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Supporting Information

Treating Water Containing Elevated Bromide and Iodide Levels with Granular Activated Carbon and Free Chlorine: Impacts on Disinfection Byproduct Formation and Calculated Toxicity

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Table of Contents

Text S1. Rapid small scale column test (RSSCT) design and operation 4

Text S2. Calibration and quality control (QC) for trihalomethane (THM) and haloacetic acid (HAA) analysis 5

Text S3. Total organic halogen (TOX) concentration calculation and example calculation of the contribution of haloacetamides (HAMs) to TOX 6

Table S1. GAC Feed Water Characteristics 7

Table S2. F400 GAC Characteristics 7

Table S3. RSSCT Operating Conditions 8

Table S4. Chlorine spike, total chlorine residual, and free chlorine residual for influent samples 8

Table S5. Quenching protocol for DBP and TOX analysis 9

Table S6. List of analytes and associated analytical methods 9

Table S7. List of DBPs targeted in this study 10

Table S8. EPA Methods 551.1 and 552.2 Calibration and Quality Control Standards 12

Table S9. Characteristics of water matrix for RSSCT influent and three effluent with ambient or spiked bromide and iodide levels 14

Table S10. Halogen incorporation into TOX following chlorination 15

Table S11. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three effluent of ambient sample 16

Table S12. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three effluent of 200-0 sample 18

Table S13. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three effluent of 200-20 sample 20

Table S14. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three effluent of 1000-100 sample 22

Table S15. Molar contribution of targeted DBPs to TOCl/TOBr/TOI 24

Table S16. Percent recovery and error for five selected bromoform calibration curve points and surrogate standard recovery 25

Figure S1. Process flow diagram of the water treatment plant (WTP) 26

Figure S2. Experimental workflow 26

Figure S3. Calibration curve for bromoform using EPA Method 551.1 by gas chromatography analysis. 27

Figure S4. Effect of bromide and iodide on speciated total organic halogen (TOX) formation in chlorinated GAC influent and effluent. Results for GAC effluent are shown after treatment of indicated number of bed volumes. Error bars represent standard deviations of duplicate measurements. 27

Figure S5. Effect of bromide and iodide on the formation of (a) total targeted DBPs and (b) priority unregulated DBPs (i.e. IAA, I-THM, HK, HAL, HAM, HAN, and HNM) in chlorinated GAC influent and effluent. 28

Figure S6. Effect of DOC concentration on DBP formation in GAC influent and effluent at four tested bromide and iodide levels. DOC concentrations correspond to the GAC influent and GAC effluent collected at bed volumes of 9,550, 16,550, and 31,500 BV 29

Figure S7. Effect of UV_{254} on DBP formation in GAC influent and effluent at four tested bromide and iodide levels. UV_{254} correspond to the GAC influent and GAC effluent collected at bed volumes of 9,550, 16,550, and 31,500 BV 31

Figure S8. Correlations between DBP and TOX formation in GAC influent and effluent at four tested bromide and iodide levels. TOX concentrations correspond to the GAC influent and GAC effluent collected at bed volumes of 9,550, 16,550, and 31,500 BV. Sample collected at BV=9550 for 1000-100 sample is excluded from the correlation for all DBPs. 33

Figure S9. Impact of bromide/DOC concentration ratio on bromine incorporation factor (BIF) for trihalogenated DBPs (THNMs, THALs, and THANs). 34

Figure S10. Impact of bromide/DOC concentration ratio on bromine incorporation factor (BIF) for dihalogenated DBPs (DHNMs and DHALs). 34

Figure S11. Impact of bromide/DOC concentration ratio on bromine incorporation factor (BIF) for THMs, THAAs, THALs, DHAAs, DHANs, and DHNMs in our study and Krasner et al. (2016). 35

Figure S12. Correlations between calculated toxicity and TOBr concentration in GAC influent and effluent at four tested bromide and iodide levels. 36

Figure S13. Contributions of individual DBP classes to TOX, calculated cytotoxicity, and calculated genotoxicity in GAC influent and effluent samples at three tested bed volumes (BVs). Bromide and iodide concentrations spiked into water samples before chlorination were 0 μg/L and 0 μg/L, respectively (ambient condition). 37

Figure S14. Contributions of individual DBP classes to TOX, calculated cytotoxicity, and calculated genotoxicity in GAC influent and effluent samples at three tested bed volumes (BVs). Bromide and iodide concentrations spiked into water samples before chlorination were 200 μg/L and 0 μg/L, respectively (200-0 condition). 38

Figure S15. Contributions of individual DBP classes to TOX, calculated cytotoxicity, and calculated genotoxicity in GAC influent and effluent samples at three tested bed volumes (BVs). Bromide and iodide concentrations spiked into water samples before chlorination were 1000 μg/L and 100 μg/L, respectively (1000-100 condition). 39

Reference 40

Text S1. Rapid small scale column test (RSSCT) design and operation

The RSSCT column was made of polytetrafluoroethylene (PTFE) tubing (I.D. = 6.35 mm, Table S3) and cut to size to provide enough length for the GAC bed and the glass wool packing at both ends.

The RSSCT column was prepared according to the following procedure:

(1) The day before each RSSCT column was prepared, HPLC grade methanol was pumped through the RSSCT setup for 15 min, followed by pumping freshly generated deionized water through the RSSCT setup overnight (for at least 8 h).

(2) Teflon tubing was fitted with stainless steel Swagelok nuts and ferrules. The bottom of the column was connected to the rest of the RSSCT set-up and the top was disconnected and left open to the atmosphere.

(3) Freshly generated deionized water was then pumped to the top of the column.

(4) Degassed and wetted glass wool was packed tightly into the bottom of the column. Any remaining air bubbles were removed with a pre-cleaned needle and syringe.

(5) A clean disposable glass pipette was then used to load the pre-weighed (Table S3) and previously wetted and degassed granular activated carbon (GAC) into the column. During the loading process, the GAC was continuously submerged by periodically pumping deionized water to the top of the column and touching the glass pipette of GAC to the top of the meniscus. The GAC then easily descended to the bottom of the column by gravity.

(6) When the GAC was completely loaded, the GAC bed was measured to ensure the length matched the pre-calculated bed length (Table S3). Often, the bed is slightly longer, in which case, the correct bed depth can be reached by tapping the outside of the column.

(7) Degassed and wetted glass wool was tightly packed into the top of the column. The GAC bed length was subsequently measured and confirmed again.

(8) The top of the column was then attached to the rest of the RSSCT setup.

The design parameters and operating conditions for each RSSCT are summarized in Table S3. RSSCT operation was conducted by checking the column at least twice a day following the procedure:

(1) A dissolved organic carbon (DOC) sample of the column effluent was filtered through a 0.45 μm PVDF syringe filter and collected in a pre-cleaned amber glass vial. All samples were collected

with zero headspace and adjusted to pH 2.0 using 6 M hydrochloric acid for storage. All DOC samples were analyzed within 2 weeks of collection.

(2) UV254 was measured immediately after filtration (and without acidification) using a 5-cm path length quartz cell and Hach® DR 5000™ spectrophotometer.

(3) The column flow rate was manually checked three times using a 10-mL graduated cylinder and verified by weight. If the flowrate was not correct, it was adjusted and re-measured until correct.

(4) Effluent sample bottles were swapped out with new, pre-cleaned sample bottles. Samples were collected with zero headspace.

Text S2. Calibration and quality control (QC) for trihalomethane (THM) and haloacetic acid (HAA) analysis

Primary dilution standards (PDS) for calibration standards, internal standards, and surrogate standards (Table S8) were prepared by diluting purchased primary standards in acetone or methyl-*tert* butyl ether (MTBE); and PDS for quality control (QC) were prepared by diluting purchased secondary source standards in acetone or MTBE. PDS were stored separately at < -10 ˚C until use. Calibration standards and QC standards were made by spiking PDS into specially prepared reagent water and liquid-liquid extracted using the same procedure as all samples. Calibration curves for THMs using EPA Method 551.1 included eight points and covered a concentration range from 0.1 to 100 μg/L; while calibration curves for HAAs using EPA Method 552.2 included seven points and covered a concentration range from 2.5 to 100 μg/L. Calibration curves were analyzed at the beginning of each sample set. An example calibration curve for bromoform using EPA Method 551.1 is depicted in Figure S3. QC standards were prepared from QC PDS solutions at a concentration approximately in the middle of the calibration curve range. Due to the arduous nature of the liquid-liquid extraction procedures and the number of steps involved, surrogate standards were used for both EPA Method 551.1 and 552.2 to validate the extraction of all samples. Surrogate standards were spiked from surrogate PDS standards into each calibration standard, QC standard, and sample, and quantified simultaneously. Additionally, to validate gas chromatography (GC) performance for HAA9 analysis, internal standard compounds were spiked into sample solvent extractions before GC analysis.

Text S3. Total organic halogen (TOX) concentration calculation and example calculation of the contribution of haloacetamides (HAMs) to TOX

TOX concentrations are presented using (1) mass concentration units (μg/L) and (2) molar concentration units (μM); i.e.,

TOX (μg/L) = TOCl as Cl (μg/L) + TOBr as Br (μg/L) + TOI as I (μg/L);

TOX (μM) = TOX (μg/L as Cl)/35.45 (μg Cl/μmol)

We also calculated the contribution of DBP classes to TOX. An example calculation of the contribution of haloacetamides (HAM) to TOX:

$$\%\text{HAM to TOX} = \frac{\sum(a+b+c)[CH_xCl_aBr_bI_cC(=O)NH_2]}{[TOCl]+[TOBr]+[TOI]} * 100\%$$

where x is the number of hydrogen atoms; a, b and c are the number of chlorine, bromine and iodine atoms, respectively, for each individual HAM; and $[CH_xCl_aBr_bI_cC(=O)NH_2]$ is the molar concentration of an individual HAM. [TOCl], [TOBr], and [TOI] are the molar concentrations of TOCl, TOBr, and TOI, respectively.

The molar contribution of targeted DBPs to TOCl/TOBr/TOI was shown in Table S11. An example calculation of the contribution of haloacetamides (HAM) to TOCl:

$$\%\text{HAM to TOCl} = \frac{\sum a*[CH_xCl_aBr_bI_cC(=O)NH_2]}{[TOCl]} * 100\%$$

where a is the number of chlorine for each individual HAM; and $[CH_xCl_aBr_bI_cC(=O)NH_2]$ is the molar concentration of an individual HAM. [TOCl] is the molar concentrations of TOCl.

Table S1. GAC Feed Water Characteristics

Parameter	Average
DOC (mg/L)	1.4
UV_{254} (cm^{-1})	0.024
SUVA (L/mg-m)	1.7
pH	6.7
Turbidity (NTU)	< 0.1
Bromide (µg/L)	22
Iodide (µg/L)	< 5

Table S2. F400 GAC Characteristics

GAC Parameter	Value
Iodine Number*	1000 mg/g (minimum)
Moisture by Weight	2% (maximum)
Effective Size	0.55 – 0.75 mm
Uniformity Coefficient	1.9 (maximum)
Abrasion Number	75 (minimum)
Screen Size by Weight, US Standard Mesh	
Retained on #12 mesh	5% (maximum)
Through #40 mesh	4% (maximum)
Apparent Density (after tamping)	0.54 g/cm^3
BET Surface Area	953 m^2/g
Micropore Volume[1]	3.45×10^{-1} g/cm^3
DFT Mesopore Volume[2]	1.35×10^{-1} g/cm^3
BJH Mesopore Volume[3]	1.62×10^{-1} g/cm^3

*: ASTM D4607

1: Micropore volume measured for pores with widths less than 20 Å

2: Mesopore volume measured for pores with widths from 20 to 360 Å

3: Mesopore volume measured for pores with widths from 20 to 500 Å

189 **Table S3.** RSSCT Operating Conditions

RSSCT Parameter	**Index**
Simulated empty bed contact time (EBCT) (min)	10
GAC Type	F400
U.S. Mesh Size	100 x 200
Dry Bed Density (g/cm^3)	0.5
Bed Depth (cm)	13.1
Column Diameter (mm)	6.4
Pump Flowrate (mL/min)	3.5
Hydraulic Loading Rate (m/hr)	6.7
Bed Volume (mL)	4.1
Column Run Time (day)	32
Volume of Water Treated (gal)	32

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192 **Table S4.** Chlorine spike, total chlorine residual, and free chlorine residual for influent samples

Cl_2 Residuals after 24 h for Influent Samples			
Sample	Cl_2 Spike (mg/L)	Total Cl_2 residual (mg/L)	Free Cl_2 residual (mg/L)
Ambient sample_influent_replicate 1	2.13	0.95	0.95
Ambient sample_influent_replicate 2	2.13	0.96	0.95
Ambient sample_influent_replicate 3	2.13	0.96	0.95
200-0 sample_influent_replicate 1	2.16	0.94	0.93
200-0 sample_influent_replicate 2	2.16	0.94	0.94
200-0 sample_influent_replicate 3	2.16	0.95	0.94
200-20 sample_influent_replicate 1	2.18	0.94	0.94
200-20 sample_influent_replicate 2	2.18	0.95	0.95
200-20 sample_influent_replicate 3	2.18	0.95	0.94
1000-100 sample_influent_replicate 1	2.33	0.91	0.91
1000-100 sample_influent_replicate 2	2.33	0.92	0.91
1000-100 sample_influent_replicate 3	2.33	0.92	0.92

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194 **Table S5.** Quenching protocol for DBP and TOX analysis

Analyte	Quenching Reagent	pH adjustment
THMs	Ammonium chloride in dry phosphate buffer mix	4.5-5.5
HAAs	Ammonium chloride	NA
Priority unregulated DBPs*	Ammonium chloride	3.5-4.0
Priority unregulated DBPs and TOX*	Ascorbic acid	3.5-4.0

195 * Details about quenching and preservation procedures for priority unregulated DBPs and TOX are provided by
196 Cuthbertson et al. (2019).(1)

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201 **Table S6.** List of analytes and associated analytical methods

Analyte	Method
Dissolved organic carbon (DOC)	SM 5310 B with a Shimadzu VCH TOC Analyzer
UV_{254}	SM 5910 B
pH	SM 4500-H+ B
Chloride, bromide, iodide	SM 4110 using ion chromatography
Free chlorine, high range (>2 mg Cl_2/L)	SM 4500-Cl
Free chlorine, low range (<2 mg Cl_2/L)	SM 4500-Cl, Hach Pocket Colorimeter II, Chlorine kit
Trihalomethanes (THM4)	EPA Method 551.1
Haloacetic acids (HAA9)	EPA Method 552.2
57 priority unregulated DBPs	Liquid-liquid extraction, GC-MS[1]
Total organic halogen (TOX)	Combustion-ion chromatography/inductively coupled plasma-mass spectrometer (ICP-MS)[1]

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Table S7. List of DBPs targeted in this study

DBP Class	DBP Name	DBP Acronym	Minimum Detection Limit (ng/L)	Minimum Reporting Limit (ng/L)
Trihalomethanes (THMs)	Chloroform	TCM	NA	2,500
	Bromodichloromethane	BDCM	NA	1,000
	Dibromochloromethane	DBCM	NA	1,000
	Bromoform	TBM	NA	1,000
Haloacetic Acids (HAAs)	Chloroacetic acid	CAA	NA	8,800
	Bromoacetic acid	BAA	NA	4,300
	Dichloroacetic acid	DCAA	NA	4,700
	Bromochloroacetic acid	BCAA	NA	4,250
	Dibromoacetic acid	DBAA	NA	4,220
	Trichloroacetic acid	TCAA	NA	4,340
	Bromodichloroacetic acid	BDCAA	NA	3,370
	Chlorodibromoacetic acid	CDBAA	NA	2,790
	Tribromoacetic acid	TBAA	NA	3,570
Haloacetonitriles (HANs)	Chloroacetonitrile	CAN	8	100
	Bromoacetonitrile	BAN	48	100
	Dichloroacetonitrile	DCAN	5	100
	Bromochloroacetonitrile	BCAN	5	100
	Dibromoacetonitrile	DBAN	38	100
	Trichloroacetonitrile	TCAN	5	100
	Tribromoacetonitrile	TBAN	50	100
	Iodoacetonitrile	IAN	31	100
Haloketones (HKs)	Chloropropanone	CP	24	100
	1,1-Dichloropropanone	11DCP	26	100
	1,3-Dichloropropanone	13DCP	35	100
	1,1-Dibromopropanone	11DBP	20	100
	1,1,1-Trichloropropanone	111TCP	6	100
	1,1,3-Trichloropropanone	113TCP	2	100
	1-Bromo-1,1-dichloropropanone	1B11DCP	3	100
	1,1,3,3-Tetrachloropropanone	1133TeCP	9	100
	1,1,3,3-Tetrabromopropanone	1133TeBP	22	100
Halonitromethanes (HNMs)	Dichloronitromethane	DCNM	28	100
	Bromochloronitromethane	BCNM	24	100

	Dibromonitromethane	DBNM	4	100
	Trichloronitromethane (Chloropicrin)	TCNM	6	100
	Bromodichloronitromethane	BDCNM	50	100
	Dibromochloronitromethane	DBCNM	50	100
	Tribromonitromethane	TBNM	50	100
Haloaldehydes (HALs)	Chloroacetaldehyde	CAL	50	100
	Bromoacetaldehyde	BAL	25	100
	Iodoacetaldehyde	IAL	25	100
	Dichloroacetaldehyde	DCAL	50	100
	Bromochloroacetaldehyde	BCAL	50	100
	Dibromoacetaldehyde	DBAL	50	100
	Trichloroacetaldehyde	TCAL	3	100
	Bromodichloroacetaldehyde	BDCAL	3	100
	Dibromochloroacetaldehyde	DBCAL	3	100
	Tribromoacetaldehyde	TBAL	3	100
Haloacetamides (HAMs)	Chloroacetamide	CAM	300	750
	Bromoacetamide	BAM	500	5000
	Iodoacetamide	IAM	400	750
	Dichloroacetamide	DCAM	16	100
	Bromochloroacetamide	BCAM	22	100
	Chloroiodoacetamide	CIAM	38	100
	Bromoiodoacetamide	BIAM	50	100
	Diiodoacetamide	DIAM	23	100
	Dibromoacetamide	DBAM	41	100
	Trichloroacetamide	TCAM	7	100
	Bromodichloroacetamide	BDCAM	30	100
	Dibromochloroacetamide	DBCAM	23	100
	Tribromoacetamide	TBAM	40	100
Iodo-Trihalomethanes (I-THMs)	Dichloroiodomethane	DCIM	12	100
	Bromochloroiodomethane	BCIM	39	100
	Chlorodiiodomethane	CDIM	39	100
	Dibromoiodomethane	DBIM	15	100
	Bromodiiodomethane	BDIM	90	100
	Triiodomethane (iodoform)	TIM	47	100
Iodinated Acetic Acids (IAAs)	Iodoacetic acid	IAA	5	25
	Chloroiodoacetic acid	CIAA	5	25
	Bromoiodoacetic acid	BIAA	5	25
	Diiodoacetic acid	DIAA	5	25

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Table S8. EPA Methods 551.1 and 552.2 Calibration and Quality Control Standards

Stock Solution	Manufacturer	Compound
EPA Method 551.1 (Primary) Stock Standard Solution (in acetone)	Absolute Standards	Chloroform
		Bromodichloromethane
		Dibromochloromethane
		Bromoform
		Dichloroacetonitrile
		Bromochloroacetonitrile
		Dibromoacetonitrile
		Trichloroacetonitrile
		Chloropicrin
		1,1-Dichloropropanone-2
		1,1,1-Trichloropropanone
EPA Method 551.1 Quality Control (Secondary) Stock Standard Solution (in acetone)	Absolute Standards; compounds are the same as primary stock standard solution	
EPA Method 551.1 Surrogate Standard Solution (in acetone)	AccuStandard	Decafluorobiphenyl
EPA Method 551.1 Internal Standard Solution (in acetone)	Restek	Bromofluorobenzene
EPA Method 552.2 (Primary) Stock Standard Solution (in methyl-tert butyl ether)	Absolute Standards	Chloroacetic acid
		Bromoacetic acid
		Dichloroacetic acid
		Bromochloroacetic acid
		Dibromoacetic acid
		Trichloroacetic acid

		Bromodichloroacetic acid
		Chlorodibromoacetic acid
		Tribromoacetic acid
EPA Method 552.2 Quality Control (Secondary) Standard Solution (in methyl-tert butyl ether)	Ultra Scientific	Chloroacetic acid
		Bromoacetic acid
		Dichloroacetic acid
		Bromochloroacetic acid
		Dibromoacetic acid
		Trichloroacetic acid
		Bromodichloroacetic acid
		Chlorodibromoacetic acid
		Tribromoacetic acid
EPA Method 552.2 Surrogate Standard Solution (in methyl-tert butyl ether)	Crescent Chemical	2,3-Dibromopropionic acid
EPA Method 552.2 Internal Standard Solution (in methyl-tert butyl ether)	Ultra Scientific	1,2,3-Trichloropropane

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207 **Table S9**. Characteristics of water matrix for RSSCT influent and three effluent with ambient or
208 spiked bromide and iodide levels

Experimental Condition	RSSCT Bed Volume	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg-m)	Bromide (µg/L)	Iodide (µg/L)	Bromide/DOC Ratio (mg/mg)
Ambient	Influent	1.4	0.024	1.7	22	< 5	0.02
	9,550	0.5	0.005	0.9	24	< 5	0.05
	16,500	0.9	0.011	1.3	24	< 5	0.03
	31,500	1.2	0.015	1.3	24	< 5	0.02
200-0 (200 µg/L Br^- & 0 µg/L I^-)	Influent	1.4	0.024	1.7	215	< 5	0.15
	9,550	0.5	0.006	1.1	220	< 5	0.43
	16,500	0.9	0.011	1.3	220	< 5	0.25
	31,500	1.2	0.015	1.3	220	< 5	0.19
200-20 (200 µg/L Br^- & 20 µg/L I^-)	Influent	1.4	0.024	1.7	222	19	0.16
	9,550	0.5	0.005	0.9	214	21	0.43
	16,500	0.9	0.011	1.3	215	21	0.24
	31,500	1.2	0.015	1.3	215	20	0.18
1000-100 (1000 µg/L Br^- & 100 µg/L I^-)	Influent	1.4	0.024	1.7	1026	95	0.73
	9,550	0.5	0.006	1.2	1030	103	1.98
	16,500	0.9	0.011	1.3	1024	104	1.18
	31,500	1.2	0.015	1.3	1026	104	0.88

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213 **Table S10**. Halogen incorporation into TOX following chlorination

Experimental Condition	Bed Volume	Halogen incorporation into TOX on a Molar Basis			TOX molar concentration (μM)
		TOCl[1]	TOBr	TOI	
Ambient	Influent	88%	10%	2.1%	2.3
	9,550	79%	20%	1.3%	0.67
	16,550	84%	16%	0.6%	1.2
	31,500	86%	13%	0.6%	1.6
200-0	Influent	42%	56%	1.8%	2.3
	9,550	46%	52%	1.7%	0.66
	16,550	47%	52%	0.7%	1.3
	31,500	47%	52%	0.5%	1.6
200-20	Influent	44%	54%	2.4%	2.5
	9,550	49%	49%	2.1%	0.70
	16,550	45%	54%	0.8%	1.2
	31,500	44%	55%	0.6%	1.6
1000-100	Influent	12%	84%	3.5%	2.8
	9,550	67%	31%	1.4%	1.8
	16,550	23%	76%	1.4%	1.5
	31,500	19%	80%	1.3%	1.7

214 [1] Chlorine incorporation into TOX on a molar basis: TOCl (μmol/L)/TOX (μmol/L)*100%,
215 where TOX (μmol/L) = TOCl (μmol/L) + TOBr (μmol/L) + TOI (μmol/L).

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217 **Table S11**. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three
218 effluent of ambient sample

DBP Class	DBP	GAC Influent (μg/L)	GAC Effluent BV=9,550 (μg/L)	GAC Effluent BV=16,550 (μg/L)	GAC Effluent BV=31,500 (μg/L)
THMs	TCM	14.4 ± 1.4	1.7	4.6	8.0
	BDCM	7.1 ± 0.5	2.6	4.4	5.7
	DBCM	2.3 ± 0.1	2.0	2.7	4.2
HAAs	DCAA	5.1	ND[1]	ND	2.7 ± 0.007
	BCAA	ND	ND	2.8 ± 0.02	2.6 ± 0.04
	TCAA	3.1	ND	ND	ND
HANs	DCAN	1.3 ± 0.05	0.2 ± 0.01	0.4 ± 0.01	0.5 ± 0.007
	BCAN	0.7 ± 0.06	0.3 ± 0.03	0.5 ± 0.01	0.4 ± 0.02
	DBAN	0.4 ± 0.04	0.3 ± 0.05	0.4 ± 0.04	0.3 ± 0.01
	TBAN	0.4 ± 0.004	0.4 ± 0.001	0.4	0.4 ± 0.001
HKs	111TCP	1.1 ± 0.02	0.2 ± 0.008	0.3 ± 0.03	0.4 ± 0.01
HNMs	TCNM	0.1 ± 0.007	ND	ND	ND
	BDCNM	0.6 ± 0.0006	0.6 ± 0.0001	0.6 ± 0.0001	0.6 ± 0.0002
	DBCNM	ND	0.9 ± 0.0003	0.9 ± 0.0003	ND
HALs	CAL	NR[2]	NR	NR	NR
	TCAL	2.6 ± 0.04	0.7	1.3 ± 0.02	1.6 ± 0.02
	BDCAL	0.4 ± 0.01	0.2	0.2 ± 0.001	0.2 ± 0.009
	DBCAL	0.3 ± 0.007	0.3	0.3 ± 0.004	0.3 ± 0.001
HAMs	DCAM	2.3 ± 0.4	0.4 ± 0.002	0.6 ± 0.05	0.8 ± 0.04
	BCAM	0.8 ± 0.1	0.3 ± 0.01	0.4 ± 0.03	0.4 ± 0.04
	DBAM	0.2 ± 0.04	0.1 ± 0.004	0.2 ± 0.01	0.1 ± 0.02
	TCAM	0.2 ± 0.03	ND	ND	ND
	BDCAM	0.2 ± 0.007	0.2 ± 0.002	0.2 ± 0.003	0.2 ± 0.003
	DBCAM	0.2 ± 0.003	0.2 ± 0.0006	0.2 ± 0.007	0.2 ± 0.005

I-THMs	DCIM	0.5 ± 0.02	ND	ND	ND
	BCIM	0.2 ± 0.02	ND	0.2 ± 0.01	0.2 ± 0.003
	DBIM	0.2 ± 0.0006	ND	0.2 ± 0.002	0.2 ± 0.001
IAAs	IAA	0.02 ± 0.001	ND	ND	ND
	CIAA	0.05 ± 0.004	ND	ND	ND
TOX	TOCl as Cl	72.9 ± 5.6	18.7 ± 4.9	36.6 ± 4.4	48.7 ± 0.06
	TOBr as Br	18.6 ± 0.2	10.4 ± 0.3	15.5 ± 0.2	16.6 ± 0.7
	TOI as I	6.1 ± 1.0	1.1 ± 0.2	1 ± 0.07	1.2 ± 0.08

[1]ND = not detected

[2]NR = not reported due to an interference with CAL

222 **Table S12**. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three
223 effluent of 200-0 sample

DBP Class	DBP	GAC Influent (μg/L)	GAC Effluent BV=9,550 (μg/L)	GAC Effluent BV=16,550 (μg/L)	GAC Effluent BV=31,500 (μg/L)
THMs	TCM	3.1	ND[1]	ND	1.6
	BDCM	10.1	1.7	3.7 ± 0.2	6.1
	DBCM	16.5	5.0	8.9 ± 0.4	13.5
	TBM	10.5	5.7	9.2 ± 0.6	12.1
HAAs	BCAA	4.0	ND	3.3	3.3
	DBAA	4.7	2.5	3.5	3.9
	BDCAA	ND	ND	ND	2.9
	CDBAA	4.1	ND	ND	2.5
HANs	DCAN	0.4 ± 0.005	0.1 ± 0.006	0.2 ± 0.004	0.2 ± 0.006
	BCAN	1.3 ± 0.007	0.3 ± 0.02	0.5 ± 0.008	0.5 ± 0.03
	DBAN	1.4 ± 0.01	0.4 ± 0.006	0.6 ± 0.008	0.5 ± 0.03
	TBAN	0.5 ± 0.0003	0.5 ± 0.0001	0.5 ± 0.0008	0.5 ± 0.001
HKs	11DBP	0.2 ± 0.002	0.2 ± 0.002	0.2 ± 0.001	ND
	111TCP	0.3 ± 0.005	ND	0.1 ± 0.0001	0.1 ± 0.001
HNMs	DBNM	0.4 ± 0.001	0.4 ± 0.0006	0.4 ± 0.0002	ND
	BDCNM	0.6 ± 0.0001	ND	0.3 ± 0.04	ND
	DBCNM	0.9 ± 0.0008	ND	ND	ND
	TBNM	2.3 ± 0.002	ND	ND	ND
HALs	CAL	NR[2]	NR	NR	NR
	DBAL	0.2 ± 0.04	ND	0.1 ± 0.01	0.1 ± 0.007
	TCAL	0.7 ± 0.02	ND	0.4 ± 0.003	0.3 ± 0.008
	BDCAL	0.5 ± 0.01	0.2	0.2 ± 0.003	0.2 ± 0.005
	DBCAL	0.6 ± 0.006	0.3	0.4 ± 0.005	0.3 ± 0.003
	TBAL	0.2	0.2	0.2 ± 0.002	ND

HAMs	DCAM	0.6 ± 0.03	0.1 ± 0.009	0.2 ± 0.0007	0.3 ± 0.02
	BCAM	1.2 ± 0.02	0.2 ± 0.01	0.3 ± 0.004	0.5 ± 0.004
	DBAM	2.8 ± 0.008	0.6 ± 0.04	1.1 ± 0.03	1.4 ± 0.0004
	BDCAM	0.2 ± 0.001	0.2 ± 0.003	0.2 ± 0.003	0.2 ± 0.0007
	DBCAM	0.3 ± 0.001	0.2 ± 0.003	0.2 ± 0.005	0.2 ± 0.0007
	TBAM	0.3 ± 0.005	0.2 ± 0.0006	0.3 ± 0.004	0.3 ± 0.004
I-THMs	DCIM	0.2 ± 0.004	ND	ND	ND
	BCIM	0.3 ± 0.008	ND	0.2 ± 0.0004	0.2 ± 0.004
	DBIM	0.3 ± 0.0005	0.2 ± 0.001	0.2 ± 0.002	0.2 ± 0.0008
IAAs	IAA	0.02 ± 0.0004	ND	ND	ND
	CIAA	0.006 ± 0.004	ND	ND	ND
	BIAA	0.02 ± 0.005	ND	ND	ND
TOX	TOCl as Cl	34.6 ± 3.2	10.8 ± 6.4	20.9 ± 3.2	25.9 ± 1.1
	TOBr as Br	103.3 ± 4.4	27.2 ± 0.8	52.3 ± 1.7	65.0 ± 1.6
	TOI as I	5.4 ± 2.1	1.4 ± 0.1	1.1 ± 0.005	0.9 ± 0.03

[1]ND = not detected

[2]NR = not reported due to an interference with CAL

227 **Table S13**. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three
228 effluent of 200-20 sample

DBP Class	DBP	GAC Influent (μg/L)	GAC Effluent BV=9,550 (μg/L)	GAC Effluent BV=16,550 (μg/L)	GAC Effluent BV=31,500 (μg/L)
THMs	TCM	3.1	ND[1]	ND	1.5 ± 0.2
	BDCM	10.4	2.1	3.7	5.9 ± 0.5
	DBCM	18.0	5.8	8.9	13.0 ± 1.3
	TBM	12.2	7.0	9.0	12.0 ± 1.2
HAAs	BCAA	6.2	4.1 ± 0.06	4.5 ± 0.08	4.6
	DBAA	5.6	2.9 ± 0.09	3.8 ± 0.08	4.4
	CDBAA	3.9	ND	ND	2.5
HANs	DCAN	0.4 ± 0.01	0.1 ± 0.007	0.2 ± 0.005	0.2 ± 0.002
	BCAN	1.3 ± 0.007	0.3 ± 0.04	0.5 ± 0.01	0.5 ± 0.01
	DBAN	1.4 ± 0.01	0.4 ± 0.03	0.6 ± 0.003	0.5 ± 0.01
	TBAN	0.5 ± 0.0005	0.5 ± 0.0002	0.5	0.5 ± 0.008
HKs	11DBP	0.2 ± 0.0007	0.2 ± 0.003	0.2 ± 0.001	ND
	111TCP	0.3 ± 0.02	ND	0.1 ± 0.001	0.1 ± 0.0008
HNMs	DBNM	0.4 ± 0.003	0.4 ± 0.0004	0.4 ± 0.002	ND
	BDCNM	0.6 ± 0.0001	ND	ND	ND
	DBCNM	0.9	ND	ND	ND
	TBNM	2.3 ± 0.002	ND	ND	ND
HALs	CAL	NR[2]	NR	NR	NR
	DBAL	0.3	ND	0.2 ± 0.1	0.1 ± 0.01
	TCAL	0.8 ± 0.05	ND	0.4 ± 0.004	0.2 ± 0.008
	BDCAL	0.6 ± 0.05	0.2	0.2 ± 0.01	0.2 ± 0.005
	DBCAL	0.6 ± 0.03	0.3	0.4 ± 0.004	0.3 ± 0.008
	TBAL	0.2 ± 0.001	0.2	0.2 ± 0.0004	ND
HAMs	DCAM	0.6 ± 0.07	0.1 ± 0.003	0.1 ± 0.02	0.2 ± 0.04

	BCAM	1.3 ± 0.02	0.2 ± 0.003	0.3 ± 0.03	0.4 ± 0.1
	DBAM	3.0 ± 0.02	0.5 ± 0.01	1.0 ± 0.1	1.3 ± 0.5
	BDCAM	0.2 ± 0.008	0.2 ± 0.0006	0.2 ± 0.001	0.2 ± 0.009
	DBCAM	0.3 ± 0.001	0.2 ± 0.003	0.2 ± 0.001	0.2 ± 0.03
	TBAM	0.3 ± 0.004	0.2 ± 0.001	0.3 ± 0.0003	0.3 ± 0.03
I-THMs	DCIM	0.3 ± 0.003	ND	ND	ND
	BCIM	0.4 ± 0.004	0.2 ± 0.009	0.2 ± 0.002	0.2 ± 0.003
	DBIM	0.3 ± 0.002	0.2 ± 0.004	0.3 ± 0.0007	0.3 ± 0.0005
IAAs	IAA	0.0009	ND	ND	ND
TOX	TOCl as Cl	38.6 ± 7.7	12.1 ± 2.1	18.3 ± 0.6	23.2 ± 2.0
	TOBr as Br	105.7 ± 33.0	27.5 ± 0.7	50.1 ± 0.4	65.4 ± 1.5
	TOI as I	7.5 ± 0.2	1.9 ± 0.1	1.2 ± 0.03	1.1 ± 0.2

[1]ND = not detected

[2]NR = not reported due to an interference with CAL

232 **Table S14**. DBP and TOX concentration (± standard deviation) (μg/L) for GAC influent and three
233 effluent of 1000-100 sample

DBP Class	DBP	GAC Influent (μg/L)	GAC Effluent BV=9,550 (μg/L)	GAC Effluent BV=16,550 (μg/L)	GAC Effluent BV=31,500 (μg/L)
THMs	BDCM	2.8	ND[1]	1.3	1.9
	DBCM	10.4	2.0	6.0	8.2
	TBM	52.8	14.4	34.5	41.5
HAAs	BCAA	6.4 ± 1.2	8.4	6.0	5.2 ± 0.04
	DBAA	10.0 ± 0.9	4.1	5.7	7.1 ± 0.1
	CDBAA	3.0 ± 0.3	ND	ND	ND
	TBAA	13.5 ± 1.1	ND	6.4	6.8 ± 0.2
HANs	DCAN	0.1 ± 0.003	ND	0.1	ND
	BCAN	0.5 ± 0.03	0.2 ± 0.0003	0.4 ± 0.002	0.3 ± 0.006
	DBAN	2.4 ± 0.3	0.7 ± 0.005	0.8 ± 0.03	0.7 ± 0.03
	TBAN	0.5 ± 0.002	0.4 ± 0.002	0.5 ± 0.0008	0.5 ± 0.0005
HKs	11DBP	0.3 ± 0.01	0.2 ± 0.001	0.2 ± 0.0006	ND
	111TCP	0.1	ND	ND	ND
HNMs	DBNM	0.4 ± 0.009	0.4 ± 0.001	0.4 ± 0.002	ND
HALs	CAL	NR[2]	NR	NR	NR
	DBAL	0.9 ± 0.09	ND	lost	0.2 ± 0.02
	TCAL	ND	ND	0.2	0.5 ± 0.08
	BDCAL	ND	ND	0.1	ND
	DBCAL	0.4 ± 0.01	0.3	0.3 ± 0.002	0.3 ± 0.004
	TBAL	0.3 ± 0.02	0.2	0.2 ± 0.002	ND
HAMs	DCAM	ND	ND	0.1	ND
	BCAM	0.3 ± 0.0003	0.1 ± 0.009	0.3 ± 0.02	0.2 ± 0.006
	DBAM	2.9 ± 0.1	0.6 ± 0.06	1.1 ± 0.04	1.4 ± 0.06
	BDCAM	0.2 ± 0.0003	ND	0.1	ND

	DBCAM	0.2 ± 0.002	0.2 ± 0.002	0.2 ± 0.0002	0.2 ± 0.001
	TBAM	0.6 ± 0.008	0.2 ± 0.009	0.3 ± 0.007	0.4 ± 0.01
I-THMs	DCIM	0.2 ± 0.008	ND	ND	ND
	BCIM	0.5 ± 0.02	0.2 ± 0.007	0.2 ± 0.002	0.2 ± 0.005
	DBIM	0.7 ± 0.04	0.3 ± 0.006	0.3 ± 0.007	0.3 ± 0.006
	BDIM	0.4 ± 0.004	ND	ND	ND
TOX	TOCl as Cl	12.2 ± 3.0	44.0 ± 0.2	12.0 ± 2.1	11.2 ± 0.6
	TOBr as Br	185.9 ± 7.0	46.2 ± 0.7	88.4 ± 2.2	107.2 ± 0.9
	TOI as I	12.3 ± 1.3	3.3 ± 0.3	2.6 ± 0.3	2.8 ± 1.0

[1]ND = not detected

[2]NR = not reported due to an interference with CAL

237 **Table S15**. Molar contribution of targeted DBPs to TOCl/TOBr/TOI

Experimental condition	**Bed volumes**	**Molar contribution of targeted DBPs to:**			**TOX molar concentration (μM)**
		TOCl[1]	**TOBr**	**TOI**	
Ambient	Influent	37%	42%	8.6%	2.3
	9,550	25%	48%	0.0%	0.67
	16,550	26%	53%	18%	1.2
	31,500	31%	55%	15%	1.6
200-0	Influent	40%	44%	7.9%	2.3
	9,550	19%	54%	6.0%	0.66
	16,550	24%	48%	17%	1.3
	31,500	37%	54%	20%	1.6
200-20	Influent	39%	47%	6.8%	2.5
	9,550	26%	69%	9.7%	0.70
	16,550	27%	52%	19%	1.2
	31,500	36%	53%	21%	1.6
1000-100	Influent	44%	49%	7.8%	2.8
	9,550	5.1%	54%	6.9%	1.8
	16,550	28%	61%	8.7%	1.5
	31,500	34%	59%	8.1%	1.7

238 [1]An example calculation is shown in Text S3.

Table S16. Percent recovery and error for five selected bromoform calibration curve points and surrogate standard recovery

Spiked Conc. (µg/L)	Calculated Conc. (µg/L)	% Recovery	% Error	Spiked Surrogate Conc. (µg/L)	Calculated Surrogate Conc. (µg/L)	% Surrogate Recovery
2.519	2.568	101.97%	-1.97%	10	10.237	102.37%
5.037	5.237	103.96%	-3.96%	10	9.402	94.02%
15.111	15.297	101.23%	-1.23%	10	9.554	95.54%
50.370	50.221	99.70%	0.30%	10	10.573	105.73%
100.740	100.783	100.04%	-0.04%	10	9.848	98.48%

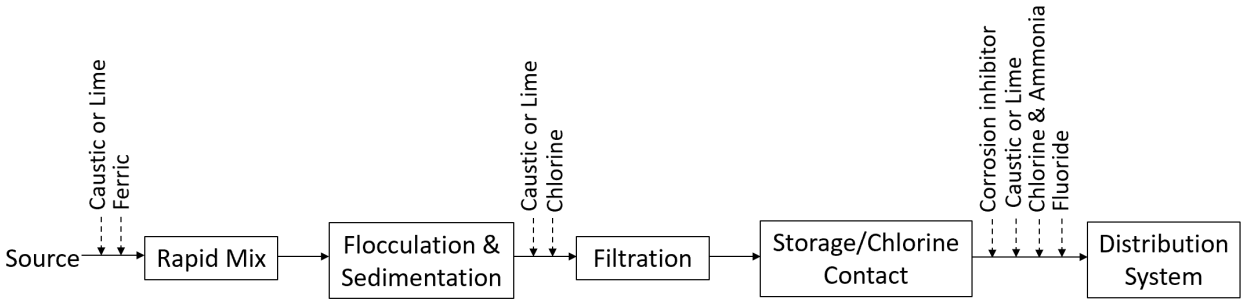


Figure S1. Process flow diagram of the water treatment plant (WTP)

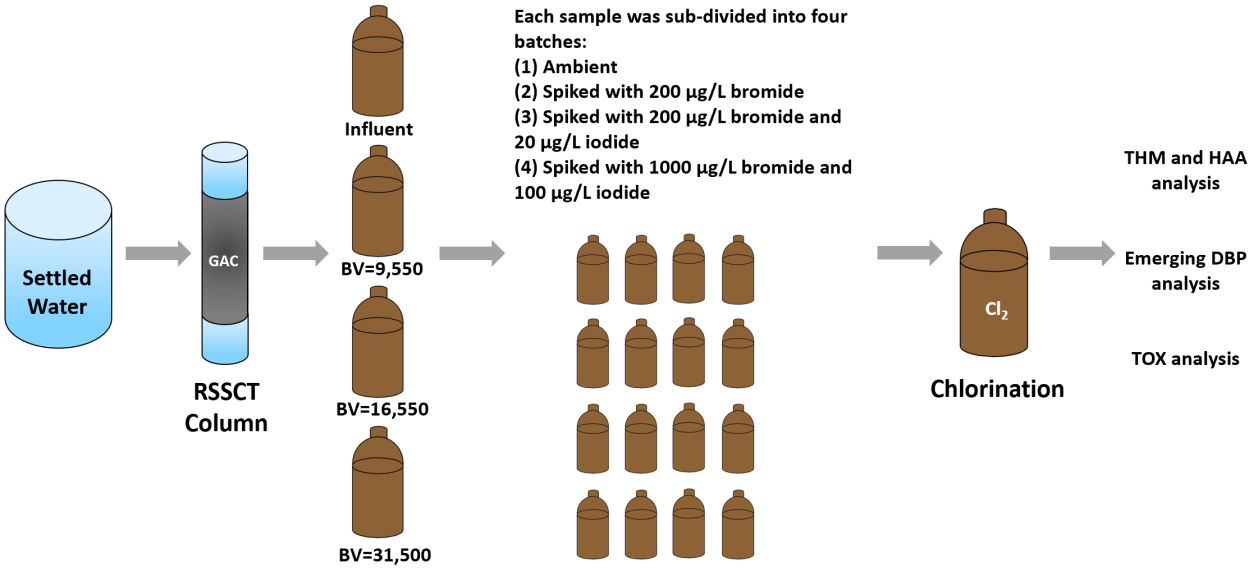


Figure S2. Experimental workflow

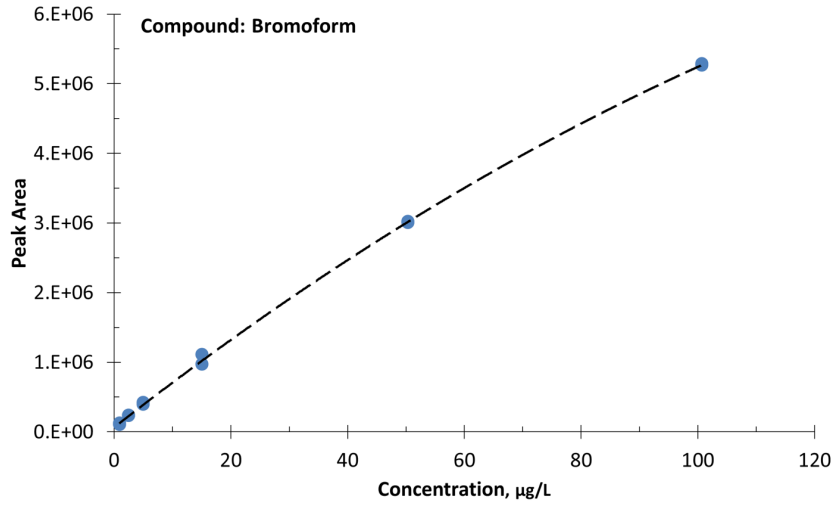


Figure S3. Calibration curve for bromoform using EPA Method 551.1 by gas chromatography analysis.

Percent recovery and error for five selected bromoform calibration curve points and surrogate standard recovery is shown in Table S16.

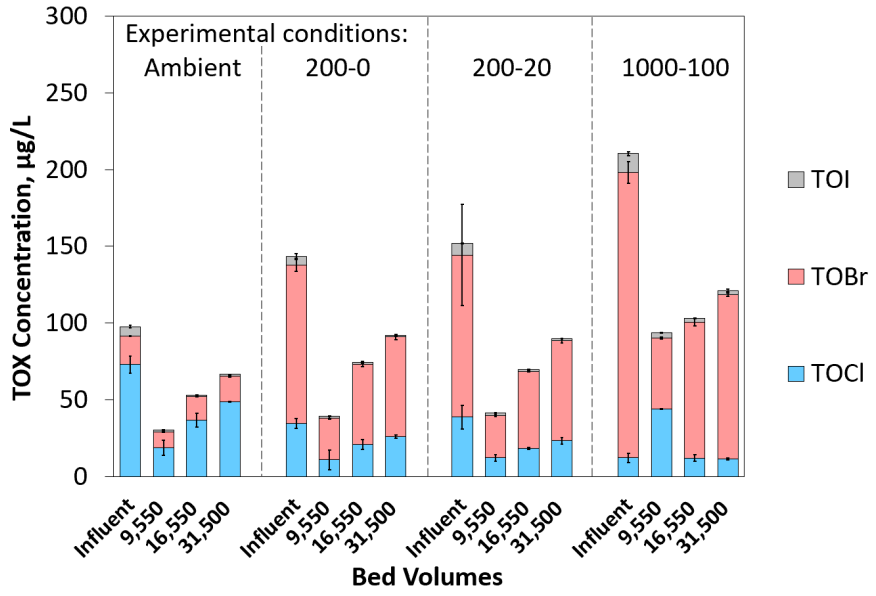


Figure S4. Effect of bromide and iodide on speciated total organic halogen (TOX) formation in chlorinated GAC influent and effluent. Results for GAC effluent are shown after treatment of indicated number of bed volumes. Error bars represent standard deviations of duplicate measurements.

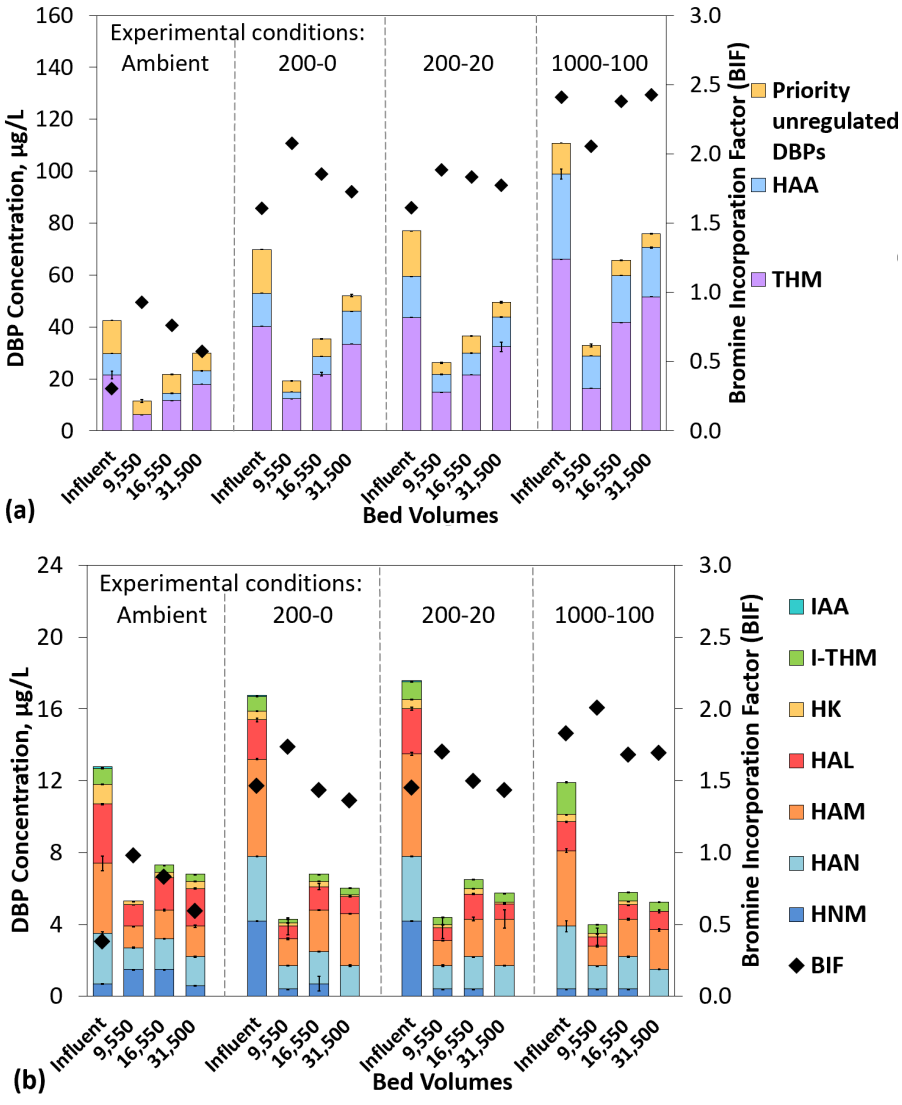


Figure S5. Effect of bromide and iodide on the formation of (a) total targeted DBPs and (b) priority unregulated DBPs (i.e. IAA, I-THM, HK, HAL, HAM, HAN, and HNM) in chlorinated GAC influent and effluent.

BIF values are indicated by black diamonds. Results for GAC effluent are shown after treatment of indicated number of bed volumes. Error bars represent standard deviations of duplicate measurements.

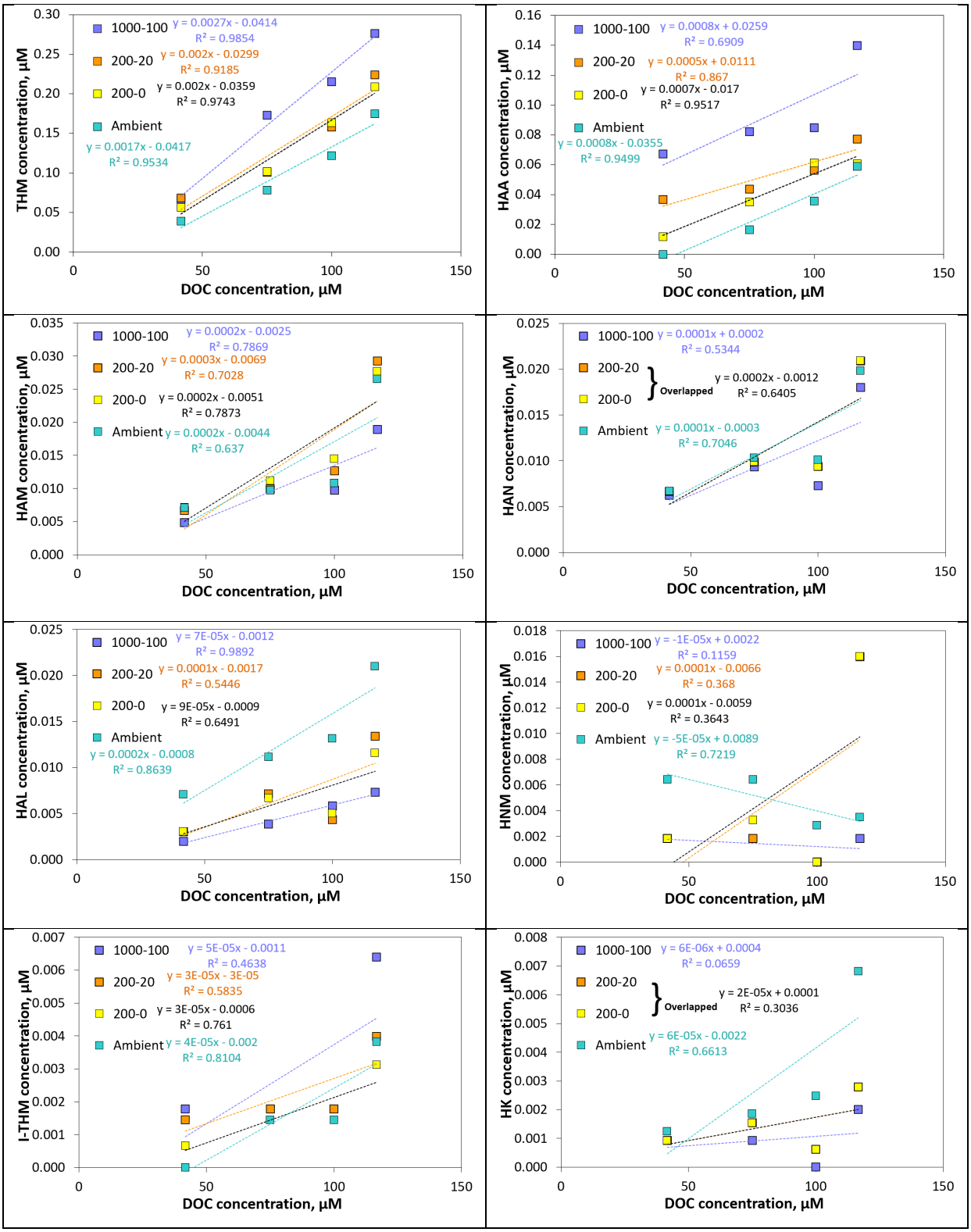


Figure S6. Effect of DOC concentration on DBP formation in GAC influent and effluent at four tested bromide and iodide levels. DOC concentrations correspond to the GAC influent and GAC effluent collected at bed volumes of 9,550, 16,550, and 31,500 BV

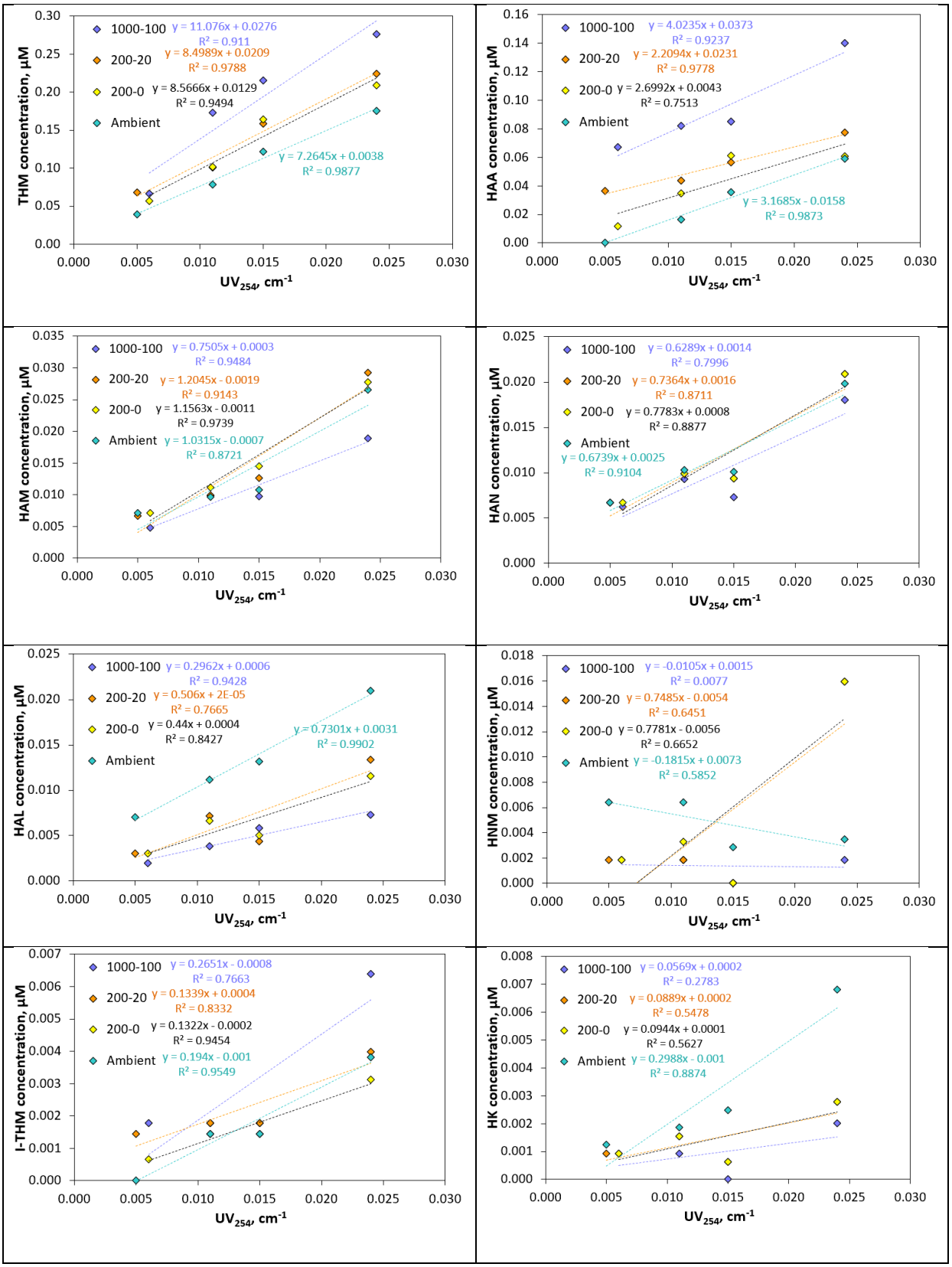

THM concentration, µM
1000-100 y = 11.076x + 0.0276 R² = 0.911
200-20 y = 8.4989x + 0.0209 R² = 0.9788
200-0 y = 8.5666x + 0.0129 R² = 0.9494
Ambient y = 7.2645x + 0.0038 R² = 0.9877
HAA concentration, µM
1000-100 y = 4.0235x + 0.0373 R² = 0.9237
200-20 y = 2.2094x + 0.0231 R² = 0.9778
200-0 y = 2.6992x + 0.0043 R² = 0.7513
Ambient y = 3.1685x - 0.0158 R² = 0.9873
HAM concentration, µM
1000-100 y = 0.7505x + 0.0003 R² = 0.9484
200-20 y = 1.2045x - 0.0019 R² = 0.9143
200-0 y = 1.1563x - 0.0011 R² = 0.9739
Ambient y = 1.0315x - 0.0007 R² = 0.8721
HAN concentration, µM
1000-100 y = 0.6289x + 0.0014 R² = 0.7996
200-20 y = 0.7364x + 0.0016 R² = 0.8711
200-0 y = 0.7783x + 0.0008 R² = 0.8877
Ambient y = 0.6739x + 0.0025 R² = 0.9104
HAL concentration, µM
1000-100 y = 0.2962x + 0.0006 R² = 0.9428
200-20 y = 0.506x + 2E-05 R² = 0.7665
200-0 y = 0.44x + 0.0004 R² = 0.8427
Ambient y = 0.7301x + 0.0031 R² = 0.9902
HNM concentration, µM
1000-100 y = -0.0105x + 0.0015 R² = 0.0077
200-20 y = 0.7485x - 0.0054 R² = 0.6451
200-0 y = 0.7781x - 0.0056 R² = 0.6652
Ambient y = -0.1815x + 0.0073 R² = 0.5852
I-THM concentration, µM
1000-100 y = 0.2651x - 0.0008 R² = 0.7663
200-20 y = 0.1339x + 0.0004 R² = 0.8332
200-0 y = 0.1322x - 0.0002 R² = 0.9454
Ambient y = 0.194x - 0.001 R² = 0.9549
HK concentration, µM
1000-100 y = 0.0569x + 0.0002 R² = 0.2783
200-20 y = 0.0889x + 0.0002 R² = 0.5478
200-0 y = 0.0944x + 0.0001 R² = 0.5627
Ambient y = 0.2988x - 0.001 R² = 0.8874
UV254, cm-1

Figure S7. Effect of UV_{254} on DBP formation in GAC influent and effluent at four tested bromide and iodide levels. UV_{254} correspond to the GAC influent and GAC effluent collected at bed volumes of 9,550, 16,550, and 31,500 BV

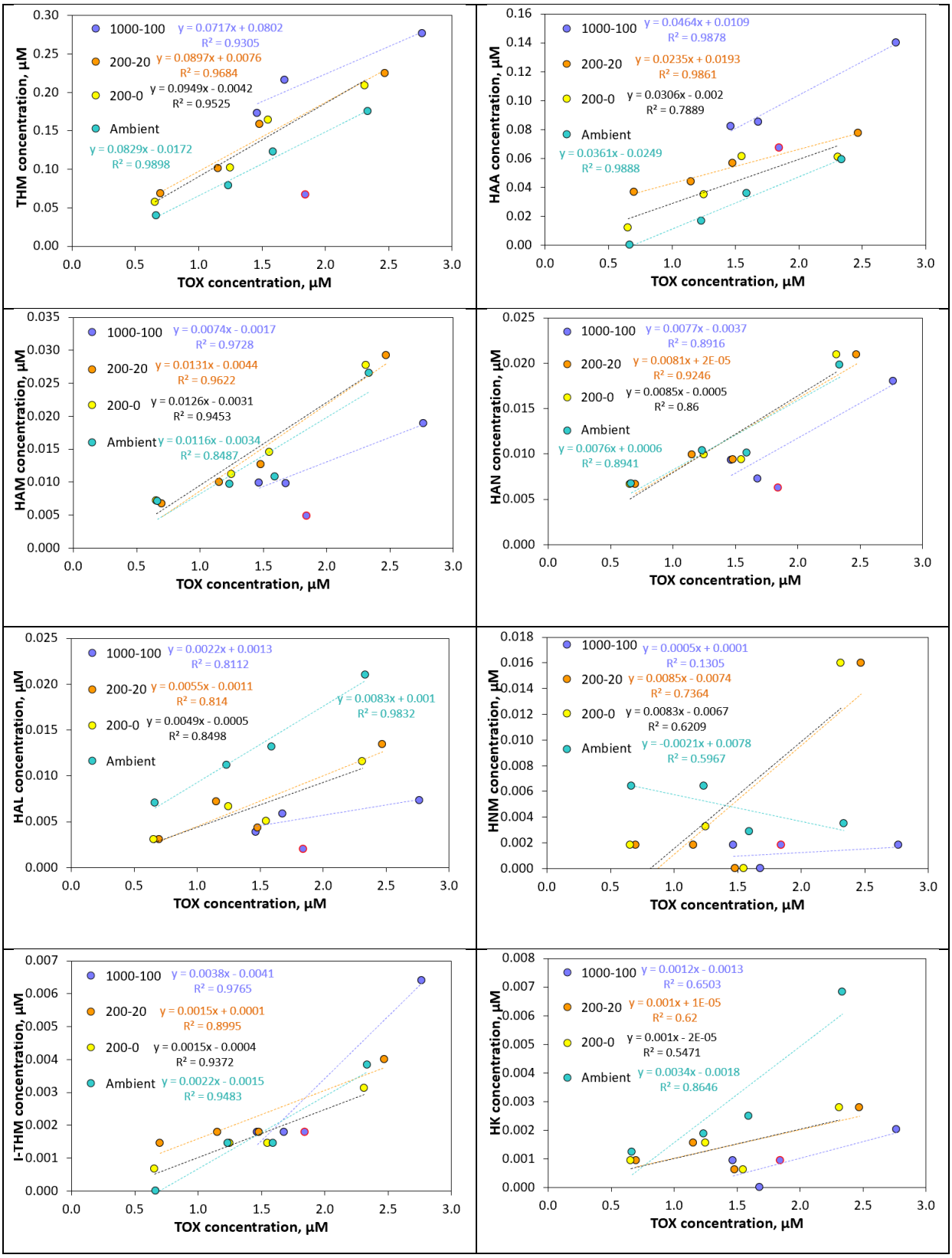

THM concentration, µM
TOX concentration, µM
1000-100 y = 0.0717x + 0.0802 R² = 0.9305
200-20 y = 0.0897x + 0.0076 R² = 0.9684
200-0 y = 0.0949x - 0.0042 R² = 0.9525
Ambient y = 0.0829x - 0.0172 R² = 0.9898
HAA concentration, µM
1000-100 y = 0.0464x + 0.0109 R² = 0.9878
200-20 y = 0.0235x + 0.0193 R² = 0.9861
200-0 y = 0.0306x - 0.002 R² = 0.7889
Ambient y = 0.0361x - 0.0249 R² = 0.9888
HAM concentration, µM
1000-100 y = 0.0074x - 0.0017 R² = 0.9728
200-20 y = 0.0131x - 0.0044 R² = 0.9622
200-0 y = 0.0126x - 0.0031 R² = 0.9453
Ambient y = 0.0116x - 0.0034 R² = 0.8487
HAN concentration, µM
1000-100 y = 0.0077x - 0.0037 R² = 0.8916
200-20 y = 0.0081x + 2E-05 R² = 0.9246
200-0 y = 0.0085x - 0.0005 R² = 0.86
Ambient y = 0.0076x + 0.0006 R² = 0.8941
HAL concentration, µM
1000-100 y = 0.0022x + 0.0013 R² = 0.8112
200-20 y = 0.0055x - 0.0011 R² = 0.814
200-0 y = 0.0049x - 0.0005 R² = 0.8498
Ambient y = 0.0083x + 0.001 R² = 0.9832
HNM concentration, µM
1000-100 y = 0.0005x + 0.0001 R² = 0.1305
200-20 y = 0.0085x - 0.0074 R² = 0.7364
200-0 y = 0.0083x - 0.0067 R² = 0.6209
Ambient y = -0.0021x + 0.0078 R² = 0.5967
I-THM concentration, µM
1000-100 y = 0.0038x - 0.0041 R² = 0.9765
200-20 y = 0.0015x + 0.0001 R² = 0.8995
200-0 y = 0.0015x - 0.0004 R² = 0.9372
Ambient y = 0.0022x - 0.0015 R² = 0.9483
HK concentration, µM
1000-100 y = 0.0012x - 0.0013 R² = 0.6503
200-20 y = 0.001x + 1E-05 R² = 0.62
200-0 y = 0.001x - 2E-05 R² = 0.5471
Ambient y = 0.0034x - 0.0018 R² = 0.8646

Figure S8. Correlations between DBP and TOX formation in GAC influent and effluent at four tested bromide and iodide levels. TOX concentrations correspond to the GAC influent and GAC effluent collected at bed volumes of 9,550, 16,550, and 31,500 BV. Sample collected at BV=9550 for 1000-100 sample is excluded from the correlation for all DBPs.

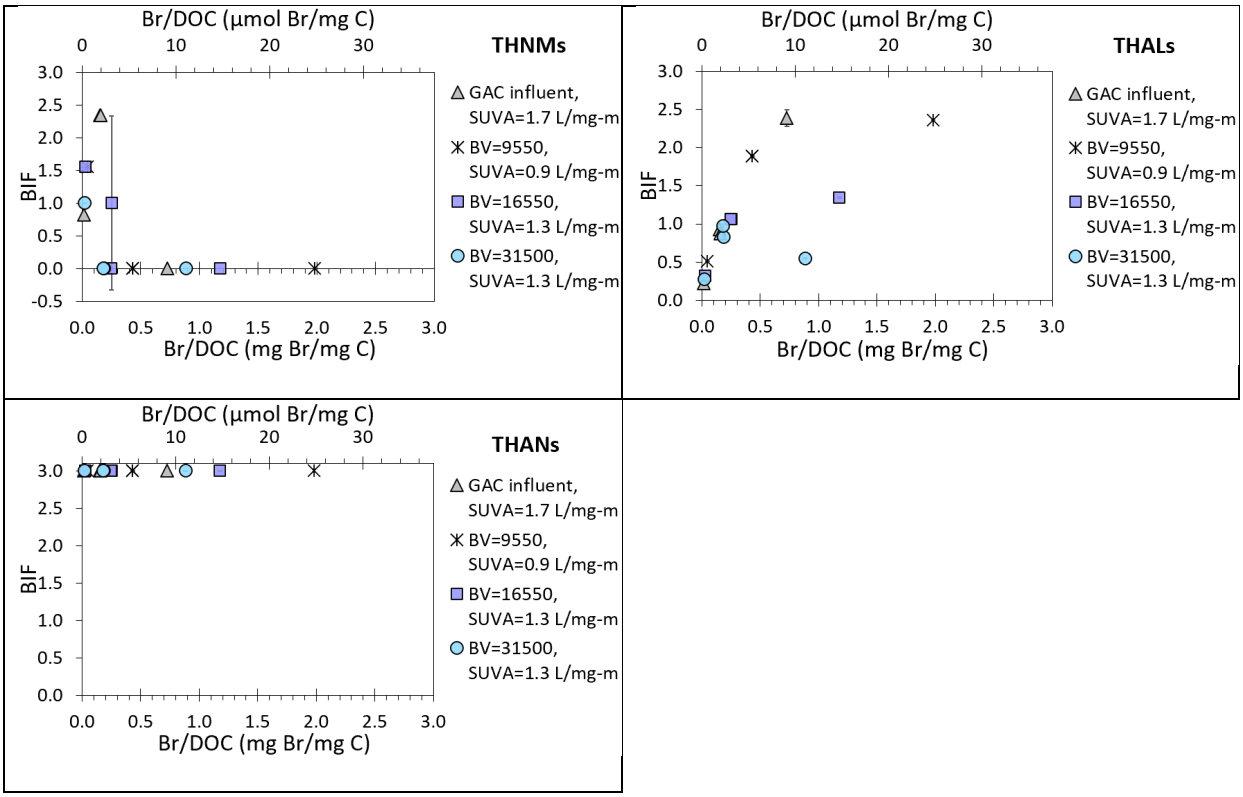


Figure S9. Impact of bromide/DOC concentration ratio on bromine incorporation factor (BIF) for trihalogenated DBPs (THNMs, THALs, and THANs).

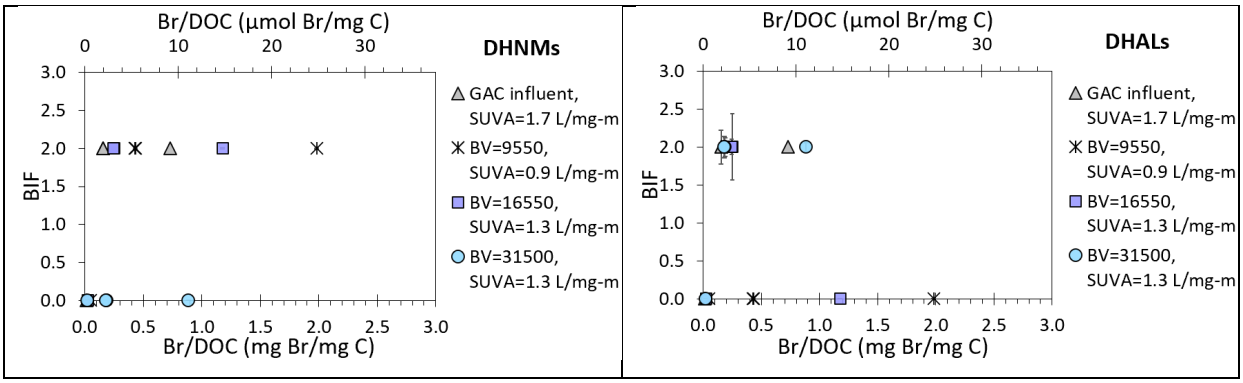


Figure S10. Impact of bromide/DOC concentration ratio on bromine incorporation factor (BIF) for dihalogenated DBPs (DHNMs and DHALs).

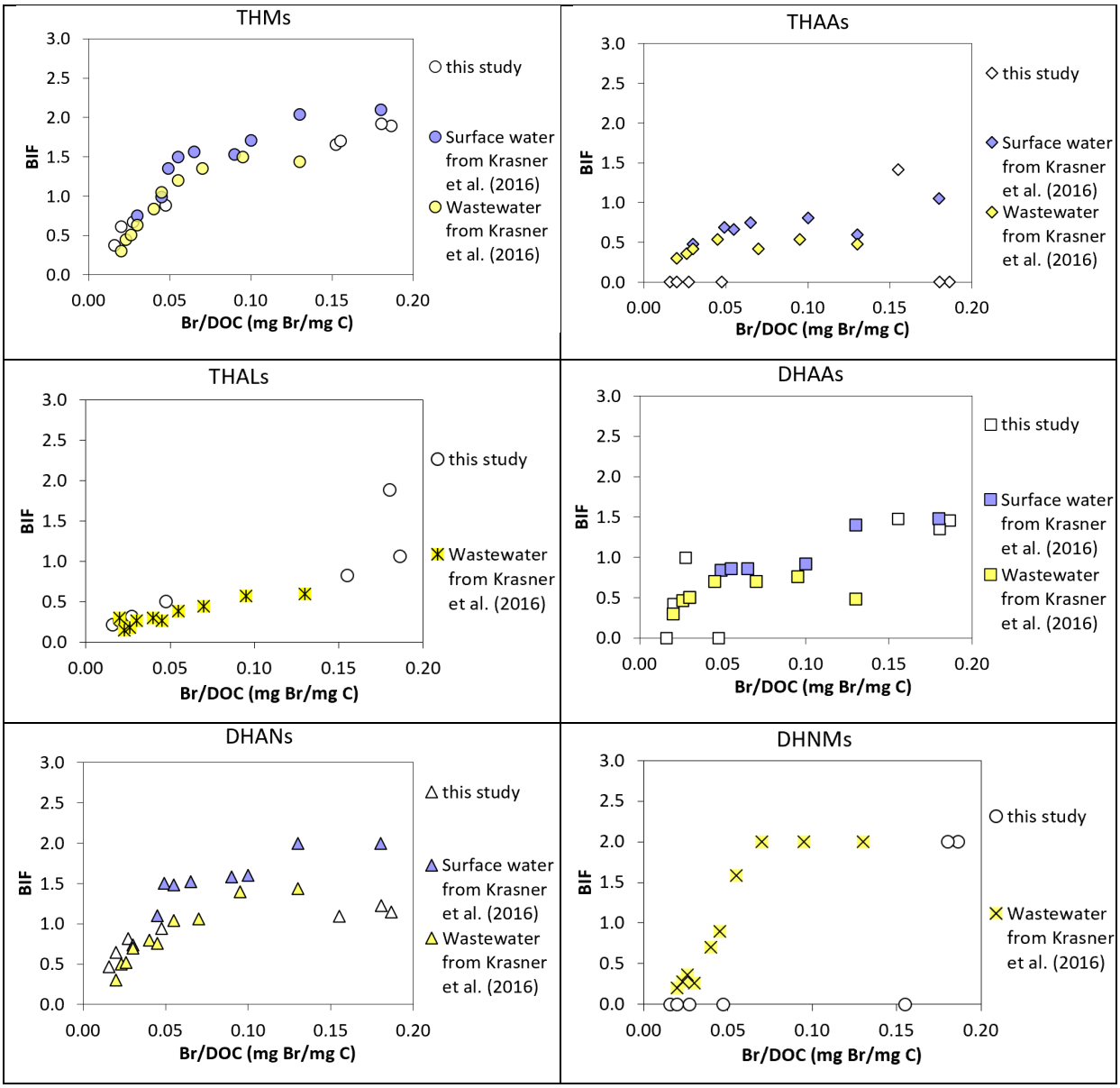
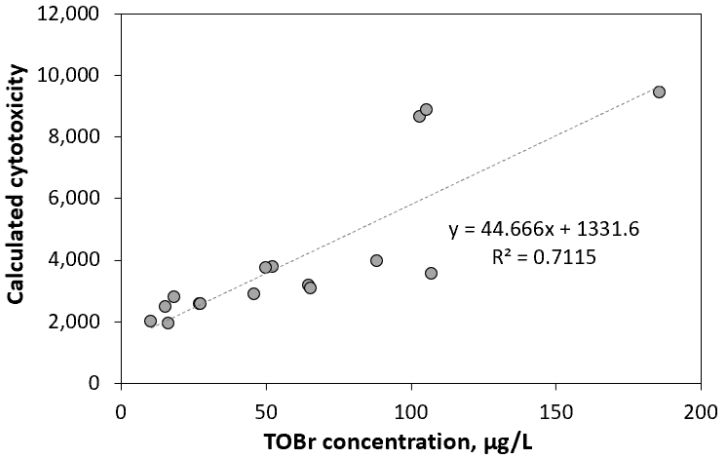


Figure S11. Impact of bromide/DOC concentration ratio on bromine incorporation factor (BIF) for THMs, THAAs, THALs, DHAAs, DHANs, and DHNMs in our study and Krasner et al. (2016).

In our study, DOC = 1.4 mg/L, UV_{254} = 0.024 cm^{-1}, SUVA = 1.7 L/mg-m for GAC influent.

In Krasner et al. (2016),(2) DOC = 3.0 mg/L, UV_{254} = 0.045 cm^{-1}, SUVA = 1.5 L/mg-m for GAC influent of surface water.

In Krasner et al. (2016),(2) DOC = 5.7 mg/L, UV_{254} = 0.121 cm^{-1}, SUVA = 2.1 L/mg-m for GAC influent of wastewater.



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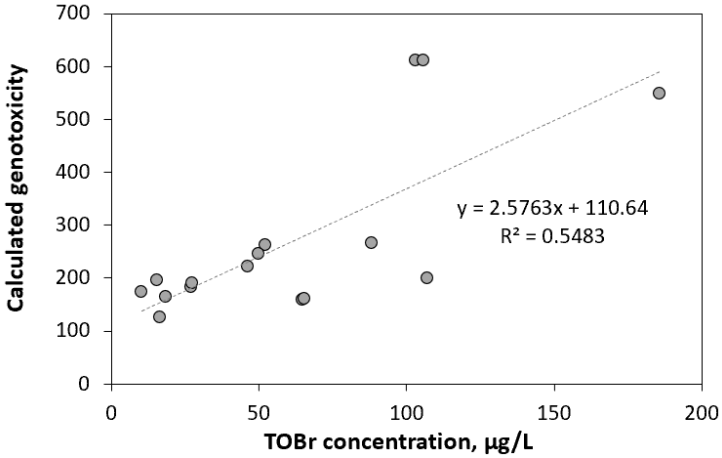

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308 **Figure S12.** Correlations between calculated toxicity and TOBr concentration in GAC influent
309 and effluent at four tested bromide and iodide levels.

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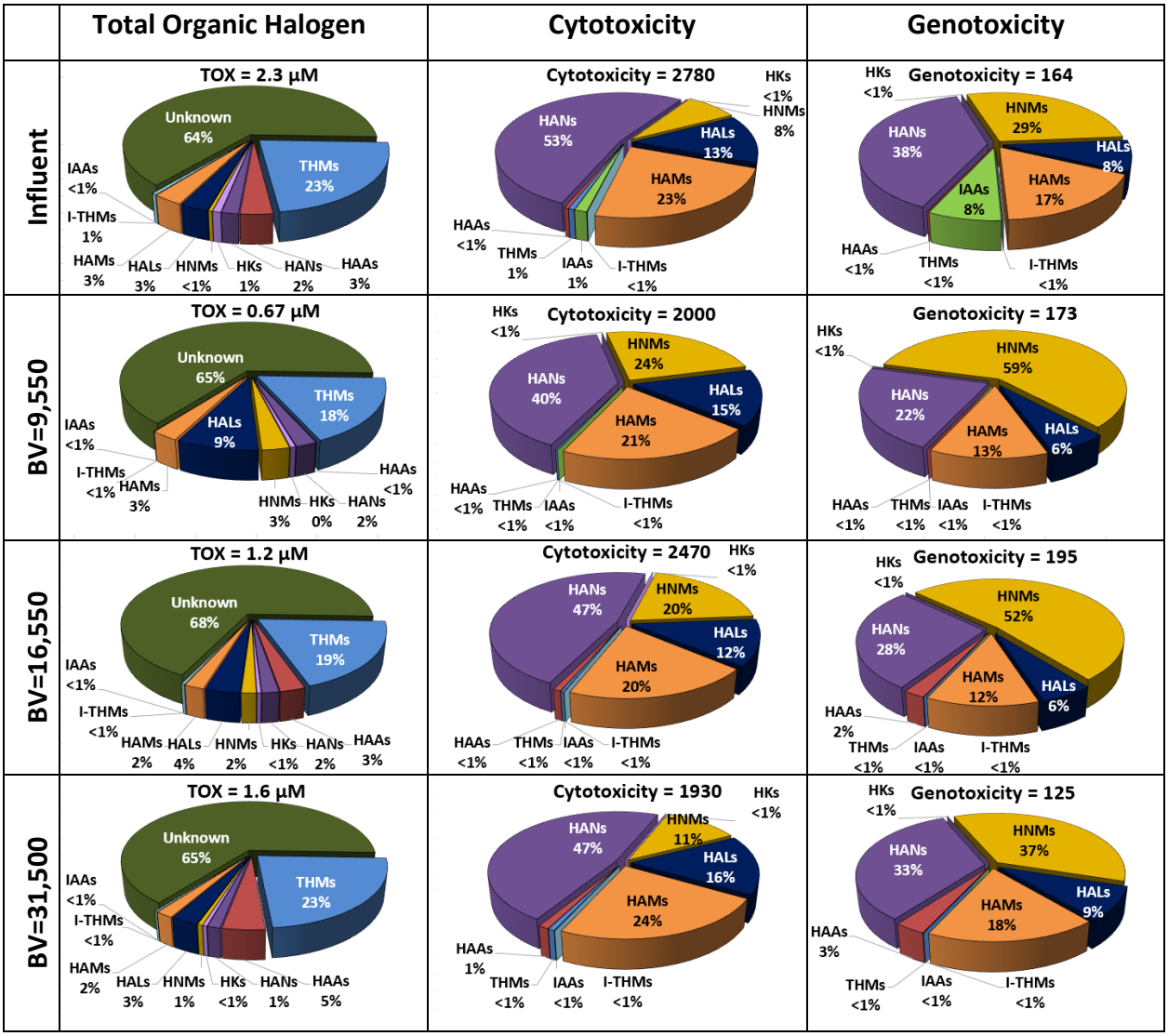

Figure S13. Contributions of individual DBP classes to TOX, calculated cytotoxicity, and calculated genotoxicity in GAC influent and effluent samples at three tested bed volumes (BVs). Bromide and iodide concentrations spiked into water samples before chlorination were 0 µg/L and 0 µg/L, respectively (ambient condition).

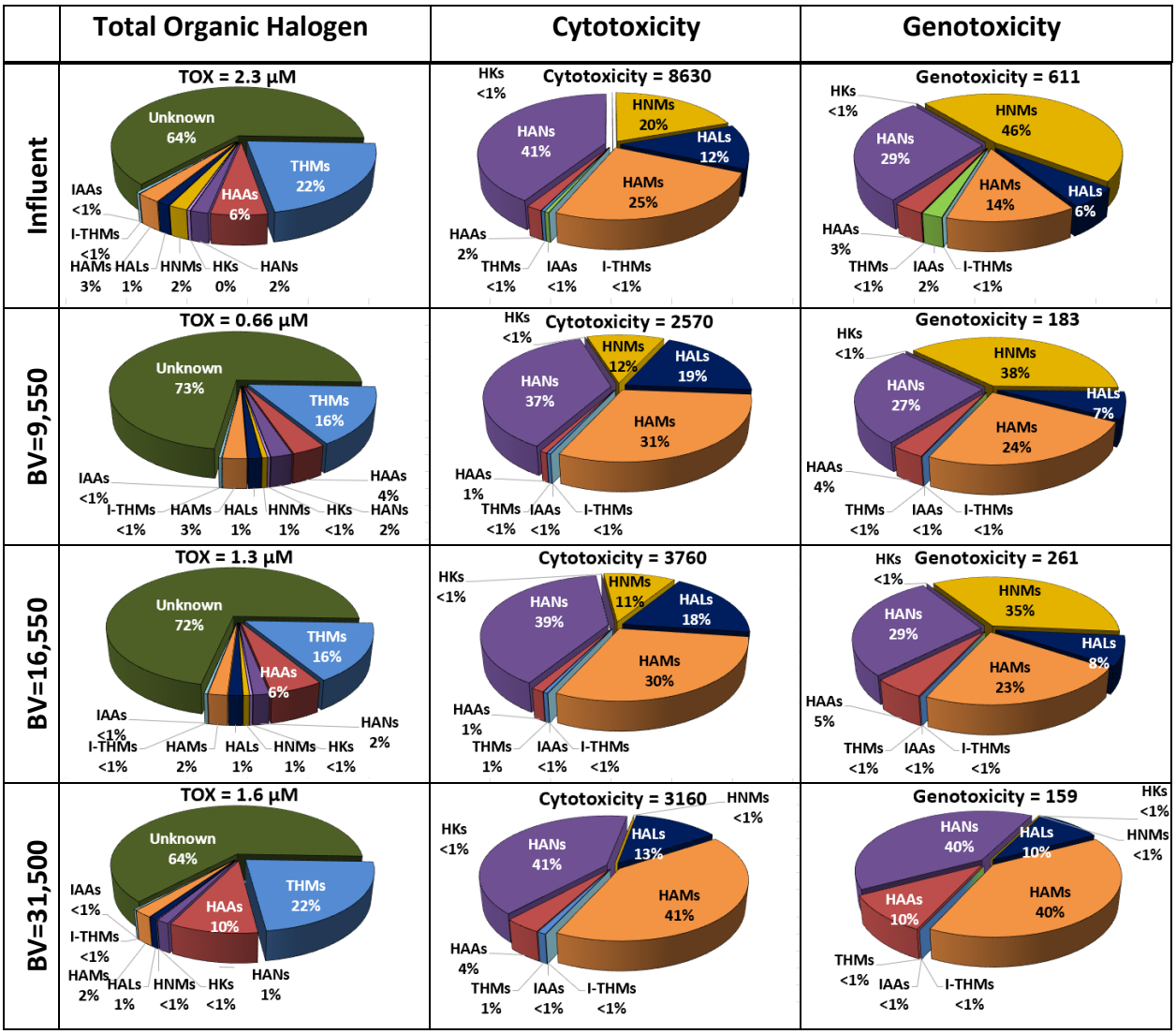

Figure S14. Contributions of individual DBP classes to TOX, calculated cytotoxicity, and calculated genotoxicity in GAC influent and effluent samples at three tested bed volumes (BVs). Bromide and iodide concentrations spiked into water samples before chlorination were 200 µg/L and 0 µg/L, respectively (200-0 condition).

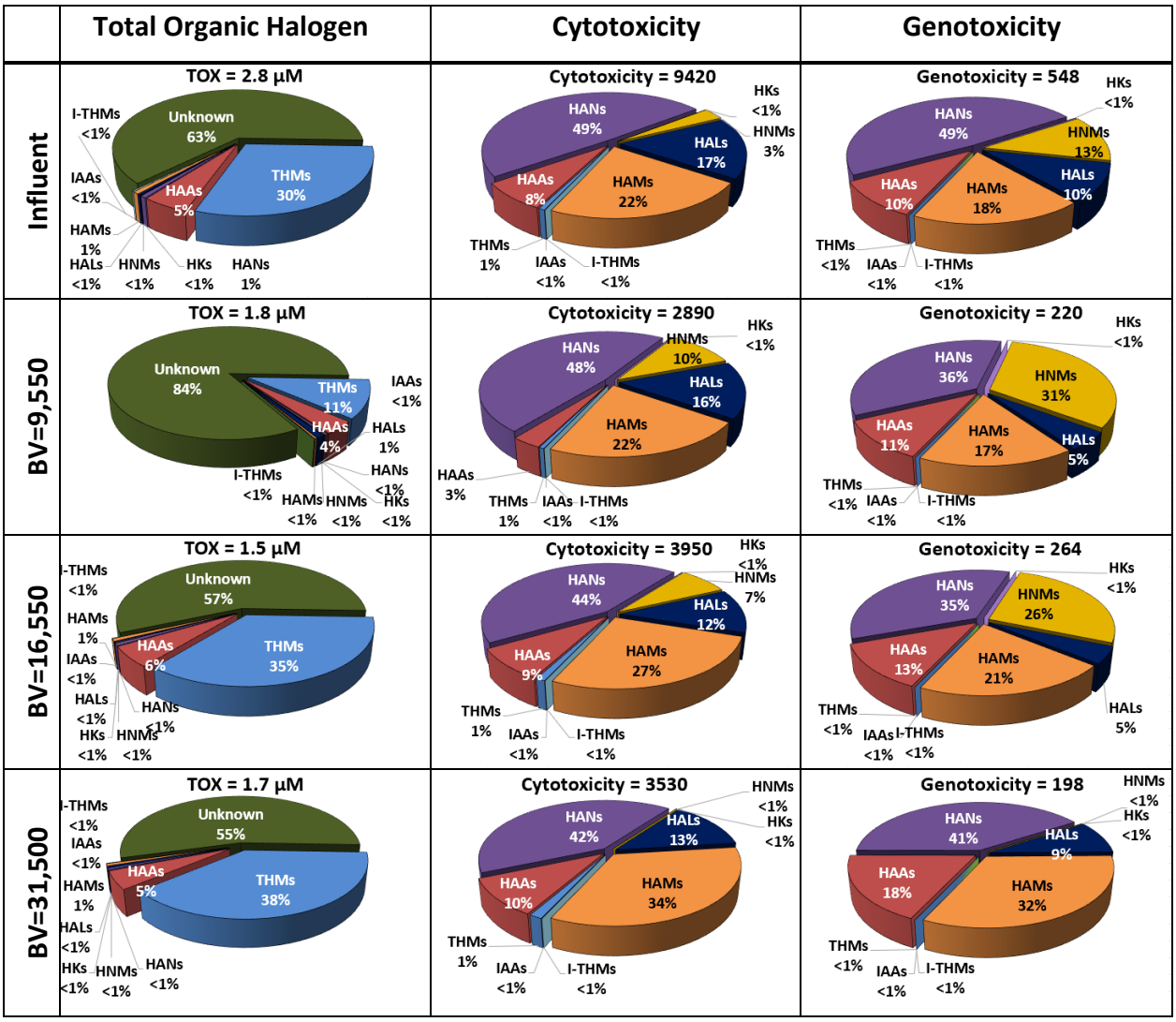

Figure S15. Contributions of individual DBP classes to TOX, calculated cytotoxicity, and calculated genotoxicity in GAC influent and effluent samples at three tested bed volumes (BVs). Bromide and iodide concentrations spiked into water samples before chlorination were 1000 µg/L and 100 µg/L, respectively (1000-100 condition).

327 **Reference**

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