Supplementary Information for:

Evaluating and modeling the activated carbon adsorption of wastewater-derived *N*-Nitrosodimethylamine precursors

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Table SI-1. RSSCT column properties for simulated 10- and 20-minute EBCTs.

	10-minute column	**20-minute column**
Carbon used:	HD3000	HD3000
Simulated full-scale EBCT (min):	10	20
Actual bench-scale EBCT (min):	0.84	1.68
Bench-scale column bed length (cm):	9.45	18.91
Full-scale particle diameter (mm):	1.29 (8x30 mesh)	
Bench-scale particle diameter (mm):	0.11 (100x200 mesh)	
Scaling factor:	11.88	
Bench-scale column aspect ratio:	44	
Bench-scale flow rate (mL/min):	2.00	
Bench-scale hydraulic loading rate (m/hr):	6.74	
Bench-scale Reynolds number:	0.6	

Ground carbon was loaded into 4.76 mm inside-diameter Teflon columns at different bed lengths for columns with simulated 10- and 20-minute EBCTs and run in parallel. A Cole-Parmer Masterflex 7521-40 pump driver and 7090-62 Teflon diaphragm pump head circulated water through the system.

Table SI-2. Comparison of raw water DBP formation values for different batches under FP and UFC conditions using monochloramine and free chlorine. Concentration in µg/L, yield in µg/mg, ± 1 standard deviation from duplicate trials.

Batch		**WW-Jun**	**WW-Oct**	**WW-Dec**	**DW-Dec**
Monochloramine FP					
NDMA		**0.960**	**0.590**	**0.747 ± 0.012**	**0.017**
	yield	0.17	0.11	0.13 ± 0.03	0.017
TTHM		**29.1 ± 3.7**	**33.4 ± 3.2**	**63.4**	**23.3**
	yield	5.1 ± 0.5	6.2 ± 0.5	11	23
HAA5		**47.0 ± 12.5**	**40.0 ± 0.2**	**85.0**	**19.8**
	yield	8.2 ± 2.4	7.5 ± 0.1	15	19
HAA9		**60.3 ± 19**	**48.2 ± 0.13**	**93.9**	**24.1**
	yield	11 ± 3.7	9.0 ± 0.1	16	24
HAN		**7.90 ± 2.7**	**7.07 ± 0.38**	**14.3**	**3.16**
	yield	1.4 ± 0.5	1.3 ± 0.1	2.5	3.1
Free chlorine FP					
TTHM		**739 ± 63**	**686 ± 14**	-	-
	yield	128 ± 7.6	128 ± 0.7		
HAA5		**489 ± 3.7**	**454**	-	-
	yield	85 ± 2.9	86		
HAA9		**625 ± 23**	**577**	-	-
	yield	109 ± 6.8	109		
Monochloramine UFC					
NDMA		**0.260**	**0.420**	-	-
	yield	0.046	0.079		
TTHM		**9.68**	**2.69**	**3.79**	**4.15**
	yield	1.7	0.49	0.61	4.1
HAA5		**3.40**	**13.8**	**11.5**	**4.80**
	yield	0.60	2.5	1.8	4.7
HAA9		**3.37**	**16.2**	**12.7**	**7.78**
	yield	0.60	3.0	2.0	7.6
HAN		**0.502**	**0.910**	**0.305**	**0.229**
	yield	0.09	0.17	0.050	0.22
Free chlorine UFC					
TTHM		**291**	**237**	-	-
	yield	52	44		
HAA5		**150**	**162**	-	-
	yield	27	30		
HAA9		**219**	**239**	-	-
	yield	39	44		
HAN		**34.3**	**25.9**	-	-
	yield	6.1	4.7		

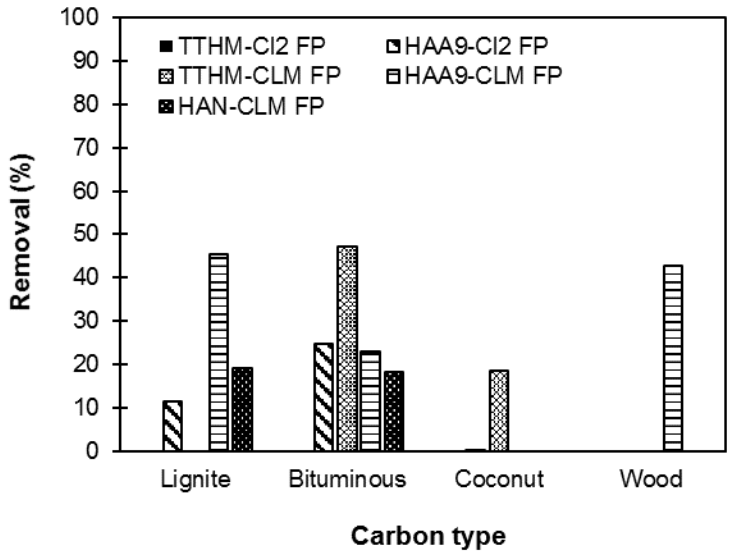

Figure SI-1. Batch TTHM FP, HAA9 FP, and HAN FP removals under chlorination (Cl2) and chloramination (CLM) conditions using four carbon types at 5 mg/L PAC dose.

Table SI-3. Molal volumes, diffusivities and functional diameters in water of select pharmaceuticals known to yield NDMA upon chloramination.

Pharmaceutical	Type	Molar mass (g/mol)	NDMA molar yield (%)	Molal volume (cm^3/g-mol)[d]	Diffusivity in water (cm^2/s)[e]	Functional diameter in water (Å)[f]
Ranitidine	Antacid and antihistamine	314.1	99 [a]	360.5	7.12E-06	6.0
Methadone	Narcotic	309.4	23-70 [b]	398.9	6.89E-06	6.2
Tetracycline	Antibiotic	444.4	23 [a]	414.9	6.80E-06	6.3
Doxylamine	Antihistamine	270.4	10 [a]	336.8	7.29E-06	5.9
Minocycline	Antibiotic	457.5	8.2 [c]	444.2	6.64E-06	6.5
Chlorpheniramine	Antihistamine	274.8	5.5 [a]	310.9	7.48E-06	5.7
Nizatidine	Antacid	331.5	5 [a]	375.8	7.03E-06	6.1
Carbinoxamine	Antihistamine	290.8	1 [a]	332.5	7.32E-06	5.9
Diphenhydramine	Antihistamine	255.4	0.3 [a]	317.5	7.43E-06	5.8

[a] Data from Shen and Andrews[1]
[b] Data from Hanigan et. al.[2]
[c] Data from Le Roux et. al.[3]
[d] Calculated using atomic volumes from Welty[4] and Perry and Chilton[5]
[e] Diffusivities calculated using Reddy-Doraiswamy correlation[6]
[f] Diameters calculated from Stokes-Einstein radius.

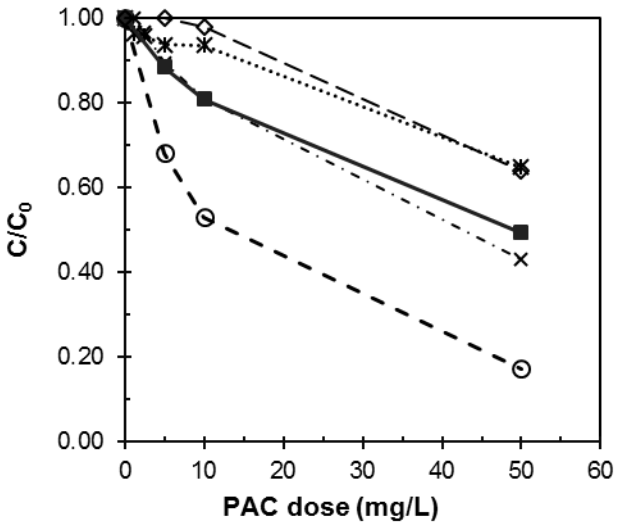

Figure SI-2. Lignite AC removal (HD3000) of chlorinated DBP precursors compared to DOM in WW-Jun. DOC = 5.8 mg/L, OFI = 1473. ····✳···· DOC; – ·✕· UVA; – ⊖ – OFI; —■— HAA9-Cl_2 FP; —◈— TTHM-Cl_2 FP**.**

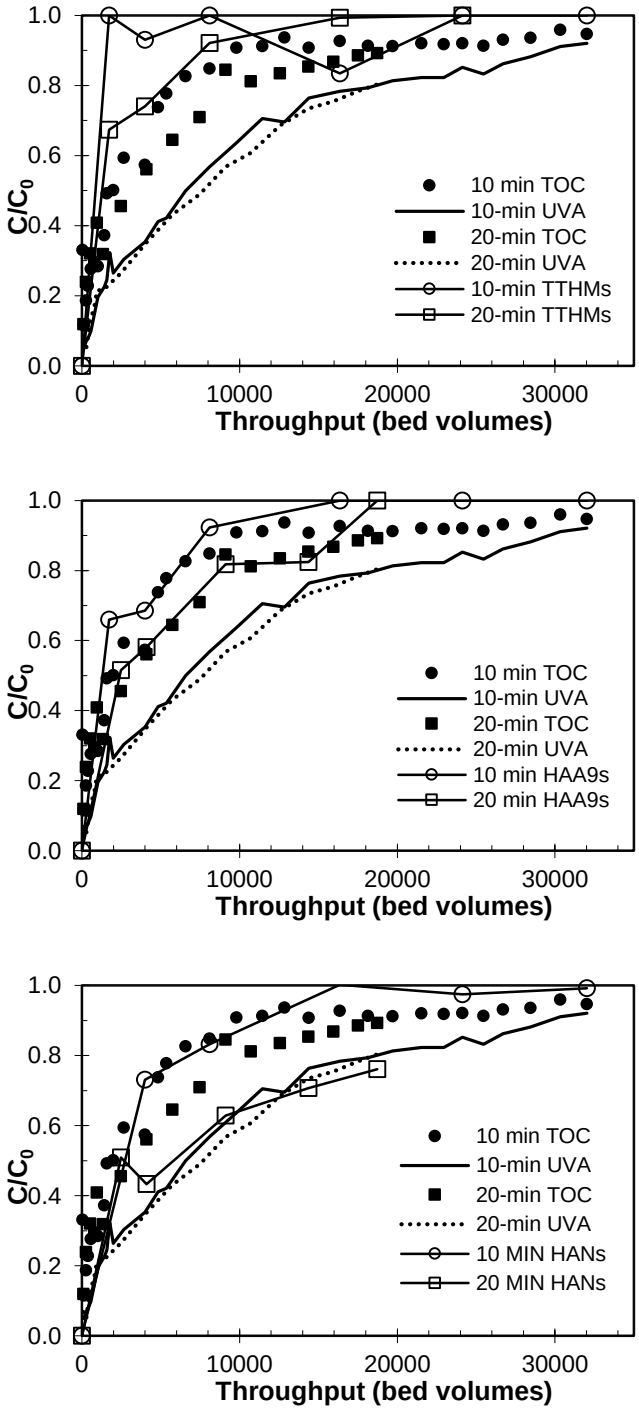

Figure SI-3. TTHM, HAA9, and HAN monochloramine FP breakthrough curves compared to TOC and UVA at 10- and 20-minute EBCTs. Influent TOC = 5.28 mg/L, UVA = 0.102 cm-1, TTHM FP = 33.4 µg/L, HAN FP = 7.07 µg/L, HAA9 FP = 48.2 µg/L.

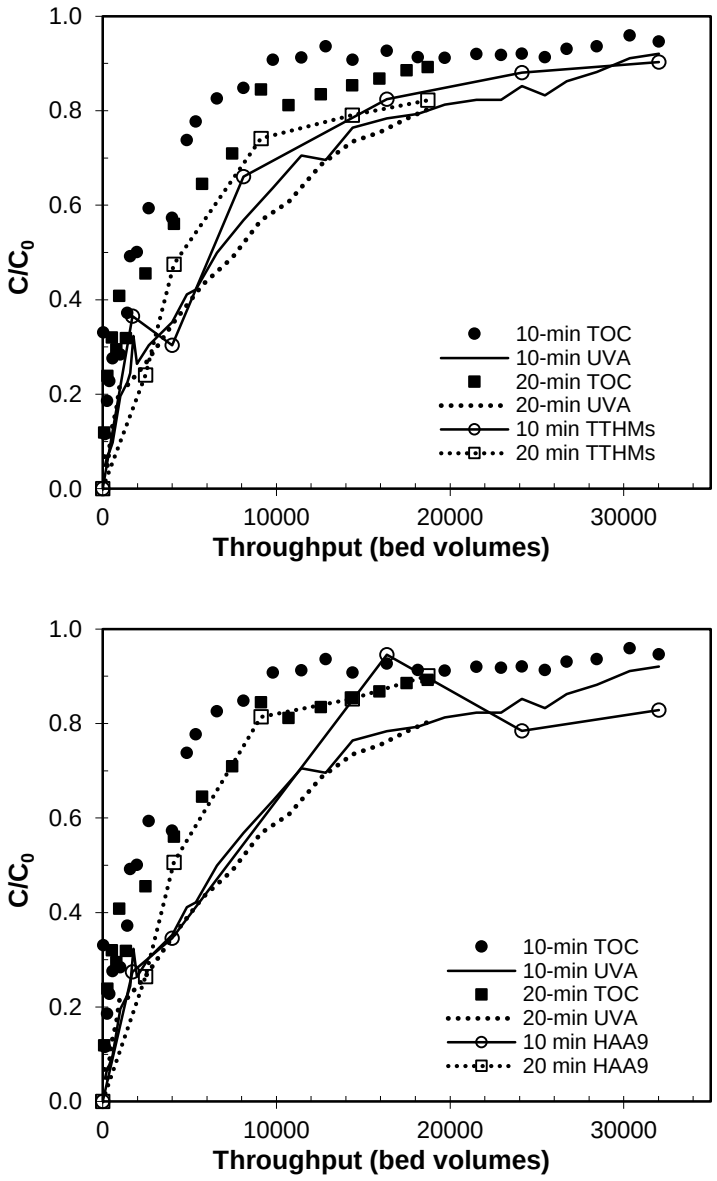

Figure SI-4. TTHM and HAA9 free chlorine formation potential breakthrough curves compared to TOC and UVA for 10 and 20 minute EBCTs. Raw water TOC = 5.28 mg/L, UVA = 0.102 cm-1, TTHM FP = 686 µg/L, HAA9 FP = 577 µg/L.

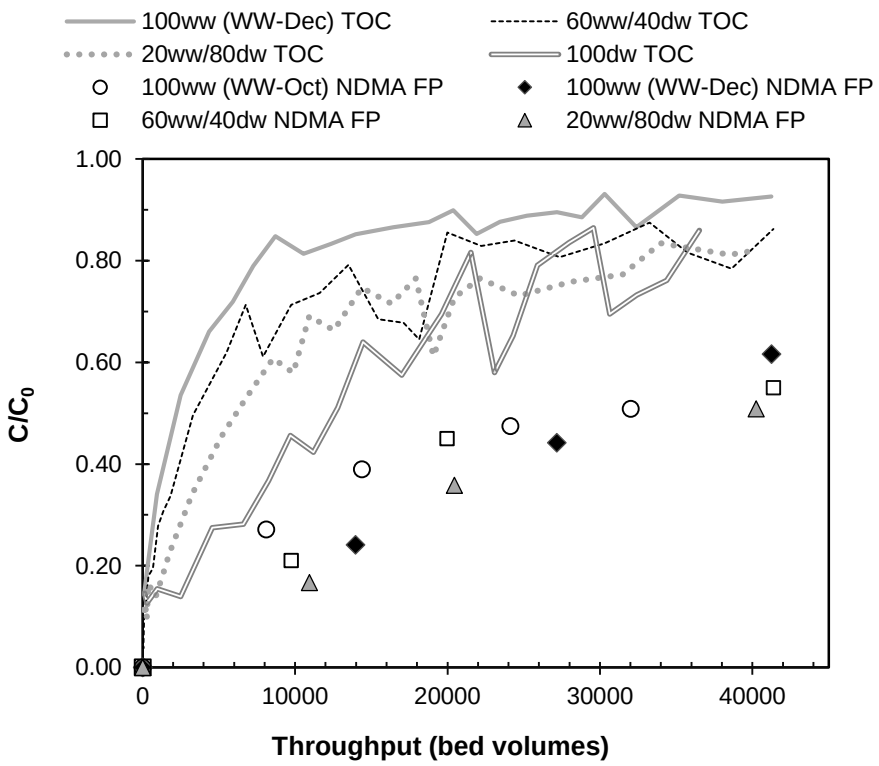

Figure SI-5. Normalized TOC and NDMA FP breakthrough for range of blended waters. 100ww (WW-Oct) NDMA FP = 590 ng/L, TOC = 5.28 mg/L; 100ww (WW-Dec) NDMA FP = 747 ng/L, TOC = 6.1 mg/L; 60ww/40dw NDMA FP = 400 ng/L, TOC = 4.1 mg/L; 20ww/80dw NDMA FP = 120 ng/L, TOC = 2.2 mg/L; 100dw NDMA FP = 37 ng/L, TOC = 1.0 mg/L.

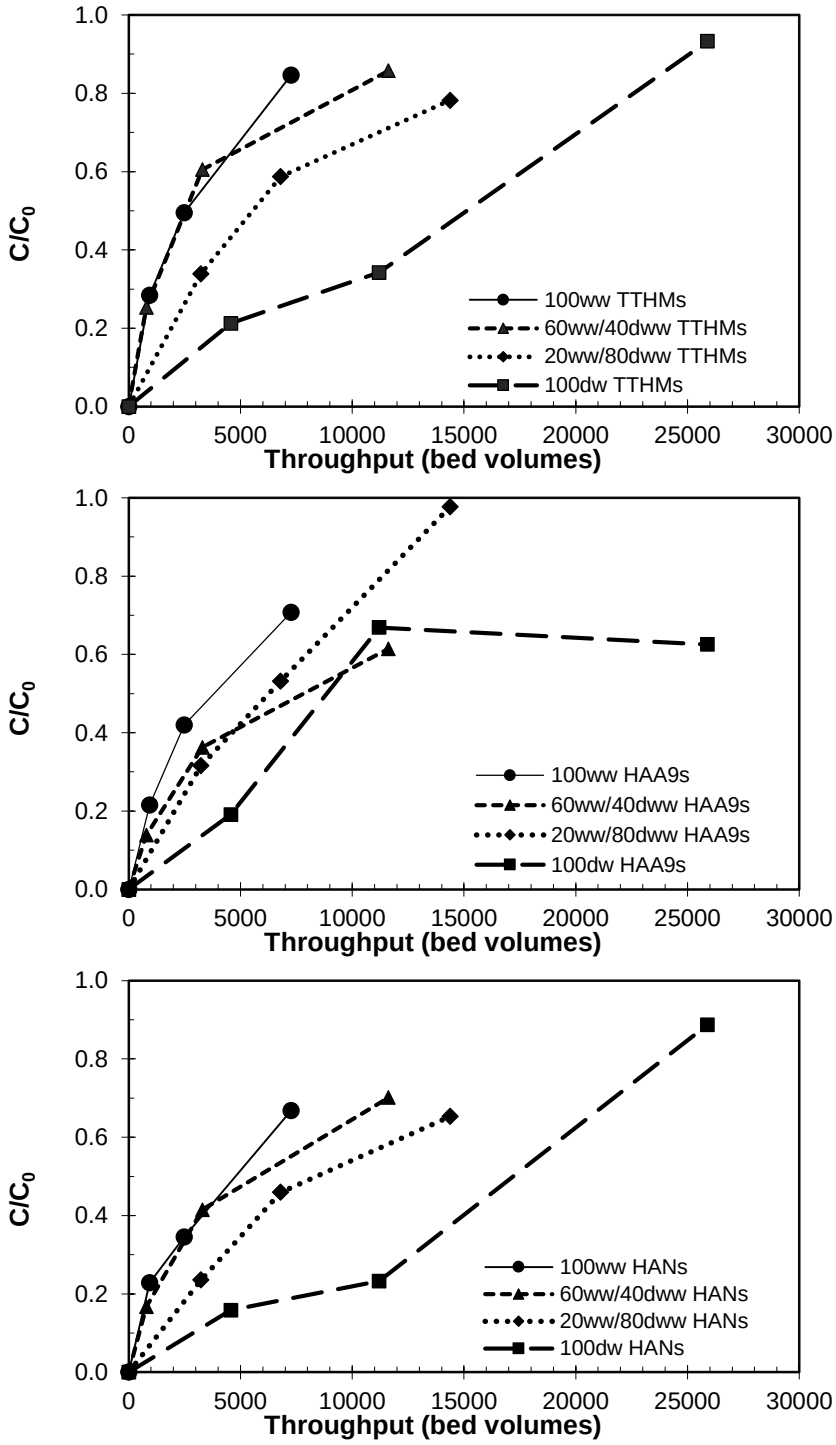

Figure SI-6. Breakthrough of chloraminated TTHM, HAA9, and HAN for varying wastewater content influents.

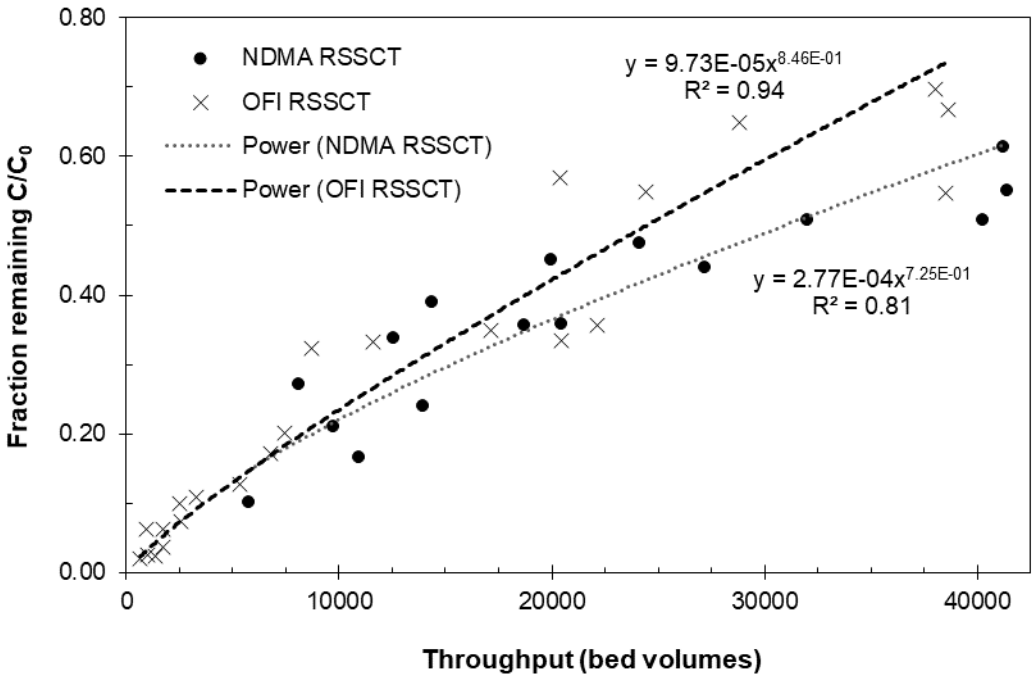

Figure SI-7. Normalized NDMA FP and OFI breakthrough data with effluent points from all bench-scale wastewater RSSCTs (blended and non-blended) considered together. Proposed power functions valid for TOC_0 = 2.2-6.1 mg/L, NDMA FP_0 = 120-747 ng/L, and OFI_0 = 316-1438 RU.

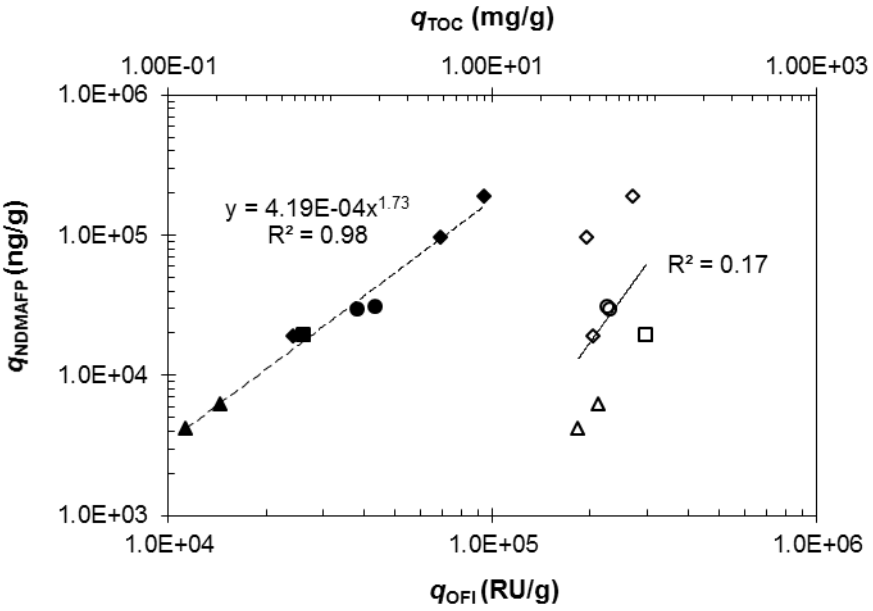

Figure SI-8. Correlation of GAC surface loading rates for OFI and TOC to NDMA FP. Solid symbols correspond to q_{OFI} on lower axis, hollow symbols correspond to q_{TOC} on upper axis. ♦ 100ww batch (WW-Jun); ● 100ww RSSCT (WW-Dec); ■ 60ww/40dw RSSCT; ▲ 20ww/80dw RSSCT; ----- q_{OFI} correlation; —— q_{TOC} correlation.

Fluorescence spectroscopy methods

Excitation and emission profiles (EEMs) were collected by measuring emission scans between 300 nm and 560 nm (at 2 nm increments), at excitation wavelengths every 10 nm between 250 nm and 450 nm using a 5 nm bandpass and 0.25 second integration time. EEMs were corrected and analyzed using MATLAB software (Mathworks, MA) in accordance with methods outlined by Korak and colleagues.[7] Inner filter corrections were made with a UV-Vis absorbance scan collected using a Cary-100 Spectrophotometer (Agilent Technologies, CA). Ultrapure 18.2 MΩ-cm blanks, Raman peaks, and lamp scans were collected before each fluorescence analysis and used during correction analysis and as instrument quality control measures.

FP and UFC testing procedure

All reagents used were certified ACS grade, supplied from Fisher Scientific. Only amber glassware was used for FP and UFC testing. Glassware was triple-rinsed with 18.2 MΩ-cm ultrapure water, heated to 550 degrees C for 3 hours, and cooled before use. Influent and batch test waters were filtered through a 1.2 µm glass filter before dosing.

All FP and UFC tests were performed at neutral pH and 23±1°C. Monochloramine FP tests were performed with fresh NH_2Cl solution prepared before each use. Laboratory grade NaOCl (5.65-6% w/v) was added to refrigerated, ultrapure 18.2 MΩ-cm water with dissolved ammonium chloride and adjusted to pH 9 with sodium hydroxide pellets. A stock concentration of 14 g/L was used during batch testing. The procedure was adjusted to use a 1.4 g/L stock solution during RSSCTs and pilot-testing since the lower stock solution was found to be more stable. NH_2Cl solution was used immediately. Samples were spiked with monochloramine to achieve 140 mg/L total chlorine as Cl_2 according to the stock strength used. Phosphate buffer prepared with equal parts mono- and di-basic sodium phosphates and adjusted to pH 7 was also added to the sample at a ratio of 1% volume by volume.

Free chlorine FP tests were performed using standard chlorine solution, prepared in advance by diluting NaOCl solution in ultrapure 18.2 MΩ-cm water and mixing with 1 molar borate buffer to achieve an initial 0.077 molar NaOCl solution. Chlorine concentration was tested before use and the solution was remade if the concentration dropped below 4000 mg/L as Cl_2. All chlorine samples were dosed at 1% volume by volume with no headspace.

A three day UFC test was performed as it was considered to be more representative of the distribution system conditions than the UFC 24 hour hold time. Monochloramine and chlorine solutions were prepared as outlined above. A three-day demand study was performed on each water for which a full UFC test was performed. Samples were then dosed accordingly, using the same procedure for chlorine and monochloramine.

Estimating molecular size from diffusivity

Molecular sizes were calculated using the following equations.

Reddy-Doraiswamy correlation[6] for diffusivity in water:

$D = 5.07 \times 10^{-5} {V_b}^{-1/3}$ (T = 20ºC)

where,

D = Diffusivity (cm^2/s)

V_b = Molal volume at normal boiling point (cm^3/g-mol)

Stokes-Einstein equation:

$$r = \frac{k_B T}{6\pi D\mu}$$

where,

r = molecular radius (cm)

k_B = Boltzmann's constant (1.38×10^{-16} cm^2-g-s^{-2}-K^{-1})

T = temperature (K)

μ = viscosity of water (0.01 g/s-cm)

Experimental methods RSD values

FP testing
The method RSD for NDMA FP (n=3) was approximately 2%. The average method RSD for TTHM, HAA9, and HAN FPs from duplicates on multiple waters (WW-Jun and WW-Oct) was less than 20% for chloramination and less than 10% for chlorination.

PAC batch testing
The method RSD for TOC based on duplicate measurements at the 5 mg/L dose across all carbons was approximately 5%. The method RSD for NDMAFP based on duplicate trials using HD3000 at the 5 mg/L dose was determined to be approximately 23%.

RSSCTs
Comparison of the WW-Oct and WW-Dec results yielded an evaluation of method reproducibility with an average RSD value of 3% for TOC when comparing BV_{20} and BV_{50} results. NDMA FP showed greater variation between wastewater runs with an average RSD value of 18%. This wider range of reproducibility for NDMA FP is expected due to additional random error contributions from FP testing and greater variability of influent NDMA precursor concentrations than influent TOC.

Literature Cited

1 R. Shen and S. a. Andrews, *Water Res.*, 2011, **45**, 944–952.

2 D. Hanigan, E. M. Thurman, I. Ferrer, Y. Zhao, S. Andrews, J. Zhang, P. Herckes and P. Westerhoff, *Environ. Sci. Technol. Lett.*, 2015, **2**, 151–157.

3 J. Le Roux, H. Gallard and J. P. Croué, *Water Res.*, 2011, **45**, 3164–3174.

4 J. R. Welty, C. E. Wicks and R. E. Wilson, *Fundamentals of Momentum, Heat, and Mass Transfer*, John Wiley & Sons Inc., New York, NY, 3rd edn., 1984.

5 R. H. Perry and C. H. Chilton, *Chemical Engineers' Handbook*, McGraw Hill, New York, NY, 1974.

6 K. A. Reddy and L. K. Doraiswany, *I&EC Fundam.*, 1967, **6**, 77–79.

7 J. A. Korak, A. D. Dotson, R. S. Summers and F. L. Rosario-Ortiz, *Water Res.*, 2014, **49**, 327–338.