products, and flame retardants. Some of these CECs are highly reactive with molecular ozone while others are more susceptible to oxidation by hydroxyl radicals, which form as a by-product of ozone decomposition (Lee et al., 2013). One of the CECs that is regularly detected in treated wastewater is 1,4-dioxane. This compound was widely used as an industrial solvent stabilizer and is commonly detected in surface water, groundwater, and treated wastewater (Stepien et al., 2014). Graywater produced from laundry wash water has also been identified as a significant source of 1,4-dioxane as this compound is a constituent of many laundry detergents and bleach products (Szczuka et al., 2020; Tanabe & Kawata, 2008). Many states have established drinking water and groundwater limits for 1,4-dioxane, but it is not yet regulated at the federal level. For example, potable water reuse facilities in California must exhibit at least 0.5-log removal of 1,4-dioxane by the selected advanced oxidation process (AOP) (California Department of Public Health, 2014), and there exists a 1 µg/L treatment goal for drinking water treatment facilities (California Water Boards, 2010). Treatment techniques for 1,4-dioxane removal in water reuse applications include AOPs such as UV advanced oxidation or ozone with hydrogen peroxide (US EPA, 2007).

The operation of ozone systems has also been shown to directly impact the performance of the downstream biofiltration (Bourgin et al., 2018). Ozone produces assimilable organic carbon that is biodegraded in the biologically active filters (BAFs). BAFs can also potentially remove dissolved metals and CECs. N-nitrosodimethylamine (NDMA) is a CEC which belongs to a group of compounds called nitrosamines, which is commonly removed biologically through BAFs (Bourgin et al., 2018; Gerrity et al., 2015; Nawrocki & Andrzejewski, 2011; Sundaram et al., 2020; Zeng et al., 2016). NDMA is formed as a disinfection by-product of chloramination and ozonation with common precursors including nitrogen-containing organic compounds such as personal care products, pharmaceuticals, and pesticides (Krasner et al., 2013). The formation of NDMA may also be influenced by several water quality and operating parameters including ammonia concentration, bromide concentration, precursor concentration, pH, and applied ozone dose (Sgroi et al., 2014). One study investigating the relative contribution of NDMA precursors by different water sources suggested that nutrient removal wastewater effluent produced lower levels of NDMA upon ozonation when compared with conventional wastewater effluent (Zeng, Glover et al., 2016; Zeng, Plewa et al., 2016). Marti et al. (2015) also showed that ozone reactive precursors react to form higher NDMA concentrations when ozonated in wastewater when compared with deionized water as a result of catalyzing reactions and hydroxyl radical scavenging. The acclimation of biomass and biological removal of NDMA in the BAFs requires several months of filter operation (Sundaram et al., 2020). This degradation likely occurs as a result of co-metabolism as no organisms have been identified which can use NDMA as a sole carbon source (Fournier et al., 2009). This study will examine the performance of the biofilters during plant startup and the parameters which influence the formation and biodegradation of NDMA.

Granular-activated carbon (GAC) adsorption is commonly implemented in water reuse as another barrier against the removal of CECs and total organic carbon (Sundaram & Pagilla, 2019). As mentioned previously, limited TOC removal is the primary drawback to ozone-BAF treatment processes. However, ozone and biofiltration implemented in combination with GAC provide a multiple barrier approach for bulk and trace organic contaminant removal. The removal of CECs remains a topic of great concern in water reuse applications due to the continual emergence of new contaminants such as perfluoroalkyl substances (PFAS), pharmaceuticals, and personal care products. Some of these compounds can serve as surrogates for treatment performance based on their chemical structure (Schimmoller et al., 2020). Monitoring the operation of the GAC is important to plant operation, as the replacement or regeneration of GAC media may represent a significant operations and maintenance cost at an ozone/BAF/GAC-based advanced water treatment facility.

The Sustainable Water Initiative for Tomorrow (SWIFT) is the effort of the Hampton Roads Sanitation District (HRSD) to provide sustainable water resources in the southeast Virginia region by implementing managed aquifer recharge through advanced water treatment. Pilot testing was conducted to compare the performance of membrane-based and ozone/BAF/ GAC-based treatment technologies for this purpose. The results of this testing proved that the ozone/BAF/GAC treatment train was able to meet all defined treatment goals and produced water which was more compatible with the native groundwater when compared with membrane-based treatment (Vaidya et al., 2019). Therefore, the ozone/BAF/GAC treatment train was selected for further pilot testing. This treatment train includes coagulation-flocculation-sedimentation (floc/sed), ozone oxidation and disinfection, BAF, GAC adsorption, and ultraviolet (UV) disinfection (Figure 1). The pilot was operated from July 2016 to May 2018 to collect long-term monitoring data and to support the full-scale application of this treatment process (Vaidva et al., 2019). The next phase of the initiative included the construction and operation of the SWIFT Research Center (SRC) in Suffolk, Virginia which includes the 1-MGD demonstration advanced treatment train, recharge well, and monitoring wells. The monitoring data gathered during the startup and operation of this facility can be used to better understand the ozone/BAF/GAC-based treatment process as it is applied in large scale applications with the purpose of water supply augmentation and groundwater recharge. Operational challenges identified during startup include optimizing the operation of the ozone system while controlling disinfection by-product formation and maximizing trace organic contaminant removal, monitoring BAF acclimation and CEC biodegradation during plant startup, and optimizing GAC performance. The purpose of this study is to demonstrate the effectiveness of an ozone-BAF-GAC-based advanced water treatment plant with respect to bulk organics removal, disinfection by-product mitigation, nitrosamine removal, and trace organic contaminant oxidation and adsorption.

# Methods

The SRC has been in operation and recharging the Potomac Aquifer since May 2018. This paper will present data from two distinct operating periods from May 2018 to December 2018 and April 2019 to May 2020 denoted as operating period one and two, respectively. This represents two periods of plant



Figure 1. SRC process flow diagram.

startup that occurred due to warranty repairs that were made at the SRC from December 2018 to April 2019. During this period of time, the media in the BAFs was replaced with virgin activated carbon media and the media in the GAC vessels was also replaced.

The SRC treats secondary wastewater effluent (N < 4 mg/L, P < 0.3 mg/L) from the Nansemond Wastewater Treatment Plant (NTP), owned and operated by HRSD. NTP is a fivestage Bardenpho treatment process with typical effluent characteristics outlined in Table 1. The quality of the final treated water (referred to herein as SWIFT Water) at the SRC was highly dependent on the upstream wastewater plant operation. During times of stable operation, the SRC operated according to parameters outlined in Table 2. The SRC process flow diagram can be seen in Figure 1. The SRC was permitted to meet all primary drinking water maximum contaminant levels (MCLs) and total nitrogen (TN) and total organic carbon (TOC) limits. The finished water TOC treatment goals include a daily maximum of 6 mg/L and a monthly average of 4 mg/L. This limit is consistent with the equivalent chemical oxygen demand (COD) limit of 10 mg/L that is followed by other potable reuse facilities in Virginia, including Loudoun Water and Upper Occoquan Service Authority (US EPA, 2017). The TN treatment goals include a daily maximum of 8 mg/L and a monthly average of 5 mg/L. SWIFT Water also meets the "12/10/10" disinfection rule set forth in the California Department of Public Health's guidelines for indirect potable reuse (IPR) via groundwater recharge (12-log enteric virus removal, and 10-log removal of both giardia and cryptosporidium). The complete summary of how disinfection credits are achieved at the SRC can be found in Table S1.

The coagulant, aluminum chlorohydrate (ACH), was fed with a cationic polymer to rapid mix ahead of floc/sed. There was also an optional sodium hypochlorite addition point ahead of floc/sed to pre-oxidize organics at times of elevated ozone demand. Prechlorination was only used on several occasions for short periods of time and it was controlled manually. The floc/sed process is operated with two inclined plate trains in parallel (equipment provided by Meurer Research Inc., Golden, CO). Preformed monochloramine was fed to the settled water at a dose of 3-5 mg/L Cl<sub>2</sub> to control DBP formation during ozonation. This dose was determined during pilot testing and preliminary testing at the SRC. Preformed monochloramine was formed inline by the injection of ammonia followed by the

Table 1.	Average NTP SCE of	characteristics
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	MIN	MAX	AVERAGE	ST DEV
TKN (mg-N/L)	1.24	5.11	1.83	0.53
$NO_{3}^{-}$ (mg-N/L)	0.20	3.34	1.50	0.58
$NO_2^-$ (mg-N/L)	0.01	0.16	0.03	0.03
TOC (mg/L)	8.01	16.6	10.7	1.55
Total Mn (µg/L)	11.6	454	34.0	50.0
Bromide (mg/L)	0.11	1.49	0.41	0.21
1,4-dioxane (µg/L)	0.39	1.39	0.62	0.13
NDMA (ng/L)	3.33	72.9	15.1	14.3
NMOR (ng/L)	<2	283	50.7	70.6

injection of chlorine. Softened water was used for carrier water in this system.

The ozone system, supplied by Xylem-Wedeco (Herford, Germany), was a side stream system in which approximately 50% of the flow was ozonated and subsequently combined with the bulk flow in a custom built 316 stainless steel pipeline contactor with a residence time of approximately 8 min. This residence time was sufficient for complete ozone decay during normal operating conditions. The ozone generators had a capacity of 92 kg/day at 12% weight ozone gas concentration. The ozone residual concentration was monitored at different locations in the ozone contactor using an Orbisphere C1100 dissolved ozone probe (Hach, Loveland, CO), and the applied ozone dose was adjusted automatically to achieve at least 3-log virus removal and 1.5-log giardia removal as calculated through single-point CT measurement and automated ozone dose control using Table C-13 from the EPA Guidance Manual for Disinfection Profiling and Benchmarking (recreated in SI as Table S2).

After ozonation, monochloramine was quenched with sodium bisulfite to prevent any detrimental impact to the biofilters. The flow was split evenly to the four BAFs (Xylem-Wedeco, Herford, Germany) in parallel with a design empty bed contact time of 9.4 min with one filter out of service (12 min with all filters in service). The activated carbon media in the BAFs was Calgon Filtrasorb816 (Pittsburgh, PA). Phosphorus was identified as a limiting nutrient in the BAFs, and therefore, during the second operating period, phosphoric acid was added prior to the filters. Backwashing was performed periodically based on head loss or turbidity breakthrough. Due to the high dissolved oxygen concentration in the ozone effluent, there was gas binding observed in the filters which resulted in artificially high head loss after short periods of operation. For this reason, a resting period protocol was established in which flow was stopped to the filter for approximately 10 min to allow for gas bubble release.

The next step in the treatment process was GAC adsorption in which the flow was split between two GAC contactors (WesTech, Salt Lake City, UT). The operation of the GAC adsorbers was flexible, allowing for parallel or series operation with variable flow split possible for each vessel. The GAC carbon media was Calgon Filtrasorb400M (Pittsburgh, PA). Finally, the water was processed through the UV disinfection system (Xylem-Wedeco) which was designed and validated to provide 4 logs of virus inactivation at a dose of 186 mJ/cm<sup>2</sup>. After this, sodium hydroxide was added to adjust the pH to match that of the native groundwater, and either preformed monochloramine or free chlorine was added to prevent biofouling to the wellhead.

## **Analytical methods**

Sampling was performed daily during times of aquifer recharge for constituents including bromide, bromate, and nitrogen species. Bromate was analyzed according to EPA method 300.1 with a Dionex 5000 plus with IC columns AS19 and AS24. Bromide was analyzed by EPA method 300 using a Dionex Integrion HPIC and column AS27. Samples were collected weekly for nitrosamines

PARAMETER	VALUE			
ACH dose (as product)	25 mg/L			
Cationic floc-aid polymer dose	0.75 mg/L			
NH <sub>2</sub> Cl dose	3–5 mg/L Cl <sub>2</sub>			
Ozone dose control	Residual control to achieve >3-log virus removal and >1.5-			
	log giardia removal by CT per Disinfection Profiling and			
	Benchmarking Guidance Manual			
Average O3:TOC	$0.8\pm0.2^1$			
Average applied ozone dose	$5.4 \pm 1 \text{ mg/L}^1$			
BAF EBCT	12 min			
GAC EBCT	15-30 min			
Design UV dose	$4-\log virus = 186 \text{ mJ/cm}^2$			

Table 2. Operating parameters

<sup>1</sup>Average and standard deviation for startup 2.



**Figure 2**. (a) TOC data represented by box and whisker plots—box represents interquartile range with the middle line denoting the mean, whiskers represent minimum and maximum if they are within the bounds of  $\pm 1.5 \times 10^{10}$ , any value greater than this is shown as an outlier with an open symbol. (b) Percent removal of TOC during Startup 2.

(NDMA, NMOR) and 1,4-dioxane. These compounds were analyzed according to EPA method 521 and 522, respectively, using an Agilent 7010B GC/MS Triple Quadrupole (Santa Clara, CA). Total organic carbon (TOC) was analyzed three times per week according to Standard Method 5310 using a Shimadzu TOC 4200. Total manganese and iron were analyzed weekly according to EPA method 200.7. Haloacetic acids (HAAs) and trihalomethanes (THMs) were analyzed monthly according to EPA methods 552.2 and 524.2, respectively. All of the aforementioned analyses were performed by HRSD's Central Environmental Laboratory. A suite of 96 CECs was analyzed quarterly by Eurofins Eaton Analytical (Monrovia, CA) by liquid chromatography with tandem mass spectrometry (LC-MS-MS). In addition to these, there is a list of unregulated chemicals including those which are considered public health or treatment efficacy indicator compounds, which are listed on the Contaminant Candidate Lists (CCLs) and the Unregulated Contaminant Monitoring Rule (UCMR) that were also monitored quarterly. A complete list of the compounds which were monitored, the respective analytical methods and rationale for monitoring can be found in Table S3.

#### **Results and discussion**

#### Total organic carbon

TOC was measured across the SRC process train to quantify performance of floc/sed, BAF, and GAC. This multiple barrier approach ensures efficient TOC removal at several stages in the process. Influent TOC fluctuations may be attributed to changes in treatment performance at NTP or varying inputs of refractory organic material from industrial, commercial, or domestic sources into the raw wastewater influent. Box plots showing the average range of TOC data throughout the SWIFT process are presented in Figure 2a.

The percent TOC removal achieved by each treatment process is summarized for the second operating period in Figure 2b. The apparent increase in TOC removal by GAC when temperature decreased was due to the operation of the GAC vessels changing. Floc/sed was consistently responsible for approximately 20%–30% TOC removal. After this, ozone oxidation produced organic carbon which may be amenable to biodegradation and subsequently removed through



Figure 3. BAF effluent nitrogen and manganese during acclimation (Startup 2).

biofiltration. At the beginning of plant operation, however, the elevated TOC removal provided by the BAF was most likely due to adsorption by virgin GAC media. After several months of operation, TOC removal can be attributed to the biological degradation of assimilable organic carbon. TOC removal by BAF levelled off at approximately 30% and this was only slightly decreased during winter months. This removal is consistent with removal reported for biofilters with exhausted media in previous studies (Sundaram & Pagilla, 2019). It was found during the second startup that phosphorus was likely a limiting nutrient in the BAFs based on the low concentrations in ozone effluent, and therefore, phosphoric acid was fed to the BAF influent beginning on day 190 of operation.

GAC adsorption was the final treatment barrier which provides TOC removal. The primary mechanism of TOC removal through GAC is adsorption while some biological growth and removal may also be occurring. GAC effluent TOC is important to monitor to understand when the adsorption capacity of the carbon media is exhausted and when GAC reactivation will be required to remain in compliance with the TOC and trace organic contaminant treatment objectives. During the first operating period, the two GAC vessels were operated in parallel for the entire duration of plant operation. After GAC media was replaced in GAC vessel 1, it was operated alone at the beginning of the second operating period. As TOC breakthrough was observed approaching the 4 mg/L treatment objective, GAC vessel 2 was put into service as well. The GAC vessels have since been operated in parallel with variable flow splits in order to achieve a target TOC of 4 mg/L. The flow split variations are shown in Figure S1a. GAC breakthrough curves for both periods of operation are shown in Figure S1b. As the removal is observed through GAC plateaus, it can be assumed that the adsorption capacity has been exhausted and biological removal is occurring. Theoretically, TOC removal by adsorption should only depend on the number of BV processed and should be independent of empty bed contact time (EBCT) (beyond the mass transfer zone). However, during the second startup, TOC removal by GAC 1 can be seen to have a dependence on EBCT exhibited by the disjointed breakthrough curve observed in Figure S1b as a result of changing flow. This suggests the likely development of biological activity in the GAC well prior to exhaustion of adsorption capacity. Both continuing to monitor the performance of GAC and optimizing TOC removal upstream is critical in successfully operating this ozone-BAF-GAC treatment train in order to meet SWIFT Water treatment goals.

#### Ammonia oxidation

Nitrogen compounds (NO2, NO3, NH3, TKN) have been monitored throughout the treatment process during both startup periods. There was no mechanism for significant nitrogen removal in the process, but the transformation of nitrogen reveals important information about the biological acclimation of the biofilters. With the addition of monochloramine prior to ozone, there was an added ammonia residual (0.5-1 mg/L-N) which reaches the biofilters. As the filters start to accumulate biomass, they begin to nitrify ammonia. Nitrification occurs in two steps, first ammonia is oxidized to nitrite and then nitrite is oxidized to nitrate. This transition is seen clearly by the increase in nitrite which occurred one month after startup, followed by the shift to full nitrification approximately two months after this (Figure 3). This was observed on the pilot scale as well, and the occurrence of nitrification was used as an indicator for biological activity (Vaidya et al., 2020). Other studies have also noted the usefulness of biofiltration after ozonation due to the capacity for BAFs to oxidize ammonia (Wert et al., 2007).



Figure 4. NTP SCE bromide and ozone effluent bromate. NH<sub>2</sub>Cl dose was increased from 3 to 5 mg/L when bromide spiked on day 134.

# **Dissolved metals removal**

Metals concentrations are also monitored throughout the process in order to quantify removal and to adhere to secondary MCLs. Both iron and manganese are regulated with secondary MCLs of 0.3 and 0.05 mg/L, respectively. Each of these compounds is related to esthetic concerns including color and taste of the treated water. Manganese is also potentially related to health concerns, and for this reason, it is regulated with a maximum acceptable concentration (MAC) of 0.12 mg/L in Canada (Health Canada, 2019). Oxidized metals removal is also important at the SRC to prevent fouling of downstream equipment and clogging of the recharge well. The majority of iron removal occurs physiochemically during flocculation/sedimentation (~70% removal observed) and biofiltration serves as a biological treatment barrier in this process. Most iron measurements throughout the treatment process were below the method reporting limit during the second operating period (Figures S2). It is hypothesized that the residual iron remaining in SWIFT water is complexed with organics and therefore cannot be removed via oxidation and filtration. This is a challenge often associated with the treatment of drinking water with high levels of iron and organics (Munter et al., 2005). Reckhow et al. (1991) also demonstrated the detrimental impact of organics concentration on the oxidation of iron by ozone. Excursions in the influent iron concentration can be attributed to periods of time where NTP was feeding ferric sulfate to promote chemical phosphorus precipitation upstream.

Removal of manganese is primarily achieved through chemical and biological oxidation and precipitation/adsorption in the ozone-BAF treatment step. The biological removal requires a period of acclimation which was consistent with the establishment of nitrification in the biofilters. The complete removal of manganese was observed just after the time where complete nitrification was established (Figure 3). This is consistent with expectations and observations of other studies which showed biological removal of manganese after complete oxidation of ammonia due to the necessary change in oxidation-reduction potential (ORP) (Hasan et al., 2012). The simultaneous biological oxidation of ammonium, manganese, and iron has been shown to be influenced by several parameters including the respective concentration of each constituent, dissolved oxygen, ORP, and pH (Cheng et al., 2017; Tekerlekopoulou et al., 2013). The factors which influence dissolved metal removal and re-dissolution in the biofilters are still under investigation at the SRC.

## Bromate formation and control

Bromide concentrations measured daily in the NTP effluent during the second operating period are presented in Figure 4. The bromide concentration in the NTP effluent ranged widely from 0.15 to 1.49 mg/L (average =  $0.50 \pm 0.19$  mg/L). The cause of this broad variation is the variable flow rate of landfill leachate that is discharged to NTP which introduces the primary source of bromide. During the second operating period, it was also found that there was a strong tidal influence on bromide concentration as a result of seawater inflow and infiltration. At times when all other bromide loads were constant, there was found to be a direct correlation ( $R^2 = 0.63$ ) between conductivity and bromide due to this tidal influence (Figure S3b). Therefore, online conductivity measurements became an important surrogate parameter that was used to monitor bromide real time.

Due to this elevated background bromide concentration, there was a need to consistently monitor and control bromate formation at the SRC. The resulting bromate concentration depends on several operating parameters including applied ozone dose, influent bromide concentration, and monochloramine dose. Applied monochloramine dose, NTP SCE bromide, ozone effluent bromate data are summarized for the second operating period in Figure 4. During the second startup period, testing was performed to understand a manageable level of landfill leachate, and resulting bromide load, which can be accepted at NTP. This testing showed that a bromide concentration of 0.3-0.5 mg/L was sustainable for plant operations and bromate was able to be controlled below the MCL while using preformed monochloramine to limit formation. Bromate formation was measured for a range of applied ozone doses and chloramine doses during this startup period while the bromide was increasing. Figure 5 shows that bromate could be controlled below the MCL at a leachate flow that resulted in bromide = 0.37 mg/L and applied ozone dose of 6 mg/L (0.74 O3:TOC) with a chloramine dose of 3 mg/L-Cl<sub>2</sub>.

During times of relatively stable bromide concentration, it was found that bromate formation depended mostly on the applied ozone dose. This relationship between ozone dose and bromate formation motivated testing to reduce ozone demand by preoxidizing the NTP SCE with free chlorine. Testing at the SRC has shown that preoxidation ahead of floc/sed is effective in reducing the ozone demand and thereby suppressing bromate formation. In one instance, sodium hypochlorite was fed at a dose of 4 mg/L-Cl<sub>2</sub> which decreased the ozone demand, and thus, the applied ozone dose required to achieve the same CT, by approximately 2 mg/L. The applied chlorine dose did not exceed the 1.5-h chlorine demand of the NTP SCE. As a result, bromate formation decreased by about 90%. Similar results have been observed in several studies, which demonstrated the benefits of feeding free chlorine to control bromate formation (Buffle et al., 2004; Wert et al., 2007). The major

drawback associated with using chlorine to control bromate is the potential formation of disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs). This concern is elevated when chlorinating treated wastewater effluent due to the higher bromide and organics/precursor concentrations (Krasner et al., 2009). During testing at the SRC, THMs and HAAs were formed with the addition of free chlorine to the SCE, and however, the concentrations were below the respective MCLs. Additionally, these compounds were effectively removed in the BAFs (Figure 6). Previous studies have shown that HAAs are somewhat amenable to biological removal in BAFs, but the same has not typically been observed for THMs (Arnold et al., 2018; Zeng, Glover, et al., 2016; Zeng, Plewa, et al., 2016). The mechanism by which THMs were removed by BAFs was not determined as a part of this study.

Bromate removal by GAC. During each startup period, bromate removal was observed on virgin GAC media. This may be attributed to the capacity of the surface of the virgin GAC media to catalytically reduce bromate to bromide (Asami et al., 1999; Siddiqui et al., 1999). The reduction of bromate by GAC provided a temporary barrier against bromate MCL exceedances and allowed flexibility in ozone operation during each startup period. This bromate reduction capacity was completely exhausted  $(C/C_0 = 1)$  after approximately 8000 GAC bed volumes in each startup period (Figure 7). This shows that GAC only provides short-term bromate removal and other control methods should be employed when needed. In previous studies, the bromate removal rate of virgin GAC decreased after three months of operation when the media became biologically active (Asami et al., 1999). Low (<0.5) C/C<sub>0</sub> values observed at higher bed volumes can most likely be attributed to the



Figure 5. Bromate formation while bromide = 0.37 mg/L.



**Figure 6.** DBP formation and removal during prechlorination (4 mg/L Cl<sub>2</sub>) and bromide spiking (spiked + 0.3 mg/L bromide) in NTP SCE, floc/sed effluent, ozone effluent, and BAF effluent. Values below the detection limit are shown at half of the detection limit value, and those bars are hatched. NDMA data was collected while adding 0.4 mg/L bromide and 4 mg/L Cl<sub>2</sub>.



Figure 7. Bromate removal by GAC (Startup 1). GAC bed volumes are represented as flow weighted values according to the GAC flow split at the time of sampling.

extended residence time between ozone effluent and GAC effluent sample points which may result in an apparent decrease in bromate where there was none.

**Optimizing ozone addition.** During the period of time when warranty repairs were being made at the SRC, one notable design modification that was made was the relocation of the ozone injection point. Originally, the sidestream residence time was approximately 30 s, during which significant bromate formation and ozone decay occurred. The bromate formation in the sidestream was likely due to both the elevated ozone to bromide and ozone to TOC ratios that are achieved in the sidestream. Studies have shown that bromate formation in the

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sidestream can be problematic if the residence time exceeds the design guidelines of 3 s (Wert et al., 2016). Testing during SRC startup showed that roughly half of the total bromate formation occurred in the extended sidestream piping (data not shown). Minimizing this sidestream residence time is particularly important when using ozone to achieve disinfection credit because ozone contact time in the sidestream before degassing is not included for CT credit (US EPA, 2010). For this reason, design guidelines also recommend minimizing this time as much as possible to reduce uncredited disinfection. After the injector was moved at the SRC, the residence time in the sidestream was reduced to ~1.2 s. This resulted in an approximately 24% lower average O3:TOC dose to meet the

same disinfection treatment goals. As a result, bromate control was also feasible during the second startup period with 160% higher average bromide concentration when compared with the first operating period (startup 1 average bromide =  $0.19 \pm 0.04$ , startup 2 bromide =  $0.50 \pm 0.19$ ).

## Nitrosamines

NDMA. The NTP SCE NDMA concentration varied from 3 to 73 ng/L (average =  $15.4 \pm 14.6$  ng/L). This variation may have been due to variable influent sources of NDMA or this might reflect changes in NTP operation. Several studies have shown the impact of WWTP operation on NDMA formation/ removal upstream of advanced water treatment plant (Krasner et al., 2009). The impact of NTP SCE bromide concentration on NDMA formation was investigated at the SRC due to the potential for bromide to enhance NDMA formation in the presence of specific precursors (von Gunten et al., 2010). No significant difference in NDMA formation was observed as a function of bromide concentration (correlation not shown). One study by Marti et al. (2016) showed the potential for chlorine to pre-oxidize ozone reactive NDMA precursors, but no significant difference in NDMA formation was observed during preoxidation at the SRC (Figure 6). This demonstrates the dependence of NDMA formation on ozone exposure rather than applied ozone dose, which was variable in this case to achieve the same CT disinfection credit. Additionally, preoxidation had no impact on short-term biological NDMA removal downstream. During normal operating conditions, NDMA was measured at an average concentration of  $53 \pm 21$  ng/L after ozonation. These data are summarized in Figure 8 for both the first and second operating periods. Although chloramine was fed prior to ozonation, testing has shown that chloramine does not contribute to or inhibit NDMA formation at the typical operating ozone doses (Figure S4). This was likely due to the short residence time and potentially the concurrent oxidation of chloramine reactive precursors by ozone which has been noted by several studies (Chen et al., 2018; Lee et al., 2007). The limited impact of monochloramine addition and resulting hydroxyl radical quenching, on NDMA formation also supports the claims of Pisarenko et al. (2015) that hydroxyl radicals do not contribute to NDMA formation. Additionally, preformed monochloramine was used at the SRC instead of in situ monochloramine addition in order to avoid dichloramine formation, which has been shown to form higher concentrations of NDMA (McCurry et al., 2017). At lower ozone doses, the addition of chloramine appears to contribute to marginally higher NDMA formation (Figure S4). It was also observed that there was no increased NDMA formation by ozone beyond the ozone dose where there was a measurable ozone residual. This was likely due to the maximum NDMA formation potential being reached for most precursors at this point (Marti et al., 2015).

NDMA was primarily removed in the process via cometabolic biological degradation in the BAFs and by UV photolysis at high doses. The establishment of sustained NDMA biodegradation in the BAFs may require several months of acclimation (Sundaram et al., 2020). The removal observed by BAFs immediately following the first startup can most likely be attributed to short-term adsorption of NDMA on virgin GAC media. After this, the occurrence of NDMA removal was concurrent with the development of nitrification and removal of dissolved Mn in the biofilters during both startup periods suggesting there was biological removal occurring at this time. Greater than 70% NDMA removal was achieved in one to three months for both operating periods. During the first startup operating period, there were several occurrences of decreased biological removal of NDMA (less than 50%) which may be attributed to shortterm shutdowns of the filters prior to sampling (indicated by X symbols in Figure 8). The length of biofilter shutdown ranged from 18 to 72 h. There was no observed decrease in TOC or



**Figure 8.** NDMA throughout the duration of plant operation. X symbols represent instances of poor NDMA removal attributed to BAF shutdown events during operating period 1. Vertical line represents the beginning of operating period 2 where BAF media was replaced.

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dissolved metal removal after these events. Two months after the second BAF startup, approximately 80% biological NDMA removal was achieved. Several weeks after this, the removal of NDMA through the biofilters decreased to <10%. It was identified that sodium bisulfite was being fed in excess of the concentration which is required to quench residual monochloramine after ozonation. The toxic effect of bisulfite was clearly exhibited by the poor NDMA removal, and however, there was no other indication of reduced biological activity at this time. Neither the TOC removal nor the oxidation of ammonia and dissolved metals was affected by the overfeeding of NaHSO4. The opposite result was observed on the pilot scale, where nitrification was inhibited by overdosing sodium bisulfite but NDMA removal was not impacted (Vaidya, 2020). After the NaHSO<sub>4</sub> dose was decreased at the SRC (beginning on day 298 on Figure 8), biological removal of NDMA began to recover almost immediately and >70% removal was established again after approximately three months of operation. Therefore, it can be determined that consistently maintaining the appropriate dose of sodium bisulfite for complete dechlorination is crucial in order to ensure biological activity is sustained.

During times when there was detectable NDMA after the BAFs, the additional removal observed was due to direct photolysis by UV irradiation. The actual UV dose during startup was in excess of the required value with new lamps, minimal sleeve fouling, and high UVT as a result of efficient TOC removal by virgin GAC. The maximum NDMA removal observed by UV was 90% at an average UV dose of 495 mJ/ cm<sup>2</sup> and GAC effluent UVT equal to 94.4%. Considering the high UV dose required for NDMA photolysis, this was only considered a temporary NDMA removal mechanism. The primary concern with respect to NDMA removal during startup of this treatment process was that biological removal must be

established in the BAFs prior to the point when the UV system was unable to deliver the relatively high dose required for efficient NDMA photolysis (based on GAC removal of TOC).

NMOR. N-nitrosomorpholine (NMOR) is another nitrosamine frequently detected in water reuse applications. Although no regulatory standard exists for NMOR in the United States, drinking water reuse guidelines have been established in Germany and Australia of 10 and 1 ng/L, respectively (NHMRC, 2008; Planas et al., 2008). NTP SCE NMOR concentrations observed during the second startup operating period varied widely (Figure S5). After approximately two months of operation, the influent concentration increased to approximately 300 ng/L. Following the time when this maximum concentration was observed, the influent NMOR concentration began to decrease over a period of a few weeks. Generally, this compound is not considered a disinfection byproduct like NDMA, but instead exists in wastewater effluent from anthropogenic sources (Glover et al., 2019; Krauss et al., 2009). The most common treatment technology for removal of NMOR is RO or photolysis by UV (Glover et al., 2019). There was marginal removal observed through ozonation and adsorption in GAC, and however, the majority of NMOR removal at the SRC was achieved by photolysis during UV treatment. At the time that the concentration began decreasing, desorption of NMOR from the BAF and GAC was observed due to the change in concentration gradient. Up to 41% NMOR removal was observed by ozone at an O3:TOC ratio of 0.93 in the absence of monochloramine. This is well aligned with the maximum removal noted in literature of 36% at O3:DOC of 1.16 (Hollender et al., 2009). GAC breakthrough of NMOR was observed after approximately 7000 GAC bed volumes. Additionally, greater than 2-log removal was observed through

Table 3. SWIFT water DBPs, CECs, and performance indicators

	SAMPLING	NUMBER OF					
	EVENTS (N)	DETECTIONS	MDL	MIN	MAX	AVERAGE	ST DEV
HAA5 (µg/L)	22	14	$0.2^{1}$	0.64	13.4	4.41	3.65
TTHM (µg/L)	22	4	4	4.4	10.7	7.62	2.34
Chlorate (mg/L)	10	9	0.01	0.04	1.37	0.74	0.34
Perchlorate (µg/L)	9	4	0.5	0.52	0.84	0.70	0.12
Acetaldehyde (µg/L)	8	7	5	2	5.9	3.37	1.28
Formaldehyde (µg/L)	10	7	5	18	41	32.3	8.29
Quinoline (ng/L)	9	3	5	8.1	11	10	1.37
Sucralose (ng/L)	9	4	5	270	12,000	6012	5501
Iohexol (ng/L)	9	4	10	22	160	70.3	53.9
Primidone (ng/L)	9	2	5	9.7	11	10.4	-
Cotinine (ng/L)	9	1	10	26	26	_	-
Caffeine (ng/L)	9	1	5	22	22	_	-
Acetaminophen (ng/L)	9	1	5	9.6	9.6	_	-
Ketorolac (ng/L)	9	1	5	2.3	2.3	_	-
Diltiazem	9	1	5	7.2	7.2	_	_
4-nonylphenol (ng/L)	9	1	100	1400	1400	_	-
PFOA (ng/L)	10	2	2	5.3	5.7	5.5	-

<sup>1</sup>The MDL is variable for each of the five HAAs.

UV photolysis at a dose of 280 mJ/cm<sup>2</sup> which exceeds removals reported elsewhere (Glover et al., 2019; Shah et al., 2013). The source of NMOR was not determined as a part of this study.

### Other disinfection by-products

In an effort to prevent biofouling in the SWIFT Water piping to the wellhead, the final disinfectant was changed from monochloramine to free chlorine after several low-level total coliform detections on SWIFT Water. As a result of this, chlorinated DBPs (HAAs and TTHMs) were formed at concentrations below their respective MCLs while they were not detected during periods of monochloramination (Table 3). Another noted benefit of ozone-biofiltration treatment is the reduction in DBP formation potential which allows for flexibility in final disinfectant selection and protects against MCL exceedances (Selbes et al., 2017; de Vera et al., 2016). Furthermore, pilot scale testing at HRSD has demonstrated the efficacy of soil aquifer treatment to abate these contaminants below detection limits (Pradhan, 2018).

Chlorate was also regularly detected in the finished water at concentrations ranging from 0.04 to 1.37 mg/L. Measurable concentrations of chlorate are indicative of sodium hypochlorite aging and the concentration formed often depends on parameters such as storage time, pH, concentration, ionic strength, and temperature (Stanford et al., 2011). Perchlorate also forms as a degradation product of aged hypochlorite solutions at concentrations typically lower than chlorate. Perchlorate has been measured in the finished water at an average concentration of  $0.7 \pm 0.12 \,\mu$ g/L. Neither of these compounds is regulated in the United States at the national level, and however, chlorate has a drinking water notification level of 800 µg/L in California and perchlorate has an established EPA health advisory and California MCL of 15 and 6 µg/L, respectively. In an effort to reduce the concentration formed of each of these compounds, efforts have been made to reduce the storage time of hypochlorite on site at the SRC. Additionally, air conditioning was installed in the hypochlorite storage rooms at NTP (maximum temperature = 22°C) during the second operating period to prevent degradation that results due to high temperatures. The installation of air conditioning at NTP will provide an opportunity to assess the impact of temperature on chlorate and perchlorate concentrations in the finished water.

Both acetaldehyde and formaldehyde are also consistently detected on the finished water at average concentrations of 3.37 and  $32.3 \mu g/L$ , respectively. While there are no MCLs for either of these compounds, there is a drinking water notification limit of 100  $\mu g/L$  for formaldehyde in California. These compounds are well-known by-products that form as a result of ozone reacting with natural organic matter (Schechter & Singer, 2008). Typically, aldehydes are well removed via biofiltration (Sundaram et al., 2014; Weinberg et al., 1993), and however, these compounds have been frequently detected in SWIFT Water at concentrations higher than those measured in the NTP SCE. Therefore, it was assumed that these compounds are either not being well removed biologically after ozonation, or they are being formed by another mechanism later in the treatment process. Aldehydes can also form during final chlorination as

a result of reaction of free chlorine or monochloramine with amino acids (Froese et al., 1999).

#### Contaminants of emerging concern

In addition to the aforementioned contaminants, a suite of unregulated compounds was monitored due to their wellknown occurrence in wastewater. These compounds are monitored with the purpose of both protecting public health and monitoring treatment efficacy (Crook et al., 2013). A summarized list of these compounds and rationale for monitoring can be seen in Table S4, and a complete list of these compounds can be found in Table S3. The majority of these compounds have not been detected in the SWIFT Water for the duration of plant operation, compounds which have been detected are summarized in Table 3. In general, previous studies have found that ozone is effective in mitigating a large number of these compounds at O3:TOC of 0.25-1 (Gerrity et al., 2014). However, compounds which are more ozoneresistant require a higher applied O3:TOC or a different treatment technology to be mitigated. In order to make general conclusions about the removal a large group of structurally diverse compounds by ozone, Lee et al. (2013) summarized trace organic contaminants into groups based on their reaction rate constant with both molecular ozone and hydroxyl radicals.

Compounds with high reactivity with ozone and OH\*. Compounds which are known to have high or moderate reaction rates with ozone have not been frequently detected in the SWIFT Water. Those which have been measured above the detection limit on one occasion (caffeine, acetaminophen, etc.) were likely detected as a result of sample contamination. Sulfamethoxazole has been proposed to be used as an indicator of oxidation efficacy due to its wide use as an antibiotic and common detection in wastewater effluent samples (Schimmoller et al., 2020). This compound is highly susceptible to ozone oxidation with removal of >99% reported when an ozone residual is achieved (Huber et al., 2005; Wert et al., 2009). Sulfamethoxazole has been detected in the NTP SCE during every sampling event, and it has never been detected in SWIFT Water. This is aligned with expectations as the SRC operates with an average O3:TOC of 0.8 to achieve an ozone residual for CT credit, and therefore, complete oxidation was likely achieved. Other compounds which also exhibit a relatively high reaction rate with ozone and are regularly detected in the NTP SCE, but never in SWIFT Water include diclofenac, gemfibrozil, naproxen, triclosan, and carbamazepine.

Compounds with moderate to high reactivity with OH\*. Compounds which have a low reaction rate with molecular ozone and a moderate reaction rate with hydroxyl radicals are removed partially during ozonation and potentially during later treatment steps as well. An exemplary compound in this category is 1,4-dioxane. The concentration of 1,4-dioxane measured throughout the duration of the second operating period is presented in Figure S6. The influent concentration of 1,4-dioxane averages  $0.62 \pm 0.13 \mu g/L$ . During the second

effluent. Other treatment options for 1,4-dioxane that have been considered for future implementation include biological treatment via cometabolic degradation in the BAFs and UV-AOP.

Iohexol also belongs to the group of compounds which reacts primarily with hydroxyl radicals during ozonation  $(k_{\text{OH}^*} = 5.73 \times 108 \text{ M}^{-1} \text{ s}^{-1}$ , Hu et al., 2019), and however, biological removal and adsorption have also been reported. This compound is an x-ray contrasting agent which can be used as an indicator of treatment efficacy due to its frequent detection in wastewater effluent. Given that there have been no operational changes made with regard to the ozone or biofilter operations, the detection of iohexol can be used as an indicator of GAC breakthrough of compounds with similar chemical structure. Partial breakthrough of iohexol was observed during the second operating period after approximately 6000 bed volumes treated by GAC unit 1. Sucralose is an artificial sweetener which is so ubiquitous in wastewater effluents, it has been proposed to be used as an indicator of wastewater loading to other water sources (Oppenheimer et al., 2011). Considering that sucralose is relatively resistant to oxidative and biological treatment, it serves as an indicator for GAC adsorption capacity of water soluble low molecular weight non-polar compounds in this treatment scheme (Schimmoller et al., 2020). During the second operating period, sucralose began to breakthrough after 6000-bed volumes treated by GAC unit 1. Monitoring for primidone and cotinine was conducted to understand removal of representative low molecular weight partially charged cyclic compounds which are frequently detected in treated wastewater. Primidone is removed to some extent by hydroxyl radical oxidation ( $k_{OH^*} = 6.7 \times 109 \text{ M}^{-1} \text{ s}^{-1}$ Lee et al., 2013) and GAC adsorption. Partial breakthrough was observed after 25,000 and 3000 GAC bed volumes for unit 1 and 2, respectively. The single detection of cotinine was



Figure 9. 1,4-dioxane and NMOR oxidation by ozone. Open symbols represent samples taken without NH<sub>2</sub>Cl.

startup, an average of 25% removal of 1,4-dioxane was observed

across the SWIFT process, and this was primarily attributed to

oxidation by hydroxyl radicals during ozonation,  $k_{OH} = 2.5-$ 

 $3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (von Sonntag & von Gunten, 2012). The

production of hydroxyl radicals during wastewater ozonation

occurs as a result of rapid reactions of ozone with organic

matter that produce OH\* as ozone decomposes (Nöthe et al., 2009). It should be noted that 1,4-dioxane is not particularly

susceptible to oxidation by molecular ozone,  $k_{O3} = 0.32 \text{ M}^{-1} \text{ s}^{-1}$ 

<sup>1</sup> (von Sonntag & von Gunten, 2012). Therefore, the addition of

monochloramine to control bromate formation by suppressing hydroxyl radical exposure results in decreased removal of

1,4-dioxane. This can be seen in Figure 9 where the open

symbols represent samples taken without NH<sub>2</sub>Cl, and closed

symbols represent samples taken with NH<sub>2</sub>Cl addition. The

maximum 1,4-dioxane removal observed without NH2Cl

was 54% at an O3:TOC of 0.9 and this decreased to 37% with

NH<sub>2</sub>Cl addition. This was clear evidence of NH<sub>2</sub>Cl quenching

hydroxyl radicals during ozonation. A similar effect was

observed with respect to NMOR removal by ozone, due to the

high reactivity of NMOR with hydroxyl radicals,  $k = 1.75 \times 10^9$ 

(Mezyk et al., 2007). NMOR removal decreased from 41%

to 17% with the addition of monochloramine at O3:TOC of

0.9. These compounds can be used as treatment indicators to

understand hydroxyl radical exposure and expected removal

for compounds with similar reactivity. Further testing with

alternative bromate control methods such as ozone-hydrogen

peroxide is needed to optimize bromate control and to

minimize the impact on CEC oxidation. There was also a

short-term adsorption of 1,4-dioxane observed in the GAC

during both startup periods (data not shown). This adsorption capacity was quickly exhausted after approximately 1500 GAC

bed volumes and short-term desorption was observed after

assumed to be a result of sample contamination as it is a common metabolite of tobacco.

# Conclusions

The objective of this study was to evaluate the performance of a demonstration-scale ozone-biofiltration-GAC advanced water reuse treatment plant. This evaluation highlighted the operational challenges encountered during startup related to bulk TOC removal, ammonia oxidation, dissolved metals removal, controlling bromate formation, nitrosamine formation and removal, and CEC removal.

- Floc/sed, biofiltration, and GAC adsorption provide important barriers in carbon-based treatment trains for TOC removal. Greater than 20% TOC removal was achieved by BAFs consistently even during cold weather conditions.
- Biofilter acclimation was observed during the first three months of operation in each startup period. Acclimation and biological activity were clearly demonstrated by the onset of nitrification and manganese removal.
- Bromate was effectively controlled by managing the influent bromide load and optimizing chemical control measures of monochloramination and prechlorination (up to 81% and 90% reduction in bromate formed, respectively). Prechlorination resulted in some halogenated DBP formation (HAAs/THMs), and however, these compounds were well removed by the BAFs.
- Virgin GAC media provided a short-term barrier for bromate removal during plant startup. This capacity was completely exhausted after 8000 BV during both operating periods.
- Nitrosamines, NDMA and NMOR, were both detected in the NTP SCE. NDMA was formed at an average concentration of 53 ng/L by ozonation. NDMA was effectively biodegraded in the BAFs with >70% removal achieved after approximately one to three months of operation during each startup period. Multiple parameters that influence NDMA formation and removal were identified.
- Aldehyde formation was observed although the mechanism for formation and removal was not identified. Halogenated disinfection by-product formation was observed in the finished water when free chlorination was used to prevent biofouling to the wellhead. Chlorate and perchlorate were also detected frequently in the finished water indicating that efforts should be made to reduce hypochlorite age and temperature.
- The maximum 1,4-dioxane removal observed was 54% at an O3:TOC of 0.9 which was attributed to oxidation by hydroxyl radicals formed during ozonation. This removal was decreased to 37% with the addition of monochloramine for bromate control due to the hydroxyl radical scavenging capacity of monochloramine.
- The multiple barrier approach of ozone oxidation, biofiltration, GAC adsorption, and UV photolysis provided sufficient removal of trace contaminants and indicator compounds. The breakthrough of these compounds and bulk TOC will likely determine the regeneration frequency of GAC.

This study provides important insights about the operation and optimization of ozone/biofiltration/GAC-based advanced water treatment plants for managed aquifer recharge. Demonstrating the efficacy of this treatment process at a larger scale will further support the use of non-RO based treatment for water reuse applications in the future. The shift to non-RO based advanced water treatment is of great research interest as municipalities seek more cost-effective options for water reuse. The data presented herein suggest that ozone/biofiltration/GAC-based treatment can meet all defined treatment goals set forth for managed aquifer recharge. The lessons learned in the first years of operation of the SRC have also helped inform the design of future fullscale SWIFT facilities to be constructed at HRSD wastewater treatment plants.

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# Author contributions

Samantha Hogard: Data curation (lead); methodology (lead); writing-original draft (lead). Germano Salazar-Benites: Writing-review & editing (equal). Robert Pearce: Writingreview & editing (equal). Tyler Nading: Data curation (supporting); writing-review & editing (equal). Larry Schimmoller: Writing-review & editing (supporting). Chris Wilson: Writing-review & editing (supporting). Jamie Heisig-Mitchell: Writing-review & editing (supporting). Charles Bott: Project administration (equal); supervision (equal); writing-review & editing (equal).

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