Supplementary Information for:

Trihalomethane, Dihaloacetonitrile, and Total *N*-nitrosamine Precursor Adsorption by Modified Carbon Nanotubes (CNTs) and CNT Micropillars

Erin M. Needham [a], Justin R. Chimka [b], Michael De Volder [c], and Julian L. Fairey [a,]*

[a] Department of Civil Engineering, University of Arkansas, Fayetteville, AR 72701

[b] Department of Industrial Engineering, University of Arkansas, Fayetteville, AR 72701

[c] Department of Engineering, University of Cambridge, Cambridge CB3 0FS, UK

[*] Corresponding author:

Julian L. Fairey, Ph.D., P.E.

Associate Professor, Department of Civil Engineering

Address: 4190 Bell Engineering Center, Fayetteville, AR 72701

Phone: (479) 575-4023

Fax: (479) 575-7168

Email: julianf@uark.edu

Supplementary Information content: Carbon Spectra Deconvolution; References; 13 pages, 4 tables, 4 figures

List of Supplementary Information

Chemical List

EMD Millipore sulfamic acid (>99%, ACS grade), methanol (>99.8%, HPLC grade), potassium iodide (ACS grade), iodine (99.8%), Alfa Aesar sulfanilamide (98%), VWR mercuric chloride (ACS grade), VWR potassium phosphate monobasic anhydrous (ACS grade), Fisher Chemical sodium phosphate dibasic (99.2%), JT Baker sodium borate ($Na_2B_4O_7 \bullet H_2O$, ACS grade), VWR sodium hydroxide (reagent grade), BDH glacial acetic acid (ACS grade), BDH pentane (>98%), VWR ascorbic acid (ACS grade), RICCA sodium hypochlorite solution (5%), EMD Millipore hydrochloric acid (ACS grade, 12.1 N), and AccuStandard *N*-nitrosodimethylamine (5 mg/mL in methanol). EPA Method 521 activated carbon cartridges were used for TONO analysis as described previously[3] and DBPFP tests and their necessary reagents were conducted using previously published methods.[4] All aqueous phase reagents and buffers were made in deionized water (18.2 MΩ-cm) produced from a Milli-Q Integral 3 water purification system.

Carbon Spectra Deconvolution

Carbon spectra were deconvoluted using a similar method to Needham et al.[1] The binding energy was charge corrected based on a C1s peak position of 284.4 eV, C1s peaks were deconvoluted with a Gaussian-Lorentzian mix function, and a Shirley background subtraction was applied. The peak corresponding to carbon-carbon bonds was modified with an asymmetry parameter of 0.19 and other peaks were assigned for alcohols (C-O), carbonyls (C=O), and carboxyls (COO) with a final peak corresponding to the shake-up features satellite in the higher binding energy region of the spectra. Carbon-carbon bonding was set to a binding energy of 284.4 eV. Alcohol, carbonyl, and

carboxyl groups were represented by peaks located at 285.35, 286.84, and 288.58 eV, respectively. The peak associated with shake-up features was located at 290.4 eV.

Table S1. WS-EFF Raw Water Characteristics

WS-EFF[a] Collection Date	**Oct. 11, 2016**	**Jan. 5, 2017**
pH	8.0	7.8
DOC[b] ($mg \cdot L^{-1}$)	5.09	7.11
UV_{254} (cm^{-1})	0.55	0.12
Specific Conductivity ($\mu S \cdot cm^{-1}$)	523	524
Fluoride ($mg \cdot L^{-1}$)	ND[c]	ND
Chloride ($mg \cdot L^{-1}$)	47.73	42.40
Bromide ($mg \cdot L^{-1}$)	ND	ND
Nitrate ($mg \cdot L^{-1}$)	35.05	49.48
Phosphate ($mg \cdot L^{-1}$)	9.23	8.84
Sulfate ($mg \cdot L^{-1}$)	36.84	42.29
Nitrite ($mg \cdot L^{-1}$)	0.53	ND

[a]Effluent from the West Side Wastewater Treatment Plant
[b]Dissolved Organic Carbon
[c]Not detected

Table S2. CNT Mat Dimensions

CNT Mat	Length (mm)	Width (mm)	Area (mm^2)
CNT-Mat-1	6.27	5.92	37.12
CNT-Mat-2	4.59	4.88	22.40
CNT-Mat-3	4.23	5.99	25.34
CNT-Mat-4	5.16	4.66	24.05

Table S3. AF4 Method Details

Stage	Time (min)	Tip Flow (mL•min^{-1})	Focus Flow (mL•min^{-1})	Cross Flow (mL•min^{-1})	Slot Flow (mL•min^{-1})	Profile
Focusing	0	0.2	1.8	1.0	0.5	Constant
Transition	5	0.2	1.8	1.0	0.5	Linear
Elution	6	2.0	0	1.0	0.5	Constant
	8	2.0	0	1.0	0.5	Linear
	10	1.1	0	0.1	0.5	Constant
	25	1.1	0	0.1	0.5	Linear
	26	1.0	0	0	0.5	Constant
	36	1.0	0	0	0.5	-

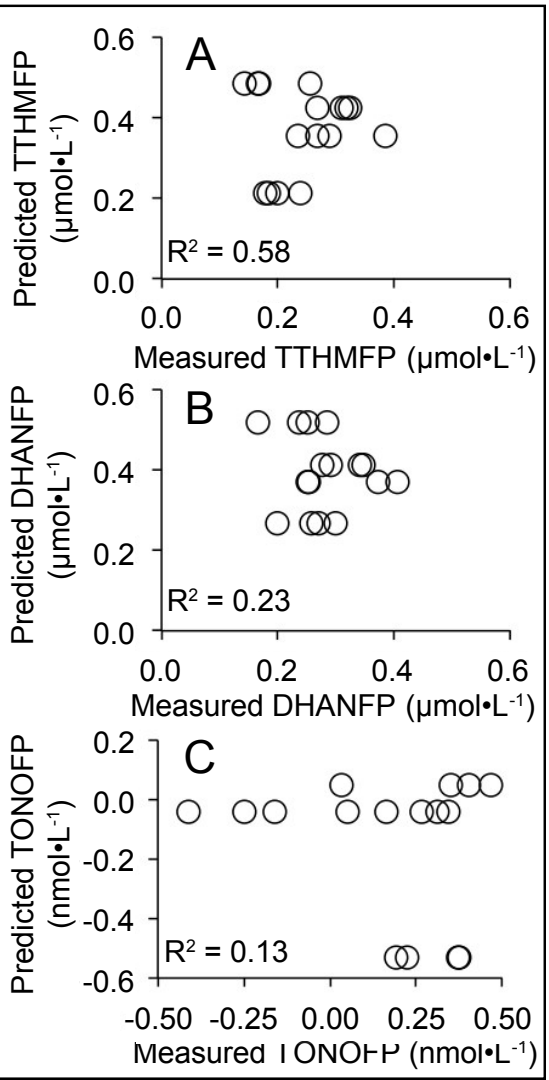


Figure S1. Multivariate models of pH-varying batch samples. All R^2 values are adjusted for the number of independent variables. Model coefficients and p-values can be found in Table 2.

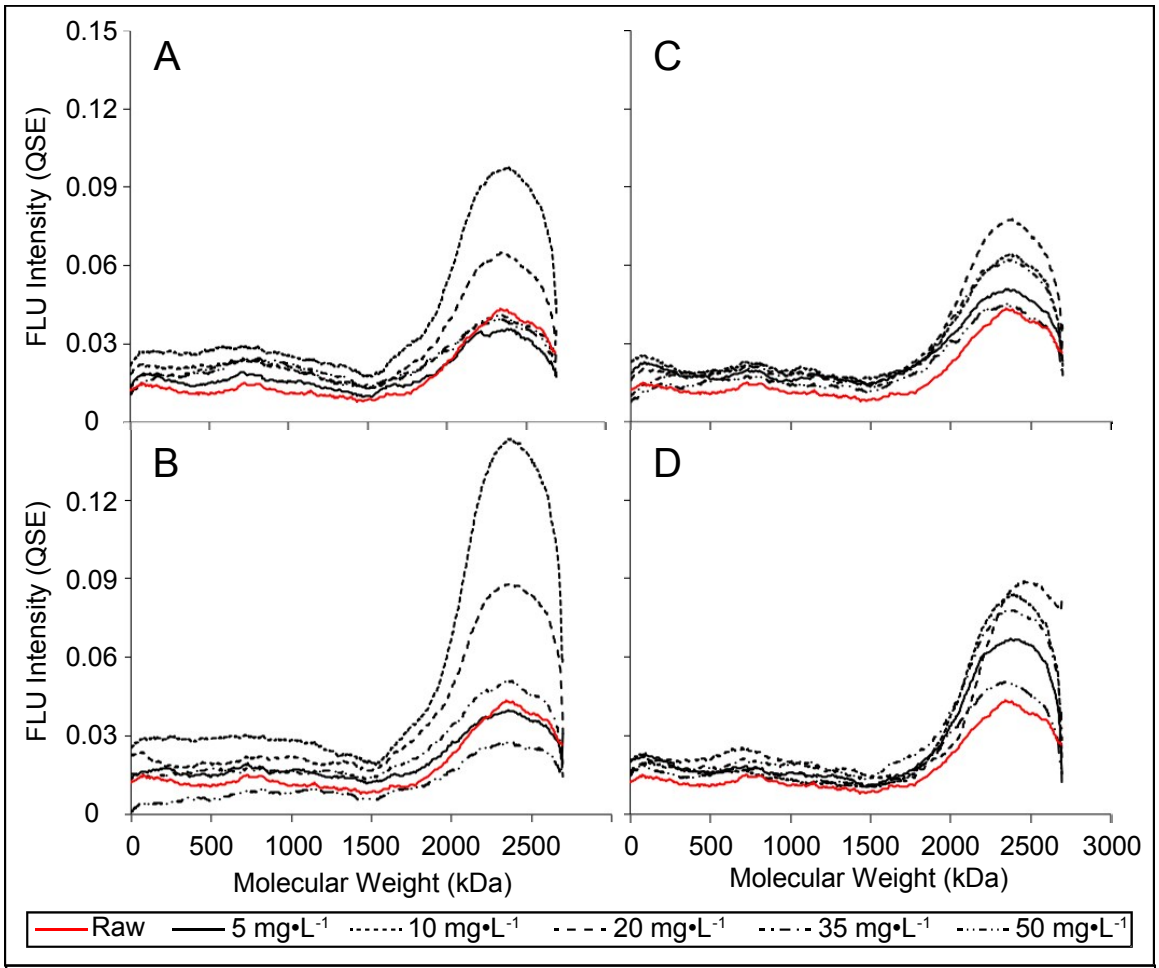
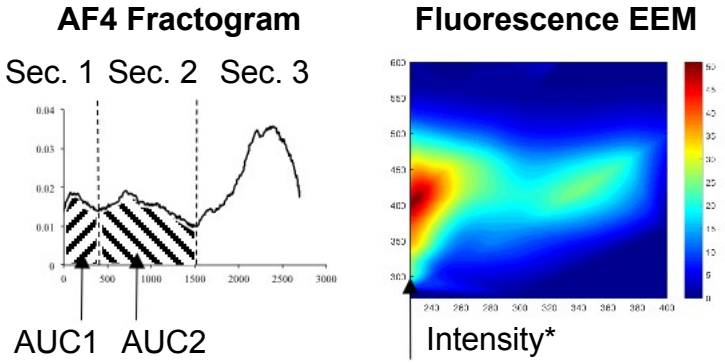


Figure S2. AF4-FLD fractograms for dose-varying batch samples with CNT 1 (Panel A), CNT 2 (Panel B), CNT 3 (Panel C), and PAC (Panel D). Raw samples (—) were not dosed with any sorbent.



$$TONOFP = 1.324\ AUC1 - 0.718\ AUC2 + 0.388\ Intensity^{*} - 5.8$$

Figure S3. Representation of the origin of variables used in the TONO precursor surrogate multivariate model. *AUC1* and *AUC2* correspond to the area under the curve of Sections 1 and 2 of the AF4 fractograms, respectively, and *Intensity** is the intensity of the fluorescence excitation-emission matrices at an excitation wavelength of 225 nm and an emission wavelength of 300 nm.

Table S4. AF4-FLD and Fluorescence EEM Data for TONOFP Surrogate Model

Sample Name	Carbon Type	Dose ($mg \cdot L^{-1}$)	AUC1[a]	AUC2[a]	Intensity*[b]
Raw	-	0	5.67	12.02	22.78
C1-5	CNT 1	5	7.20	15.73	20.86
C1-10	CNT 1	10	11.72	26.49	20.09
C1-20	CNT 1	20	9.38	20.76	17.42
C1-35	CNT 1	35	7.99	21.57	18.78
C1-50	CNT 1	50	7.50	20.82	16.20
C2-5	CNT 2	5	7.14	16.60	25.68
C2-10	CNT 2	10	12.75	28.38	23.04
C2-20	CNT 2	20	8.86	21.30	20.13
C2-35	CNT 2	35	6.85	17.15	18.99
C2-50	CNT 2	50	2.06	8.27	17.23
C3-5	CNT 3	5	8.75	17.84	25.72
C3-10	CNT 3	10	9.69	20.53	23.35
C3-20	CNT 3	20	8.40	19.50	22.87
C3-35	CNT 3	35	7.11	18.91	18.07
C3-50	CNT 3	50	5.72	15.64	14.25
C4-5	PAC	5	8.64	16.09	25.45
C4-10	PAC	10	8.35	14.37	23.19
C4-20	PAC	20	8.89	21.13	21.01
C4-35	PAC	35	8.25	19.05	15.08
C4-50	PAC	50	7.01	15.45	12.11

[a] For a description of the variables *AUC1* and *AUC2*, see Section 2.4.4 of the manuscript. [b] Fluorescence intensity at $I_{225/300}$ detailed in Section 2.5 of the manuscript.

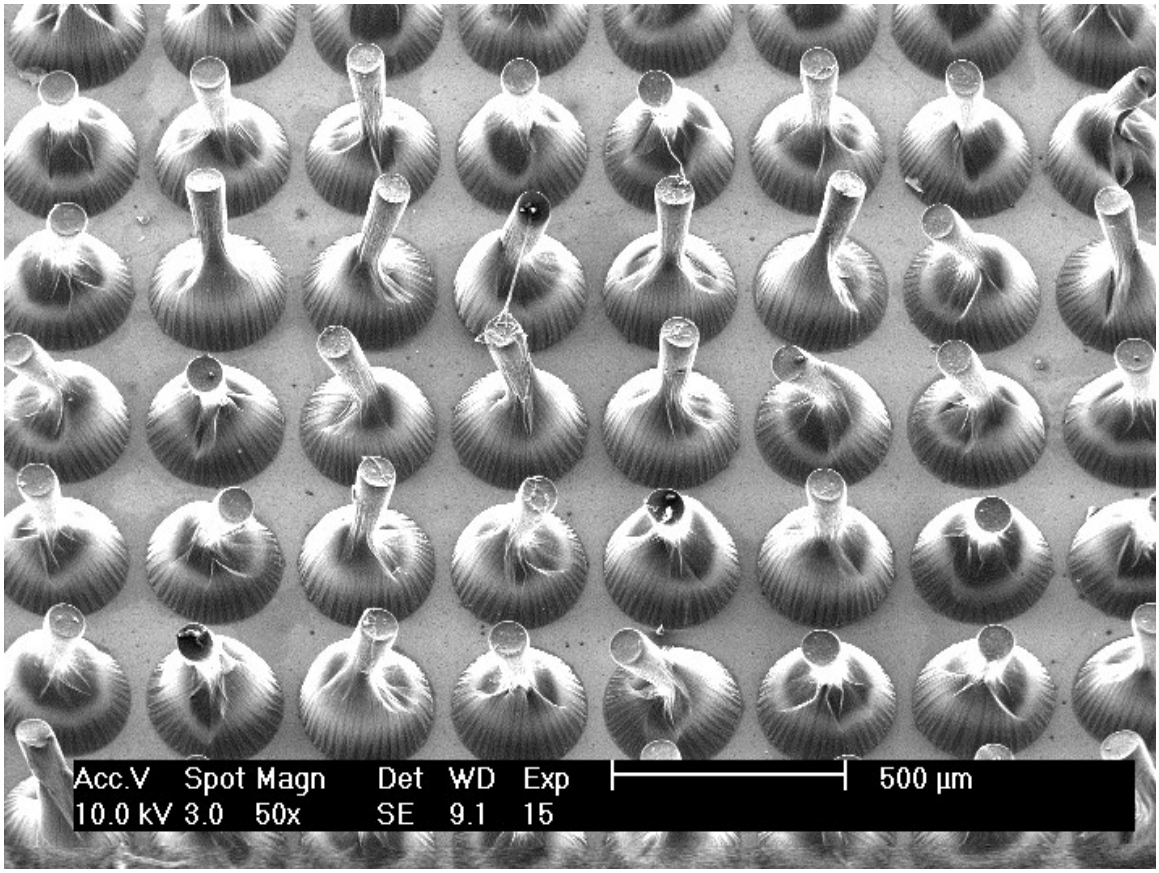


Figure S4. Scanning electron microscopy (SEM) images of CNT-Mat 1 at 50 times magnification following use in the continuous flow tests.

References

1. E. M. Needham, S. M. Sidney, J. R. Chimka and J. L. Fairey, *Environ. Sci.: Water Res. Technol.*, 2016, **2**, 1004-1013.