Controlling disinfection byproducts from treated wastewater using adsorption with granular activated carbon: Impact of pre-ozonation and pre-chlorination

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This study measured chlorine- and chloramine-reactive precursors using formation potential (FP) tests of nine U.S. Environmental Protection Agency (EPA) regulated and 57 unregulated disinfection byproducts (DBPs) in tertiary-filtered wastewater before and after pilot-scale granular activated carbon (GAC) adsorption. Using breakthrough of precursor concentration and of concentration associated calculated cytotoxicity and genotoxicity (by correlating known lethal concentrations reported elsewhere), the performance of three parallel GAC treatment trains were compared against tertiary-filtered wastewater: ozone/GAC, chlorine/GAC, and GAC alone. Results show GAC alone was the primary process, versus ozone or chlorine alone, to remove the largest fraction of total chlorine- and chloramine-reactive DBP precursors and calculated cytotoxicity and genotoxicity potencies. GAC with pre-ozonation removed the most chlorine- and chloramine-reactive DBP precursors followed by GAC with pre-chlorination and lastly GAC without pre-treatment. GAC with pre-ozonation produced an effluent with cytotoxicity and genotoxicity of DBPs from FP that generally matched that of GAC without pre-oxidation; meanwhile removal of toxicity was greater by GAC with pre-chlorination. The cytotoxicity and genotoxicity of DBPs from FP tests did not scale with DBP concentration; for example, more than 90% of the calculated cytotoxicity resulted from 20% of the DBPs, principally from haloacetaldehydes, haloacetamides, and haloacetonitriles. The calculated cytotoxicity and genotoxicity from DBPs associated with FP-chloramination were at times higher than with FP-chlorination though the concentration of DBPs was five times higher with FP-chlorination. The removal of DBP precursors using GAC based treatment was at least as effective as removal of DOC (except for halonitromethanes for GAC without pre-oxidation and with pre-chlorination), indicating DOC can be used as an indicator for DBP precursor adsorption efficacy. However, the DOC was not a good surrogate for total cytotoxicity and genotoxicity breakthrough behavior, therefore, unregulated DBPs could have negative health implications that are disconnected from general water quality parameters, such as DOC, and regulated classes of DBPs. Instead, cytotoxicity and genotoxicity correlate with the concentration of specific classes of unregulated DBPs.

1. Introduction

Disinfection with chemical oxidants has been used to combat
waterborne diseases since the late 19th century (Crittenden et al., 2012). However, the uses of chemical oxidants, such as chlorine, has led to an unintended health hazard through the formation of disinfection byproducts (DBPs) (Richardson, 2011; Richardson et al., 2007). While the U.S. Environmental Protection Agency (EPA) currently regulates 11 DBPs (four trihalomethanes [THMs], five haloacetic acids [HAAs], bromate, and chloride) (USEPA, 2019), research has shown that there are over 600 DBPs that have the potential to cause adverse health effects in humans (Richardson, 2011).

Chemical disinfectants react with background organic matter and halides (i.e., bromide and iodide) that are ubiquitously present in natural and waste waters to form halogenated DBPs (Richardson and Postigo, 2015). Nitrogen-containing organic matter, such as proteinaceous material associated with wastewater effluent, and nitrogen-containing disinfectants like chloramine can serve as precursors for nonhalogenated DBPs (Schreiber and Mitch, 2006; Shah and Mitch, 2012a). Controlling DBP formation may be one of the design and operation constraints for adoption of potable reuse treatment technologies (USEPA, 2012; Arnold et al., 2018), so a deeper understanding of their behavior through treatment is critical.

Adsorption with granular activated carbon (GAC) has been extensively studied in drinking water treatment applications for the removal of organic substances including organic matter (Roberts and Summers, 1982), regulated DBP precursors (Glaze and Wallace, 1984; Rodriguez-Fuentes et al., 2005; Singer, 1999) and micropollutants (Corwin and Summers, 2012). However, limited research has been conducted to evaluate the effectiveness of GAC for the removal of regulated and especially unregulated DBP precursors in treated wastewaters under potable reuse conditions. Recent studies regarding the treatment of regulated and emerging DBP precursors using GAC have focused on drinking water applications (Cuthbertson et al., 2019, 2020).

Most potable reuse pertaining research on controlling unregulated DBPs with GAC has focused on nitrosamines (e.g., N-nitrosodimethylamine [NDMA]) and their precursors (Gerrity et al., 2015; Sgroi et al., 2018; Zeng et al., 2016). Some wastewater-derived NDMA precursors are removed better than bulk organic matter, including dissolved organic carbon (DOC) and ultraviolet-absorbing organics (Hanigan et al., 2012; Mulhern et al., 2017). Additionally, NDMA precursor removal by GAC adsorption resembles that of micropolluent adsorption (Mulhern et al., 2017). A set of pharmaceuticals has been discovered that generates NDMA and their precursors (Gerrity et al., 2012; Shah and Mitch, 2012a). Controlling DBP formation may be one of the design and operation constraints for adoption of potable reuse treatment technologies (USEPA, 2012; Arnold et al., 2018), so a deeper understanding of their behavior through treatment is critical.

An approach for controlling DBP concentration in the plant effluent is the use of upstream oxidation to form DBPs and oxidize DBP precursors followed by GAC adsorption of the preformed DBPs and remaining DBP precursors. Ozone followed by GAC can more efficiently remove regulated DBP precursors than GAC alone (Liu et al., 2017). Jiang et al. (2017) demonstrated that total organic halogen, THMs, and HAAs concentrations and developmental toxicity were lower in effluents when chlorination preceded GAC as opposed to after GAC for drinking water. They also observed lower aromatic halogenated DBPs when pre-chlorination was used. However, another study showed that THMs and HAAs chlorination precursors broke through GAC faster than DOC (Babi et al., 2007). Pre-chlorination has recently been shown to enhance the efficacy of GAC for controlling THMs (Fischer et al., 2019). However, the impact of pre-oxidation on GAC performance for controlling DBPs, both regulated and nonregulated has not been evaluated for potable reuse in which the bromide and nitrogen rich organic matter levels are much higher.

Besides adsorption, biological activity on GAC can achieve microbial-mediated degradation for efficient and consistent DBP precursor removal (Liu et al., 2017). A few studies at pilot-scale have focused on biofiltration that employed biologically activated carbon (BAC) along with pre-ozonation for drinking water (Liu et al., 2017), without pre-ozonation for drinking water (Yu et al., 2017) and pre-ozonation for treated wastewater (Chuang and Mitch, 2017) for attenuating regulated and unregulated DBPs and their precursors. These studies did not evaluate adsorption breakthrough behavior given that monitoring for constituents began after GAC was spent and acclimated to biological growth.

The objective of this study was to systematically evaluate the GAC breakthrough of an extensive list of DBP precursors and their calculated toxicities during parallel pre-oxidation (no pre-oxidation, pre-ozonation, and pre-chlorination) GAC under a practical potable reuse scenario. This study is the first to measure chlorine- and chloramine-reactive DBP precursors of nine EPA regulated and 57 unregulated DBPs in tertiary-filtered wastewater before and after treatment with pilot-scale adsorption with GAC. The impact of pre-chlorinating and side-by-side comparison with pre-ozonation prior to GAC adsorption has not been evaluated before using treated wastewater. Ambient bromate, NDMA, THM4, and HAA5 were also measured and monitored throughout the treatment train to assess pre-oxidation implications on DBP formation. The study utilizes calculated cytotoxicity and genotoxicity quantities from methods reported elsewhere to identify and provide comparisons of the pre-oxidation GAC treatment options (Allard et al., 2015; Chuang and Mitch, 2017; Krasner et al., 2016; Lau et al., 2020; Plewa et al., 2017; Smith et al., 2010). Specifically, the toxic potentials of DBPs formed during formation potential experiments were calculated by normalizing measured concentrations to published cytotoxicity and genotoxicity lethal concentrations of individual DBPs (Wagner and Plewa, 2017).

2. Materials and methods

2.1. Pilot treatment

The pilot plant influent was tertiary-filtered municipal wastewater from a wastewater treatment plant located in Las Vegas, Nevada. At full-scale, the municipal wastewater is treated with primary treatment (bar screen, ferric chloride coagulant, grit removal, anionic polymer, primary clarification), secondary treatment (Johannesburg process for biological nitrogen and phosphorus removal) and biologically active dual-media (anthracite and sand) filtration. Water quality parameters of the pilot plant influent are listed in Table S1.
The pilot-plant utilized three identical GAC columns (Module F300; IntuiTech, Inc.; Salt Lake City, UT, USA) in parallel. One column adsorbed received raw tertiary-filtered wastewater from a full-scale wastewater plant (GACraw), another received ozonated raw water (GACO3), and a third received chlorinated raw water (GACCl2). During ozonation (with an SGC-21 ozone generator; Pacific Ozone; Benicia, CA, USA), the ozone dose was consistent at 3.9 ± 0.6 mg/L (n = 14; 0.78 ± 0.11 mg-O3/mg-DOC). A representative ozone contact curve is shown in Fig. S1A, which has a calculated ozone exposure of 0.8 mg-min/L. Pilot chlorination operated with a chlorine (Pure Bright bleach, 6.60% sodium hypochlorite; KIK Custom Products, Ontario, Canada) dose of 1 mg-Cl2/L during the first 2000 BVs and 3 mg-Cl2/L thereafter with a 15 min contact time. The chlorinated stream was dechlorinated on the GAC. Specifically, dechlorination by GACCl2 occurred as follows: chlorine residual decreased from 0.5 to 0.2 mg-Cl2/L in the first 15 cm of column and from 0.2 to <0.02 mg-Cl2/L (detection limit) after an additional 40.6 cm of column. Chlorine exposure of 11 mg-min/L was determined by calculating the area under the curve of a chlorine decay time series (Fig. S1B) when the dose was 3 mg-Cl2/L. All three columns operated at a 4 L/min flow rate, corresponding to a loading rate of 12 m/h, and were packed with 2 m of lignite GAC (Hydrocarbofloc, Alcoa; Cabot Corporation, Boston MA, USA) to operate at an empty bed contact time (EBCT) of 10 min. Hydrocarbofloc 3000 GAC has a manufacturer-reported particle size of <10% outside of 8–30 mesh, iodine # of 650 mg/g, and molasses # of 450. Additionally, the GAC has been previously characterized for specific surface area (676 m²/g) and pore volume (0.711 cm³/g) (Hanigan et al., 2012).

The pilot-plant operated continuously from June 2016 to December 2016 (7-month period). Maintenance shutdowns occurred at least weekly, or as needed, for backwashing of the GAC columns. Backwashing was done concurrently on all columns to prevent excessive head loss (i.e., 0.6 bar of pressure) and used raw water at a flow rate of 11 L/min (37 m³/h loading rate) for a total duration of 15 min.

The six sampling locations included pilot-plant influent, pre-ozonated, pre-chlorinated, GACraw effluent, GACO3 effluent, and GACCl2 effluent. Throughput was calculated by dividing the volume of treated water by the volume occupied by the GAC. Because columns did not have matching throughputs as a function of operating time due to irregular maintenance shutdowns, each of the three sets of samples that were taken on the same day corresponded to different throughputs.

An additional column operated in parallel and was filled with biological activated carbon (BAC, 10-year old exhausted GAC with an attached active biofilm) to serve as a control for biological performance. The BAC column received raw water for the first half of the 7-month period and pre-ozonated water for the second half to serve as a control for both GACraw and GACO3. This control column operated at an EBCT of 10 min, but at a slightly reduced flowrate of 2.65 L/min.

2.2. Sample collection and processing

Samples for ambient DBPs, bulk parameters, and DBP precursors were collected every 2 weeks at the beginning of the project and gradually limited to once every month. Bromate was analyzed in the raw water and before and after GACO3 only. Bromate was not expected to form during chlorination and was not measured (Fang et al., 2014). Also, selected bulk parameters that are known indicators of DBP precursors, DOC (Reckhow et al., 1990), ultraviolet absorbance at 254 nm wavelength (UV254 (White et al., 2003)), and specific ultraviolet absorbance (SUVA; UV254 divided by DOC in AU-L/mg-m) (Hua et al., 2015), were monitored or calculated concurrently with DBPs and DBP precursors to scrutinize GAC adsorption performance and approximate chemical oxidant demands.

THM and HAA precursors were quantified with formation potential (FP) chlorination experiments. FP chlorination (FP-CL) experiments were conducted as described in Standard Methods (SM 5710). Briefly, pH controlled (at pH 7 using phosphate buffer) water samples were reacted with enough free chlorine to result in a 3–5 mg-Cl2/L residual after 7 days of reaction. NDMA precursors were measured using FP chloramination (FP-CLM) experimental conditions (Mitch and Sedlak, 2004). Briefly, FP-CLM experiments were done by reacting pH controlled (at pH 7 using phosphate buffer) water samples with 140 mg-Cl2/L of freshly prepared monochloramine for 10 days. NDMA and THM samples were quenched with 25 mg/L of thiosulfate and HAA samples were quenched with 100 mg/L ammonium chloride.

Uniform formation conditions (UFCs) were used to simulate conventional chlorination or chloramination distribution conditions. NDMA UFC chloramination experiments were conducted according to previous studies by Shah and Mitch, 2012b) and Zeng and Mitch (2015), and THM and HAA UFC chlorination experiments were conducted according to Summers et al. (1996). Briefly, to determine UFC chloramination, pH controlled (at pH 8 with borate buffer) water samples were reacted with enough chloramine to result in a residual of 1.0 mg-Cl2/L after 3 days of reaction. Similarly, for UFC chlorination, pH controlled (at pH 8 using borate buffer) water samples were reacted with enough chlorine to give a residual of 1.0 ± 0.4 mg-Cl2/L after 24 h. As reported above, quenching was DBP specific. Ambient DBPs, those that were performed during pilot treatment and were present in the samples before UFC tests, were quantified but not subtracted from the FP and UFC results. Ambient concentrations however, were <0.1% of the FP.

Three sample events spaced evenly throughout the project were analyzed for precursors of seven classes of unregulated DBPs: haloacetaldehydes (HALs), halocacetamides (HAMS), haloacetonitriles (HANs), haloketones (HKs), halonitromethanes (HNMs), iodo-haloacetic acids (I-HAAs), and iodo-trihalomethanes (I-THMs). FP assay results were conducted using both chlorination and chloramination conditions as stated above. Two sets of acidified (pH to 3.5–4 with H2SO4) samples were generated for each FP experiment—one quenched with ascorbic acid and the other with ammonium chloride at a molar stoichiometric ratio of 1:1:3 for chlorination experiments and one with ascorbic acid and another without a quencher for chloramination experiments. Samples from the FP assay were chilled and shipped in coolers overnight from the Southern Nevada Water Authority: Applied Research & Development Center (Henderson, Nevada) to the University of South Carolina (Columbia, South Carolina) for unregulated DBP analyses.

2.3. Analytical methods

Analytical methods for basic water quality parameters are listed in Table S2. Bromate was analyzed per EPA Method 302.0. Regulated THM4 and HAA5 were analyzed per EPA Methods 551.1 and 552.3, respectively. HAA9 were not quantified and thus the following HAs were not included in this study: monobromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, and chlorodibromoacetic acid. A total of nine HAAs was extracted as reported in Holady et al. (2012). Experiments were analyzed using an Agilent 7890 gas chromatograph coupled to a 7010 triple quadrupole mass spectrometer equipped with a PAL3 autosampler (Agilent Technologies, Santa Clara, CA, USA), A 2 µL injection volume was used for all sample analyses set at 200 °C in splitless mode. Separation was performed using an
Agilent DB-624 column (30 m × 250 μm × 1.4 μm) with a constant helium flow rate set at 1.2 mL/min. Initial oven temp was set at 35 °C and held for 2 min, then ramped to 150 °C at 10 °C/min and held for 5 min, and then ramped to 250 °C at 25 °C/min and held for 4.5 min for a total run time of 27 min. The MS was configured for electron ionization (EI) and multiple reaction monitoring (MRM). All nitrosamines were quantified using isotope dilution. Mass spectrometer instrument parameters are listed in Table S4. A method detection limit (MDL) study (with n = 12 replicates) was performed by spiking 1 L of deionized water close to the expected reporting limit (5.0 ng/L). Using a Student T-test, method report limits (MRL) were set at 3 to 5 times the MDL. MRLs are listed in Table S3. For comparison of all results, MRLs were converted to pM (Table S6).

Unregulated DBPs (listed in Table S5) were analyzed using either of three extraction methods and two derivatization methods. TriHALs, HANS, HKS, and HNMs were extracted using liquid-liquid extraction (LLE) with 2 mL methyl-tert-butyl ether (MTBE) and 30 g sodium sulfate. HAMs, I-HAAs, brominated tri-HNMs (bromodialkylchloronitromethane, dibromochloronitromethane, and tribromonitromethane), and one HAN (tribromochloroacetonitrile) were extracted using three successive LLEs with 5 mL MTBE and 30 g sodium sulfate and concentrated under nitrogen. Both extracts were spiked with an internal standard, 1,2-dibromopropane, and analyzed using gas chromatography (GC)-mass spectrometry (MS) (Agilent 7890 gas chromatograph coupled to a 5977A mass spectrometer; Agilent Technologies, Santa Clara, CA, USA) with a Rtx-1 column (30 m × 0.25 mm × 1.4 μm film thickness; Restek Corporation, Bellefonte, PA, USA) and configured for EI and selected ion monitoring (SIM). For I-HAAs, a portion of extract underwent diazomethane derivatization prior to analysis by GC/EI-MS/MS using a Thermo Quantum GC triple quadrupole mass spectrometer coupled to a TRACE GC Ultra gas chromatograph (Thermo Fisher Scientific, Waltham, MA, USA). Mono- and di-HAL samples were analyzed using a method by Jeong et al. (2015). Briefly, samples underwent O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) derivatization followed by LLE and GC/EI-MS analysis. Additional analytical details are included in the SI.

2.4. Calculation of DBP associated toxicity and bromine substitution factor

The lethal concentrations (LCs) of various types of DBPs including THMs, HAAs, HNMs, HAMS, HANS, HALs, and NDMA in Chinese hamster ovary cells (CHO) (Wagner and Plewa, 2017) were used to calculate cytotoxicity associated with the DBP FP, as reported in various studies (Allard et al., 2015; Chuang and Mitch, 2017; Krasner et al., 2016; Plewa et al., 2017; Smith et al., 2010). The calculation involved dividing the DBP molar concentration by its LC at which 50% of the CHO cells were killed (LC50) in μM. It should be noted that HKS, and tribromoacetonitrile were not included in these calculations, as their CHO cytotoxicities have not yet been reported. Similarly, the genotoxic contributions of various DBPs were calculated similarly, using reported 50% tail DNA values (in %) from CHO single cell gel electrophoresis acute genomic DNA damage assays (Wagner and Plewa, 2017). With the assumption that genotoxicity and cytotoxicity is additive, total toxicity was calculated by adding together the calculated toxicity of individual DBP species. It is noted this toxicity calculation approach might be limited by not considering synergistic effects, differences between human and animal cells, and association with human health risk (McKenna et al., 2019). Though Lam et al. (2020) validated using the sum of cytotoxic potency weighted DBP concentrations as an estimate of the CHO cell cytotoxicity associated with known DBPs in real disinfected waters, including potable reuse waters. This approach is useful to identify DBPs for additional toxicity testing and potential trade-offs in treatment.

The bromine substitution factor (BSF) was calculated as reported in Hua and Reckhow (2012) where the scale for BSFs ranged from 0 (fully chlorinated) to 1 (fully brominated) for all DBP classes so

### Table 1

| Type | DBP Class | Raw (nM) | % removal | 50% breakthrough (BV) |
|------|-----------|---------|-----------|-----------------------|
| FP-CL | HALs      | 725 ± 43 (3) | -31 ± 18 (3) | -1 ± 20 (3) | 9200 >21,000 4500 |
|      | HAMs      | 38 ± 32 (3)  | 15 ± 27 (3)  | 3 ± 80 (3)  | 3200 4000 4500 |
|      | HANS      | 113 ± 20 (3) | 25 ± 12 (3)  | 14 ± 28 (3) | 4200 9000 4900 |
|      | HKs       | 48 ± 7 (3)   | -36 ± 29 (3) | 9 ± 12 (3)  | 6000 6300 4800 |
|      | HNMs      | 33 ± 1 (3)   | -610 ± 204 (3) | 3 ± 58 (3) | <450 <21,000 <360 |
|      | I-HAAs     | 0.3 ± 0.2 (2) | NAa | NAa | NAa |
|      | I-THMs     | 22 ± 30 (2)  | NAa | NAa | NAa |
|      | THM4       | 2000 ± 100 (9) [257 ± 20 μg/L] | 12 ± 5 (9) | -1 ± 9 (9) | 2500 3000 3000 |
|      | HAAs       | 1800 ± 100 (9) [258 ± 41 μg/L] | 16 ± 7 (9) | 0 ± 6 (9)  | 8500 5600 >18,000 |
|      | NDMA       | NAa | NAa | NAa |
|      | Total FP-CL | 4700 ± 410 (3) | 5 ± 3 (3) | 3 ± 10 (3) | 6000 17,000 5000 |
|      | FP-CLM     | 141 ± 35 (3) | -90 ± 86 (3) | -55 ± 19 (3) | 5000 <21,000 9500 |
|      | HAMs       | 173 ± 15 (3) | 14 ± 14 (3)  | -13 ± 56 (3) | 6000 4600 >18,000 |
|      | HANS       | 140 ± 40 (3) | 53 ± 15 (3)  | -36 ± 17 (3) | 5200 7100 >18,000 |
|      | HKs        | 100 ± 100 (3) | -44 ± 24 (3) | -36 ± 12 (3) | 8900 <21,000 >14,000 |
|      | HNMs       | 44 ± 19 (3)  | -175 ± 68 (3) | 21 ± 38 (3) | <450 8000 <5000 |
|      | I-HAAs     | 0.7 ± 0.3 (2) | NAa | NAa | NAa |
|      | I-THMs     | 3.2 ± 2.5 (2) | NAa | NAa | NAa |
|      | THM4       | NAa | NAa | NAa |
|      | HAMs       | NAa | NAa | NAa |
|      | HANS       | NAa | NAa | NAa |
|      | HKs        | NAa | NAa | NAa |
|      | HNMs       | NAa | NAa | NAa |
|      | NDMA       | 8.1 ± 1.1 (10) [597 ± 78 ng/L] | 88 ± 2 (9) | 56 ± 11 (9) | >21,000 1700 15,000 |
|      | Total FP-CLM| 610 ± 130 (3) | -23 ± 15 (3) | -30 ± 4 (3) | 5500 <21,000 14,000 |
| Bulk | DOC        | 4.9 ± 0.25 (23) mg/L | 0 ± 4 (23) | -2 ± 4 (23) | 2000 2800 2200 |
|      | UNA/SA     | 0.108 ± 0.004 AU | 49 ± 1 (6) | 13 ± 1 (6)  | 4500 3000 4200 |

a Data was limited (n < 2 detections) and could not be determined.

b Not monitored in this study.
that comparisons can be made within classes of mono-, di-, and tri-halogenated DBPs (see Equation S1 in the SI). BSF was only calculated for DBP classes for which all chlorinated and brominated analogues were measured, i.e., tri-HALs, tri-HAMS, tri-HNMs, THM4, di-HALs, di-HAMS, and di-HNMs.

3. Results and discussion

3.1. Bromate

Figure S2 shows bromate as a function of throughput in bed volumes (BVs) during ozonation and GAC. The raw water had low but detectable levels of bromate (4 ± 3 μg/L). Bromate formed at an average of 26 μg/L due to the reaction of 153 μg/L of bromide with 0.8 mg-Ο3/mg-DOC of ozone, a 10% molar yield relative to bromide. Only a single observation at the start of the run (450 BVs) suggested removal (of about 28%) of bromate with GAC. While GAC had been determined to be effective at removing bromate in pristine waters, the presence of organic matter greatly inhibits bromate adsorption (Krisits et al., 2000). Therefore, it is unsurprising that bromate was poorly removed by GAC in treated wastewater containing 5 mg/L of DOC (Table 1; see additional discussion on bulk parameters in the SI). Bromate mitigation strategies (e.g., pH depression, ammonia, chloramines, and hydrogen peroxide) involving bromide sequestration or manipulating the ozone/hydroxyl radical pathways have been studied for decades in drinking water applications (Buffle et al., 2004; Pinkernell and Von Gunten, 2001; and Wert et al., 2007). However, these bromate mitigation strategies have only been limitedly studied in wastewater matrices (Soltermann et al., 2017), which generally have much higher ozone demand.

3.2. THM4 and HAA5

3.2.1. GAC treatment of prechlorine-formed THMs and HAAs

Ambient concentrations of THM4 and HAA5 are shown in Fig. S3 (A and B, respectively). The concentration of THMs in the raw water was low [0.6 ± 0.1 μg/L of THM4 (n = 10)] and below the MRL for HAA5 (1 μg/L; Table S6). THMs and HAAs were formed during pilot pre-chlorination, generating an average 9 μg/L of each THM4 (n = 3) and HAA5 (n = 3) when 1 mg-Cl2/L dose was used for pre-chlorination (0–1540 BVs) and 24 ± 3 μg/L of THM4 (n = 6) and 16 ± 5 μg/L of HAA5 (n = 7) when 3 mg-Cl2/L dose was used (>1540 BVs). Complete removal of THM4 by GAC03 was observed in the beginning (<2000 BVs) and less removal occurred with increasing throughput, indicative of breakthrough. THM4 breakthrough of 50% occurred at 3000 BVs (Fig. S3) compared to 2200 BVs for bulk DOC (Table 1; see additional discussion on bulk parameters in the SI). After 5000 BVs, the concentration of THMs in the effluent was greater than in the influent, which is a behavior that has been observed in other GAC studies (Babi et al., 2007). This behavior suggests that adsorbed THMs were either displaced and desorbing in exchange with more favorably adsorbing compounds, formed chemically from chlorine reacting with adsorbed organic matter on GAC during dechlorination or via a decarboxylation process that converts HAAs to THMs (Zhang and Minaer, 2002), or some combination of the three. GAC03 removed ambient HAAs completely during the initial stages of the pilot (BV < 2000) and only allowed as much as 1.6 μg/L of HAA5 (during 4000 to 8000 BVs) into the effluent before HAA5 was removed to below their MRLs after 10,000 BVs (fig. S3B), likely due to biological degradation (Babi et al., 2007; Kim and Kang, 2008).

3.2.2. Preozonation treatment of FP chlorine-reactive precursors

Molar concentrations of THM4 and HAA5 precursors determined after FP-CL in GAC influent samples are presented in Fig. S4. Pre-ozonation slightly reduced THM4 FP-CL and HAA5 FP-CL in the influent stream (11% and 20% removal average, respectively), indicating that the reaction with ozone reduced the total number of precursors through oxidation and transformation to lower molecular weight compounds, consistent with previous work (Amy et al., 1991; De Vera et al., 2015). Deeudomwongsa et al. (2017) showed that THM formation was reduced not from direct reaction of precursors with ozone but from the reaction with hydroxyl radicals (as in O3/H2O2 in drinking water), which can be generated from the reaction of ozone and natural organic matter. While in the same study (Deeudomwongsa et al., 2017) the authors showed HAA5 formation was promoted via ozone oxidation, other studies reported similar findings to those reported herein, in that HAA precursors were removed during ozonation (De Vera et al., 2015).

GAC03 had a small but noticeable improvement to breakthrough of HAAs precursors during higher throughputs compared to other GAC processes, which could be linked to the reduced concentration of HAAs precursors in the influent (shown in Table 1 and Fig. S4). For THM4 precursors, GAC03 showed similar breakthrough performance compared to the other two GAC processes.

3.2.3. Prechlorine-GAC treatment of FP chlorine-reactive precursors

Pre-chlorination was expected to reduce THM4 FP-CL by converting THM precursors into ambient THMs or intermediate chlorinated aromatic products prior to GAC (Jiang et al., 2017). While a 6% and 7% transformation of precursors to ambient THM4 and HAA5 occurred, respectively, it did not play any appreciable role in subsequent GAC treatment. Rather, all GAC columns (pre-oxidation or not) reduced THM4 and HAA5 FP-CL to a similar degree. It is likely that the chlorine exposure during pilot pre-chlorination was not enough [11 mgCl2-min/L compared to 100 mgCl2-min/L in Jiang et al. (2017)] to influence GAC performance for removal of THM4 FP-CL. Further information on the individual species of THM4 and HAA5 FP-CL in GAC effluents is provided in the THM4 and HAA5 section in the Support Information (SI) document.

3.2.4. Preoxidation-GAC treatment of UFC chlorine-reactive precursors

UFC experiments were conducted on GAC effluent samples to determine DBP formation under chlorine exposures representative of conventional disinfection and distribution. Results of UFC experiments are shown in Fig. 1 and compared with DOC breakthrough concentrations. Distinguishable from the literature (Fischer et al., 2019), all three GAC pilots performed similarly with breakthroughs to the U.S. EPA MCL regulatory limits (80 μg/L for THM4 and 60 μg/L for HAA5) occurring at ~3000 BVs for THM4 UFC-CL but never captured for HAA5 (suggesting breakthrough >18,000 BVs). GAC03 effluent stabilized at the lowest THM4 UFC-CL (at most, 25% lower than GACraw effluent) and HAA5 UFC-CL (at most, 40% lower than GACraw effluent). In practice, this wastewater could be subjected to blending prior to introducing it to drinking water distribution systems and could result in a substantially lower level of regulated DBP formation.

3.3. NDMA

3.3.1. GAC treatment of ozone-formed NDMA

Ambient NDMA concentration as a function of throughput is shown in Fig. S5. The ambient NDMA concentration increased from 3.0 ± 0.5 ng/L (n = 6; raw) to 17 ± 3 ng/L (n = 11; GAC03 influent) during ozonation, taking the concentration above the California Environmental Protection Agency (CA/EPA) notification level (NL) of 10 ng/L. Subsequent GAC03 filtration removed 59% of NDMA to produce an effluent with 7 ± 3 ng/L (n = 11) of NDMA (on average),
with only one sample above the CA/EPA NL. GAC adsorption of NDMA has been previously proven to be an ineffective mitigation technique due to the hydrophilic nature of NDMA (Mitch et al., 2003). However, the removal of NDMA with GACO3 increased as throughput increased, from 32% to 78% NDMA removal in the span of 5 months (~20,000 BVs), likely due to increase in biological degradation (Chuang and Mitch, 2017; Gerrity et al., 2015; Zeng et al., 2016).

3.3.2. Ozone treatment of FP chloramine-reactive precursors

Concentrations of NDMA chloramine-reactive precursors (FP-CLM) through pre-oxidation and GAC treatment are shown in Fig. S6. Pilot pre-chlorination and pre-ozonation removed a large component of the total amount of NDMA FP-CLM from the influent, 56% and 88%, respectively. Pre-ozonation formed 14 ng/L of NDMA and removed 486 ng/L (on average) of NDMA FP-CLM (35 ng of precursors destroyed per 1 ng of NDMA formed). This reinforces that ozone-reactive NDMA precursors are distinctive from those reactive towards monochloramine (Farré et al., 2011; Marti et al., 2015; Pisarenko et al., 2012). Meanwhile, pre-chlorination did not form NDMA.

3.3.3. Preoxidation-GAC treatment of FP chloramine-reactive precursors

The removal of NDMA FP-CLM by GACraw and GACO3 approached steady-state values of 80% and 50%, respectively, indicating biodegradation of precursors, while GACCl2 removal efficiency decreased with time, indicating adsorption breakthrough (Fig. S6). Considering oxidation and sorption together, the NDMA FP-CLM of GACO3 effluent was lowest, stabilizing at 36 ± 7 ng/L, compared to GACraw and GACCl2 effluents, with values of 100 ng/L each (as shown in Fig. S6). The removal of NDMA FP-CLM during GACraw exceeded that of DOC and UVA254 as determined from a comparison of the results shown in Figs. S6 and S7. This relatively high performance is likely associated with the trace contaminants (e.g., ranitidine, diphenhydramine, and tetracycline) which are NDMA precursors and are removed effectively with GAC (Hanigan et al., 2012; Marti et al., 2017; Mulhern et al., 2017).

3.3.4. Preoxidation-GAC treatment of UFC chloramine-reactive precursors

Using UFC conditions, we determined that NDMA UFC-CLM was considerably lower in GACO3 effluent than in the effluent of the other two GACs (Fig. 2). Unfortunately, NDMA UFC-CLM still measured above the CA/EPA NL of 10 ng/L for all GACs throughout the full length of the run. However, because NDMA in GACO3 effluent was only 1.6 times the NL, blending with another source water could be done to meet compliance. NDMA UFC-CLM for GACCl2 effluent was lower than GACraw effluent throughout most of the column run, but their difference can be deemed insignificant since it was less than the variability due to error. The breakthrough of NDMA UFC-CLM during GACO3 occurred quickly and could not be captured because most precursors that remained after pre-ozonation were recalcitrant towards GAC adsorption.

3.4. Other unregulated DBPs

3.4.1. Influent FP chloramine- and chlorine-reactive precursors

The molar sums of regulated and unregulated DBPs formed during FP conditions with chlorine and chloramine are shown in Fig. 3A and B, respectively. More species of unregulated DBPs formed from FP with chloramine compared to chlorine (Table S6). For example, unlike unregulated DBPs formed with FP-CL, FP-CLM produced diiodoacetamide (DIAM), dichloroacetonitrile (DCAN), and TCAL in appreciable amounts (between 10 and 25 μg/L in influent samples). Also, the total concentration of HAM FP-CLM (173 ± 15 nM) was greater than HAM FP-CL (38 ± 32 nM). The major classes of DBPs formed during FP-CL were THM4, HAA5, and HALs (Fig. 3) matching the order of what has been observed for other water sources (Chuang and Mitch, 2017; Fu et al., 2017; Krasner et al., 2006).

3.4.2. Preoxidation of FP chlorine-reactive precursors

Pre-ozonation produced HAL (32 ± 18%), HK (36 ± 29%) and...
HNM (610 ± 200%) and removed HAN (25 ± 12%) chlorine-reactive precursors. While pre-oxidation did not alter the total concentration of total FP-CL (Table 1, % removal), it did systematically change the concentration of certain unregulated DBP chlorine-reactive precursors. It was thought based on the THM4 and HAA5 FP-CL data, as well as data from unregulated DBPs, that the pre-chlorination dose was not sufficiently high to alter the precursors prior to FP-CL experiments. However, it did increase the concentration of HAL, HAN, and HK FP-CLM by 55 ± 19%, 36 ± 17%, 36 ± 12%, respectively.

### 3.4.3. Preoxidation of FP chloramine-reactive precursors

Pre-ozonation increased HAL (90 ± 86%), HK (44 ± 24%), and HNM (175 ± 68%) and removed HAN (53 ± 15%) chloramine-reactive precursors. HAM precursors were neither formed nor removed during pre-ozonation. Because ozonation can produce low molecular weight aldehydes and ketones, HAL and HK precursors increased during ozonation (De Vera et al., 2015; Richardson et al., 1999; Weinberg et al., 1993). Also, HNM precursors increased after ozonation because they have an oxidized N-functional group, nitro, that can form from the reaction of amines (particularly secondary amines) with ozone (McCurry et al., 2016). Furthermore, both HAM and HAN precursors are likely oxidized to form HNM precursors since the nitrogen moiety on both HAM and HAN precursors are susceptible to ozone oxidation (De Vera et al., 2015).

### 3.4.4. GAC treatment of FP chloramine- and chlorine-reactive precursors

After GAC adsorption, unregulated DBP FP (with CL and CLM) in the GAC effluent approached that of the influent with increasing throughput, indicative of adsorption breakthrough (see Fig. S8 for normalized concentration as a function of throughput). Throughput estimated (using linear interpolation) at 50% breakthrough is shown in Table 1 (and compared in Fig. S9). Breakthrough of chloride-reactive precursors through GACraw was in the order of: HNMs DOC < THM4 < HAMs < HANs < UVA254 < HKs < HAA5 < HALs. Chloramine-reactive precursors followed a distinctive removal pattern, with breakthrough in the order of: HNMs < DOC < UVA254 < HALs – HANS – HAMs < HKs < NDMA.

### 3.4.5. Preoxidation-GAC treatment: FP chloramine- and chlorine-reactive precursors

Pre-oxidation with chlorine and ozone impacted the breakthrough of precursors. Pre-chlorination delayed the GAC breakthrough of HAL, HAN, HAM, and HK chlorine-reactive precursors (FP-CLM), but increased chlorine-reactive HAL precursors (FP-CL) (Table 1; Fig. S9). Though HAL, HAN, and HK chlorine-reactive precursors increased after pre-chlorination (Table 1), the formed precursors were more adsorbable than those in the raw water, as was deduced from the observation of breakthrough of GACCl2 compared to GACraw. Though HAM FP-CLM did not change during pre-chlorination, the chemical nature of these precursors was altered during pre-chlorination since, again, they were more susceptible to GAC adsorption than in their raw form.

Pre-ozonation delayed the GAC breakthrough of HNM, HAN, and HAL FP-CL and HNM, HAL, HK FP-CLM (Table 1). Because ozonation increased HNM FP and HK FP (-CL and -CLM), their presence was higher in the effluent of GACO3 compared to GACraw. Though HAM FP-CLM did not change during pre-chlorination, the chemical nature of these precursors was altered during pre-chlorination since, again, they were more susceptible to GAC adsorption than in their raw form.

Pre-ozonation delayed the GAC breakthrough of HNM, HAN, and HAL FP-CL and HNM, HAL, HK FP-CLM (Table 1). Because ozonation increased HNM FP and HK FP (-CL and -CLM), their presence was higher in the effluent of GACO3 compared to GACraw. Though HAM FP-CLM did not change during pre-chlorination, the chemical nature of these precursors was altered during pre-chlorination since, again, they were more susceptible to GAC adsorption than in their raw form.

Still, the combined process of O3/GAC produced an effluent with the lowest total DBP precursor levels (Fig. 3) compared to Cl2/GAC and raw/GAC. The order of breakthrough for each individual class of DBP contrasted with reported removals from pre-ozonated biofiltration that used GAC media in wastewater (Chuang and Mitch, 2017) and drinking water (De Vera et al., 2016; Fu et al., 2017). For example, GAC with pre-ozonation followed breakthrough performance (Table 1) in the order: HNMs > HALs > HAA5 > HANs > HKs > HAMs > THMs, while Chuang and Mitch (2017) reported biofiltration removals in the order: HNMs > HAMs > HALs > HKs > THMs > HAAs.

![Fig. 3. Concentration of regulated and unregulated DBPs classes following formation potential (FP) (A) chlorination and (B) chloramination in samples from pre-oxidation and post-GAC treatment. NA – not available.](image-url)
Though THMs and HAAs are commonly used as surrogates for DBP formation, a lack of correlation between regulated and unregulated DBPs has been reported in wastewater effluents (Krasner et al., 2009). Here we demonstrated that GAC adsorption does not remove all classes of DBP precursors by the same degree. Rather, all unregulated DBP classes, with the exception of HNMs, were removed more effectively (Table 1) than THMs and DOC. In wastewater, precursors containing nitrogen are highly abundant (Chen et al., 2011). As a result, there is increased likelihood to form HNMs during chlorination and chloramination in treated wastewater. Although HNM FP-CL increased with pre-ozonation, the ozone-produced HNM precursors were highly adsorbable by GAC. In fact, HNM FP-CL in the effluent of GACO3 resembled that of GACCl2 and GACraw (see Fig. S10 for a comparison of DBPs that were limitingly formed, <1 mM).

The bromine substitution factor (BSF) for DBP FP is shown in Fig. S11. The aggregated average BSF was higher after GAC treatment compared to the influent, as expected due to removal of DOC and no removal of bromide ion, i.e., increased Br⁻ to DOC ratio. This increase in BSF was more noticeable for FP-CLM (Fig. S11B) than for FP-CL and for raw/GAC and O3/GAC than for Cl2/GAC. For raw pilot influent, trihalonitromethane FP-CL and -CLM had the highest BSF compared to other DBP classes.

3.5. Estimated toxicity of DBPs

Because the calculated toxicity corresponds to DBPs formed during much higher oxidant exposures (i.e., FP) than what is typical for water treatment disinfection (e.g., UFC), calculated cytotoxicity and genotoxicity were used only to indicate relative performance of GAC adsorbents.

3.5.1. Influent cytotoxicity from FP chloramine- and chlorine-reactive precursors

The calculated cytotoxicity associated with DBPs formed during FP-CL and -CLM are displayed in Fig. 4A and B, respectively. The calculated cytotoxicity of the nine classes of DBPs according to their concentrations after FP-CL and cytotoxic potencies (Wagner and Plewa, 2017) were consistent across throughput and rank in the order of: I-THMs < I-HAAs < THMs < HAAs < HAMS < HNMs < HALs < HANs < HNMs. The calculated cytotoxicity induced by the DBPs formed in FP experiments is drastically different from their molar concentrations (i.e., compared to Fig. 3A). The two dominating classes of DBPs (on a molar basis) in the raw tertiary-filtered wastewater formed after FP-CL, THM4 and HAAS, were 80% of the total concentration, but represented less than 5% of the total summed calculated cytotoxicity (see Fig. 4). Rather, more than 90% of the calculated cytotoxicity was due to HALs, HNMs, HAMS, and HANs, which accounted for 20% of the total molar concentration. Similarly, Krasner et al. (2016) found HANs and HNMs contributed the most to the overall calculated cytotoxicity in a bench-scale study, even though their concentrations were limited compared to regulated DBPs.

3.5.2. Influent genotoxicity from FP chloramine- and chlorine-reactive precursors

The calculated genotoxicity of DBPs formed during FP-CL and -CLM are shown in Fig. 5A and B, respectively. The calculated genotoxicity of the six classes of DBPs according to their concentrations after FP-CL were not consistent across throughput but ranked in the order of I-THM < I-HAAs < HAAs < HALs < HAMS < HANs based on averages. The calculated genotoxicity induced by the DBPs formed in FP experiments is drastically different from their molar concentrations (i.e., compared to Fig. 3B). The two dominating classes of DBPs (on a molar basis) in the raw tertiary-filtered wastewater formed after FP-CL, THM4 and HAAS, were 80% of the total concentration, but represented less than 5% of the total summed calculated genotoxicity (see Fig. 5). Rather, more than 90% of the calculated genotoxicity was due to HALs, HNMs, HAMS, and HANs, which accounted for 20% of the total molar concentration. Similarly, Krasner et al. (2016) found HANs and HNMs contributed the most to the overall calculated genotoxicity in a bench-scale study, even though their concentrations were limited compared to regulated DBPs.

![Fig. 4. Calculated cytotoxicity from DBPs formed during (A) chlorination and (B) chloramination under formation potential experiments in samples from pre-oxidation and post-GAC treatment. NA = not available.](image-url)
(with HKs, THMs, and NDMA not determined) based on averages in the raw tertiary-filtered wastewater. Calculated genotoxicity after FP-CLM were not consistent across throughput and ranked in the order of: NDMA < I-HAAs < HANs < HALs < HAMs < HNMs based on averages. Specifically, the calculated genotoxicity associated with HNMs after FP-CL was 43% of the total (of the six species for which genotoxicity was available) though it only amounted to 13% in terms of concentration. Meanwhile, HAA5 after FP-CL accounted for 65% of the sum concentration of the six genotoxic DBP species, yet were less than 2% of the total calculated genotoxicity.

3.5.4. Preoxidation-GAC treatment of toxicity from FP chloramine- and chlorine-reactive precursors

Pre-ozonation increased the total calculated cytotoxicity and genotoxicity of DBPs formed after FP-CL and -CLM primarily due to the increases in HNM precursors, but it also had a synergistic effect with GAC, where GACO3 removed HNMs to a greater degree when compared to GACraw. Pre-chlorination was not consistent in the effect it had on cytotoxicity and genotoxicity, but it did consistently yield a GACO3 effluent with lower calculated toxicity than GACraw effluent. While pre-chlorination has been shown to improve DBP attenuation during GAC (Jiang et al., 2017), improving toxicity without notable reduction in total concentration is unique to this study.

In the first two sets of samples (363–450 and 5100–6700 BVs), the cytotoxicity and genotoxicity calculated from DBPs formed during FP-CLM was higher than from FP-CL, though the concentration of DBPs was five times higher for FP-CL (Figs. 4 and 5, respectively). This was contrasting to studies with a similar cytotoxicity calculation approach (Chuang and Mitch, 2017; Zeng et al., 2016). Chuang and Mitch (2017) found chloramination under simulated distribution system conditions (comparable to UFC herein) produced lower calculated cytotoxicity, ~3-80-fold, compared to chlorination in treated municipal wastewater before and after ozone and biofiltration. In this study, the calculated cytotoxicity and genotoxicity were higher for chloramination-formed DBPs because of the unique oxidation conditions. For example, we observed formation of dichloroacetamide, which is orders of magnitude more toxic (e.g., cytotoxicity of dichloroacetamide: LC50 = 1.9 × 10⁻⁶ M) than those that are more prominent, such as THMs and HAAs (e.g., cytotoxicity of chloroform: LC50 = 9.2 × 10⁻³ M) (Richardson et al., 2008; Wagner and Plewa, 2017). The calculated cytotoxicity was drastically lower during the last sampling (18,400–21,000 BVs) of FP-CLM even though the total concentration of DBP FP-CLM was not considerably reduced. This occurred because highly cytotoxic chloroacetaldehyde (cytotoxicity of chloroacetaldehyde: LC50 = 3.6 × 10⁻⁶ M) and
dibromoacetaldehyde (cytotoxicity of dibromoacetaldehyde: \( \text{LC}_{50} = 4.4 \times 10^{-9} \text{ M} \)) [Jeong et al., 2015] were below detection in the final round of samples, though they were the primary source of calculated cytotoxicity (in the tens of nM) for the first two sample campaigns.

4. Conclusions

This study measured chlorine- and chloramine-reactive DBP precursors of nine regulated and 57 unregulated DBPs in tertiary-treated wastewater before and after treatment with pilot-scale pre-oxidation followed by GAC adsorption. These results indicate GAC employed in a potable reuse application has the potential to reduce chlorine- and chloramine-reactive DBP precursors compared to no GAC application. Also, GAC employed with pre-ozonation can produce an effluent with lower HAA5 UFC, THM4 UFC, NDMA UFC and the sum of regulated and emerging DBP precursors under FP-CL and -CLM than GAC with pre-chlorination. GAC with pre-chlorination produced an effluent with less sum of regulated and emerging DBP precursors under FP-CL than without pretreatment. However, bromate mitigation strategies are likely warranted with the GAC with pre-ozonation used to treat wastewater. Though DBP precursors under FP conditions can be reduced to a greater extent by GAC with pre-oxidation when compared to GAC with no pre-oxidation, GAC with pre-ozonation can potentially produce an effluent with calculated cytotoxicity and genotoxicity that are similar to GAC with no pre-oxidation, while GAC with pre-chlorination can potentially yield an effluent with the lowest calculated toxicity. Caution is warranted if chloramines alone are to be used post disinfection since chloramines can potentially produce more species of unregulated DBPs and the calculated cytotoxicity and genotoxicity from DBPs’ formed during FP-CLM can be potentially higher than from FP-CL even though the concentration of DBPs can be five times higher for FP-CL. This study suggests that DOC can be used as an indicator for DBP treatment efficacy, however the DOC breakthrough behavior did not correlate with the total sum of calculated cytotoxicity and genotoxicity. Therefore, for potable reuse applications unregulated DBPs could have negative health implications that are disconnected from DOC and regulated classes of DBPs, which could be verified under simulated disinfection conditions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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