Supplemental Information

Reduction of Haloacetonitrile-associated Risk by Adjustment of Distribution System pH

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SI Table of Contents

Text SI-1: Trihalomethane, Haloacetamide, and Haloacetonitrile GC-ECD Method Parameters:

1. Inlet:
   200°C
   Split Mode – Split Ratio 10:1, Split Flow 9 mL/min
   Gas Saver: On – 20 mL/min after 3 min
2. Column: HP-5, 30 m x 320 µm x 0.25 µm
   Flow: 0.9 mL/min He
   Avg Velocity: 16.647 cm/sec
   Constant Flow
   Post Run: 2.3922 mL/min
3. Oven:
   Equilibration Time: 0.5 min
   Max Oven Temp: 325°C
   Oven Program:
   Initial 35°C, Hold 9 min
   Ramp to 40°C at 1°C/min and hold for 3 min
   Ramp to 120°C at 6°C/min and hold for 3 min
   Ramp to 250°C at 30°C/min and hold for 3 min
4. Detector:
   ECD, 290°C
   Makeup flow 25 mL/min N_2
   Constant Makeup Flow

Text SI-2: Haloacetic Acid GC-ECD Method Parameters:

1. Inlet:
   175°C
   Split Mode – Splitless, Pure Flow to Split Vent: 30 mL/min at 0.75 min
   Gas Saver: On – 20 mL/min after 3 min
2. Column: DB-1, 30 m x 250 µm x 1 µm
   Flow: 1.6 mL/min He
   Avg Velocity: 35.053 cm/sec
   Constant Flow
   Post Run: 2.3922 mL/min
3. Oven:
   Equilibration Time: 0.5 min
   Max Oven Temp: 325°C
   Oven Program:
   Initial 35°C, Hold 10 min

Ramp to 40°C at 1°C/min and hold for 5 min
Ramp to 110°C at 2.5°C/min and hold for 3 min
Ramp to 220°C at 20°C/min and hold for 2 min

4. Detector:
   ECD, 300°C
   Makeup flow 25 mL/min N_2
   Constant Makeup Flow

Table SI-1: Water quality parameters for finished drinking water.

NTU	0.02
TSS (mg/L)	BDL
pH	7.9
Alkalinity (mg/L as $CaCO_3$)	59.3
TOC (mg/L)	1.61
ORP (mV)	618
FCl_2 (mg/L Cl_2)	1.72
TCl_2 (mg/L Cl_2)	1.8
NH_2Cl (mg/L Cl_2)	BDL
NH_3 (mg/L N)	BDL
NO_2^- (mg/L N)*	BDL
NO_3^- (mg/L N)*	0.764
Br^- (mg/L)*	BDL
Chloride (mg/L)*	20.48
Sulfate (mg/L)*	6.60
TN (mg/L)	0.157

*NO_2^-, NO_3^-, bromide, chloride, and sulfate were measured using ion chromatography. The method detection limit is ~5 µg/L for each.

Table SI-2: CHO LC_{50} values for compounds of interest

Haloacetonitriles	
Compound	**LC_{50}**
TCAN	1.60E-04
DCAN	5.73E-05
DBAN	2.85E-06
BCAN	8.46E-06
CAN	6.83E-05
BAN	3.21E-06

Haloacetamides	
Compound	**LC_{50}**
TCAM	2.05E-04
DCAM	1.92E-05
DBAM	1.22E-05
BCAM	1.71E-05
CAM	1.48E-04
BAM	1.89E-06

Haloacetic Acids	
Compound	**LC_{50}**
TCAA	2.40E-04
DCAA	7.30E-05
DBAA	5.90E-04
BCAA	7.78E-04
CAA	8.10E-04
BAA	9.60E-06

Trihalomethanes	
Compound	**LC_{50}**
Chloroform	9.62E-04

Table SI-3: Tabulated DBP concentrations for all species measured in finished drinking water.

pH 6						
Time (hour)	1	16	24	30	48	120
Compound	Concentration (µg/L)					
Chloroform	27.7	34.7	37.2	41.0	46.4	50.9
BDCM	5.8	6.2	6.3	6.4	6.6	6.7
TCAN	3.1	4.4	4.9	5.5	6.0	6.8
DCAN	1.0	0.8	0.9	0.5	BDL	BDL
1,1-DCA	BDL	0.6	0.7	0.7	0.8	0.8
BCAN	3.7	4.4	4.9	5.0	5.3	5.4
DCAM	0.6	1.2	0.7	BDL	BDL	1.1
TCAM	BDL	0.5	0.5	0.7	0.8	0.9
MCAA	10.7	13.5	12.0	14.4	14.9	15.7
BCAA	12.1	18.4	18.5	23.8	30.3	31.9
DBAA	1.2	1.5	1.5	1.7	2.0	1.8
BDCAA	16.3	24.9	24.0	29.9	39.1	35.1
TBAA	3.1	3.9	3.9	4.1	4.9	4.4
pH 7.5						
Time (hour)	1	16	24	30	48	120
Compound	Concentration (µg/L)					
Chloroform	28.9	42.9	48.6	56.2	73.2	71.6
BDCM	6.0	6.9	7.2	7.4	8.5	8.0
TCAN	3.4	4.8	5.1	5.7	7.3	5.8
DCAN	0.7	0.5	0.6	0.5	0.5	BDL
1,1-DCA	0.6	0.7	0.8	0.8	1.1	0.9
BCAN	4.1	4.4	4.0	2.9	2.3	1.0
DCAM	1.1	1.4	1.6	2.2	2.9	3.1
TCAM	0.5	0.7	0.8	1.0	1.4	1.1
MCAA	11.4	17.3	17.8	20.2	20.1	22.1
BCAA	13.3	18.3	21.2	27.2	30.6	34.3
DBAA	1.3	1.5	1.7	2.1	2.0	2.1
BDCAA	19.8	26.7	30.3	34.9	38.2	38.6
TBAA	3.7	3.9	4.2	4.7	4.7	4.5
pH 9						
Time (hour)	1	16	24	30	48	72
Compound	Concentration (µg/L)					
Chloroform	35.1	53.5	59.8	62.2	68.2	75.2
BDCM	6.5	7.6	8.0	8.2	8.4	8.9
TCAN	3.6	3.5	3.0	2.7	1.9	1.3
DCAN	0.6	0.5	0.6	0.6	BDL	BDL
1,1-DCA	0.6	0.8	0.9	0.9	1.0	1.0
BCAN	3.9	0.8	BDL	BDL	BDL	BDL
DCAM	1.5	3.2	3.9	4.6	5.7	7.1
TCAM	0.7	1.0	0.8	1.0	1.1	1.2
MCAA	14.1	19.1	21.7	19.5	24.8	25.3
BCAA	14.9	19.5	22.6	21.9	26.7	30.0
DBAA	1.3	1.7	1.8	1.9	2.0	2.2
BDCAA	22.3	24.6	28.5	23.5	30.2	31.9
TBAA	3.5	3.7	3.7	2.7	3.6	3.8

Table SI-4: Tabulated DBP concentrations for all species measured in Suwanee River NOM.

pH 6						
Time (hour)	1	16	24	30	48	120
CPD	Concentration (µg/L)					
Chloroform	18.9	56.0	67.4	76.7	86.3	120.4
BDCM	BDL	4.1	4.1	4.1	4.2	4.2
TCAN	0.8	3.6	4.2	4.8	5.6	7.3
DCAN	0.9	1.1	1.0	0.9	1.0	0.5
1,1-DCA	BDL	BDL	BDL	BDL	BDL	BDL
BCAN	3.0	6.0	6.8	7.5	8.0	9.3
DCAM	3.4	3.5	3.9	3.9	3.9	3.8
TCAM	BDL	BDL	BDL	0.6	0.5	0.6
MCAA	BDL	BDL	BDL	BDL	BDL	BDL
BCAA	16.0	41.0	46.8	51.3	57.0	73.6
DBAA	BDL	BDL	BDL	BDL	BDL	BDL
BDCAA	22.2	80.0	97.8	109.1	124.2	154.8
TBAA	BDL	2.5	2.6	2.5	BDL	2.7
pH 7.5						
Time (hour)	1	16	24	30	48	120
CPD	Concentration (µg/L)					
Chloroform	32.1	95.8	108.9	117.6	137.2	147.0
BDCM	4.4	4.2	4.2	4.2	4.3	4.3
TCAN	1.3	4.4	4.9	5.9	5.9	7.4
DCAN	BDL	0.8	0.7	0.9	0.6	BDL
1,1-DCA	BDL	BDL	BDL	BDL	BDL	BDL
BCAN	3.9	5.8	5.2	4.9	4.2	2.2
DCAM	1.6	2.2	2.6	2.8	2.8	1.3
TCAM	BDL	BDL	0.5	0.6	0.6	0.8
MCAA	BDL	BDL	BDL	BDL	BDL	1.3
BCAA	18.5	46.0	52.2	56.8	62.8	79.5
DBAA	BDL	BDL	BDL	BDL	BDL	BDL
BDCAA	29.7	101.1	114.3	125.1	137.1	160.4
TBAA	BDL	2.2	1.8	2.2	2.2	2.3
pH 9						
Time (hour)	1	16	24	30	48	72
CPD	Concentration (µg/L)					
Chloroform	35.9	113.5	143.6	152.3	168.4	192.7
BDCM	BDL	4.2	4.2	4.2	4.4	4.3
TCAN	1.5	2.4	2.1	1.9	1.6	1.2
DCAN	0.8	0.8	0.8	0.8	0.7	0.5
1,1-DCA	BDL	BDL	BDL	BDL	BDL	BDL
BCAN	3.2	0.7	BDL	BDL	BDL	BDL
DCAM	0.5	1.2	0.7	1.4	1.5	2.7
TCAM	BDL	BDL	BDL	BDL	0.6	0.7
MCAA	BDL	BDL	BDL	BDL	1.6	1.1
BCAA	19.9	49.1	56.2	61.1	66.3	72.6
DBAA	BDL	BDL	BDL	BDL	BDL	BDL
BDCAA	18.2	53.9	60.4	65.2	68.8	73.4
TBAA	BDL	BDL	BDL	BDL	BDL	BDL

Table SI-5: Tabulated DBP concentrations for all species measured in Upper Mississippi River NOM.

pH 6						
Time (hour)	1	16	24	30	48	120
Compound	Concentration (µg/L)					
Chloroform	14.3	36.5	43.8	47.1	57.4	78.9
BDCM	3.9	4.2	4.2	4.2	4.3	4.3
TCAN	1.3	5.0	6.0	6.3	7.6	10.4
DCAN	1.0	1.0	1.0	0.9	0.7	0.5
1,1-DCA	BDL	BDL	BDL	BDL	BDL	BDL
BCAN	2.2	4.6	5.2	5.3	6.0	7.6
DCAM	BDL	5.3	4.5	4.3	4.7	4.1
TCAM	BDL	0.7	0.8	0.8	0.9	1.3
MCAA	BDL	BDL	BDL	BDL	BDL	BDL
BCAA	10.4	28.6	27.6	34.9	33.3	40.4
DBAA	BDL	BDL	BDL	BDL	BDL	BDL
BDCAA	10.9	44.0	44.9	58.4	57.6	70.3
TBAA	BDL	BDL	BDL	BDL	BDL	2.3

pH 7.5						
Time (hour)	1	16	24	30	48	120
Compound	Concentration (µg/L)					
Chloroform	19.3	57.8	70.9	72.1	81.3	105.6
BDCM	3.9	4.3	4.4	4.4	4.4	4.5
TCAN	1.9	6.4	7.3	7.5	8.2	8.7
DCAN	1.3	0.8	0.8	0.7	0.7	BDL
1,1-DCA	BDL	BDL	BDL	BDL	BDL	0.5
BCAN	2.8	4.3	3.9	3.9	3.3	1.6
DCAM	1.3	2.0	1.8	2.2	2.9	4.2
TCAM	BDL	1.0	1.0	1.2	1.4	1.8
MCAA	BDL	1.2	1.6	1.7	2.0	2.4
BCAA	10.5	33.3	37.7	39.6	45.5	64.1
DBAA	BDL	BDL	BDL	BDL	BDL	BDL
BDCAA	12.7	56.8	66.7	69.7	79.8	105.0
TBAA	BDL	BDL	2.0	2.0	2.1	BDL

pH 9						
Time (hour)	1	16	24	30	48	72
Compound	Concentration (µg/L)					
Chloroform	25.3	78.7	85.8	93.3	107.4	119.2
BDCM	4.1	4.4	4.4	4.4	4.5	4.6
TCAN	2.1	3.1	2.5	2.3	1.6	1.3
DCAN	1.2	0.8	0.9	0.8	0.7	0.6
1,1-DCA	BDL	BDL	BDL	BDL	BDL	BDL
BCAN	2.7	0.5	BDL	BDL	BDL	BDL
DCAM	BDL	4.0	5.7	6.1	8.6	9.4
TCAM	BDL	0.8	0.9	1.0	1.3	1.4
MCAA	BDL	1.7	1.9	2.0	3.0	3.6
BCAA	14.0	34.8	37.2	41.3	45.6	51.1
DBAA	BDL	BDL	BDL	BDL	BDL	BDL
BDCAA	14.5	35.6	37.0	40.4	44.1	47.5
TBAA	BDL	BDL	BDL	BDL	BDL	BDL

Table SI-6: Pearson coefficients for linear best fits between pH and DBPs in finished drinking water. 1- and 24-hour experiments were conducted in triplicate, with the average concentration shown below. Other correlations are based on only 3 data points but confirm trends apparent in the replicated experiments.

1-hour	Concentration (µg/L)			
pH	THM	HAA	HAM	HAN
6	33.52	43.36	0.95	7.77
7.5	34.88	49.39	1.57	8.23
9	41.61	56.14	2.22	8.15
Pearson R	**0.91**	**0.98**	**0.85**	**0.54**

16-hour	Concentration (µg/L)			
pH	THM	HAA	HAM	HAN
6	40.87	62.21	1.70	9.57
7.5	49.86	67.79	2.14	9.69
9	61.16	68.56	4.14	4.83
Pearson R	**1.00**	**0.92**	**0.94**	**-0.85**

24-hour	Concentration (µg/L)			
pH	THM	HAA	HAM	HAN
6	43.59	59.96	1.27	10.61
7.5	55.77	75.14	2.42	9.75
9	67.79	78.27	4.74	3.86
Pearson R	**0.99**	**0.87**	**0.97**	**-0.93**

30-hour	Concentration (µg/L)			
pH	THM	HAA	HAM	HAN
6	47.35	73.86	1.21	11.07
7.5	63.66	89.16	3.20	9.09
9	70.34	69.62	5.60	3.49
Pearson R	**0.97**	**-0.21**	**1.00**	**-0.96**

48-hour	Concentration (µg/L)			
pH	THM	HAA	HAM	HAN
6	52.98	91.18	1.25	11.79
7.5	81.70	95.65	4.30	10.15
9	76.65	87.32	6.83	2.63
Pearson R	**0.77**	**-0.46**	**1.00**	**-0.94**

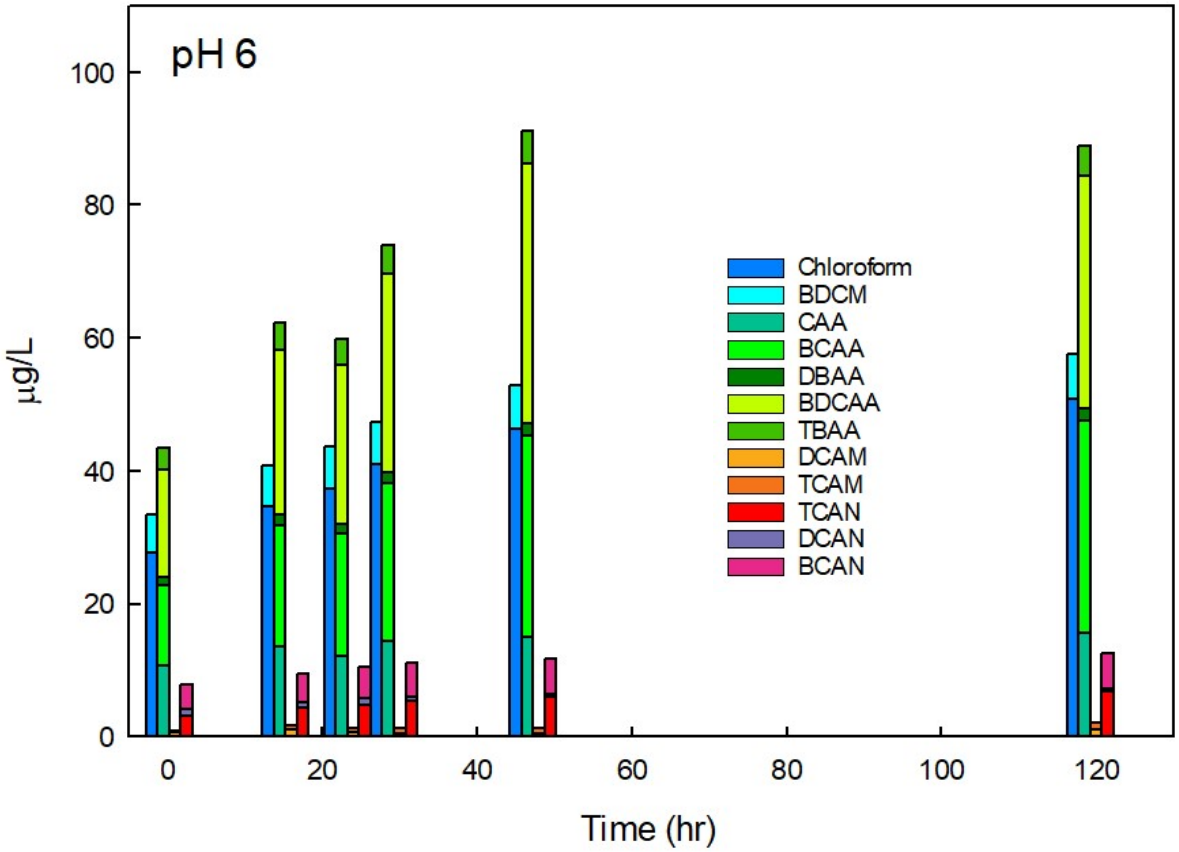

Figure SI-1: DBPs in finished drinking water at pH 6 stacked by common functional group.

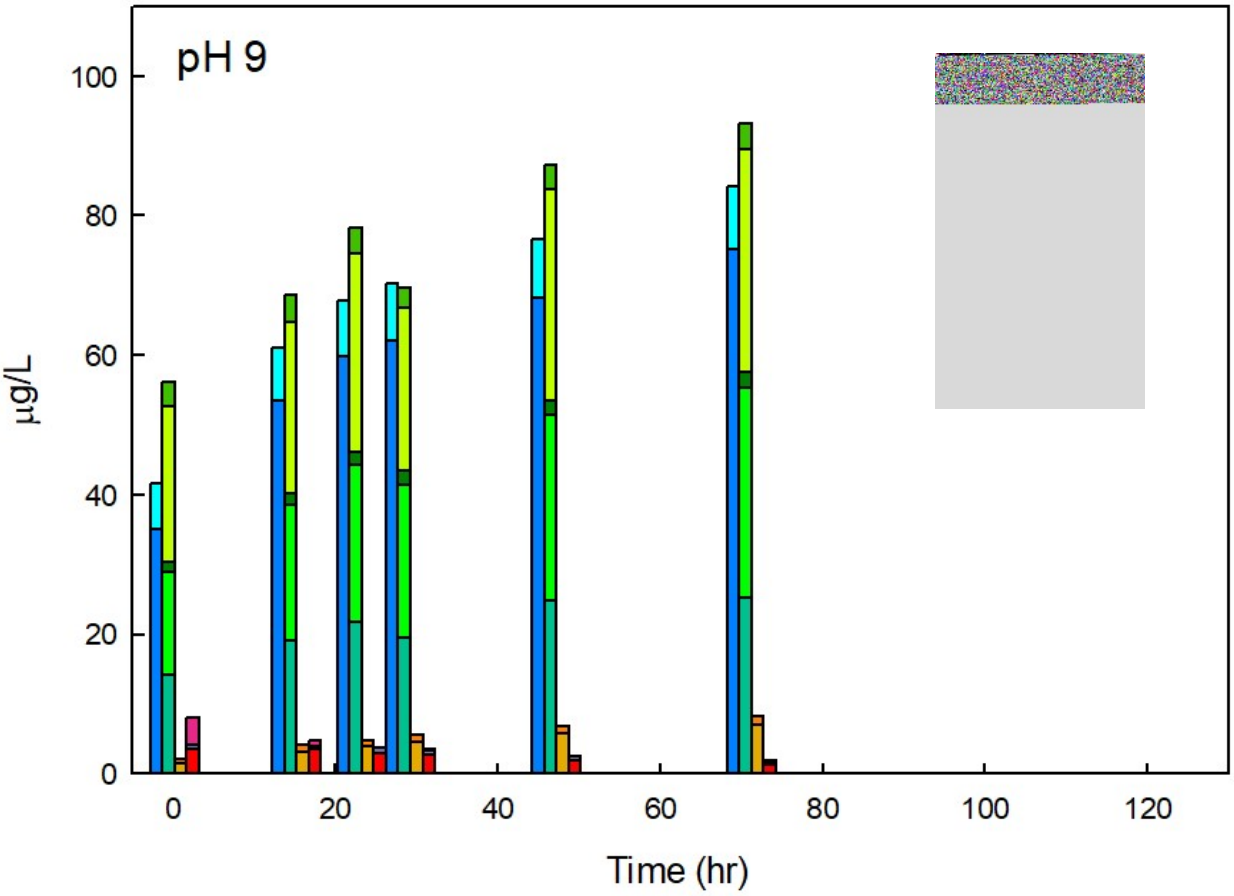

Figure SI-2: DBPs in finished drinking water at pH 9 stacked by common functional group.

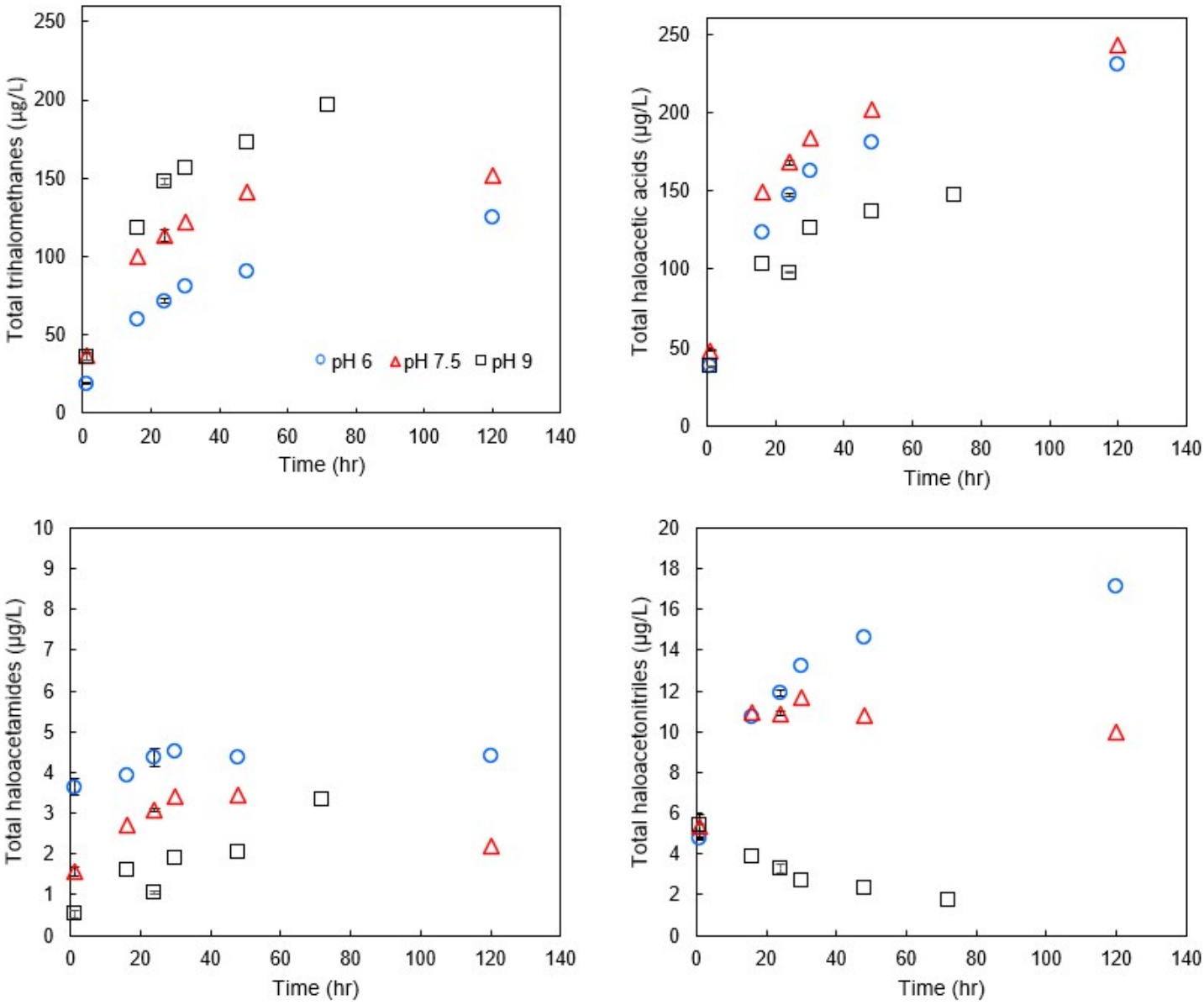

Figure SI-3: DBP formation over time by class at pH 6, 7.5, and 9 for Suwannee River NOM.

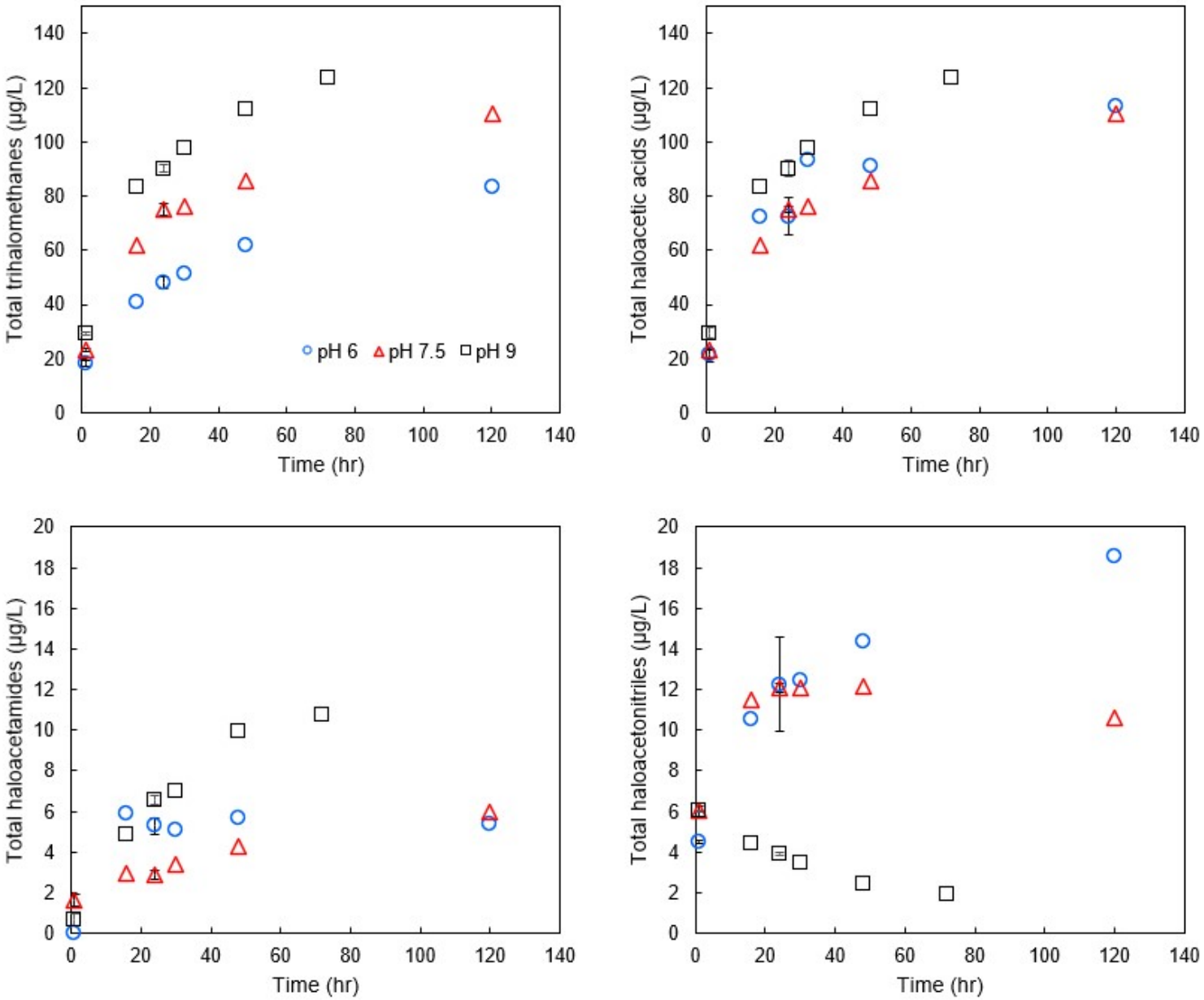

Figure SI-4: DBP formation over time by class at pH 6, 7.5, and 9 for Upper Mississippi River NOM.

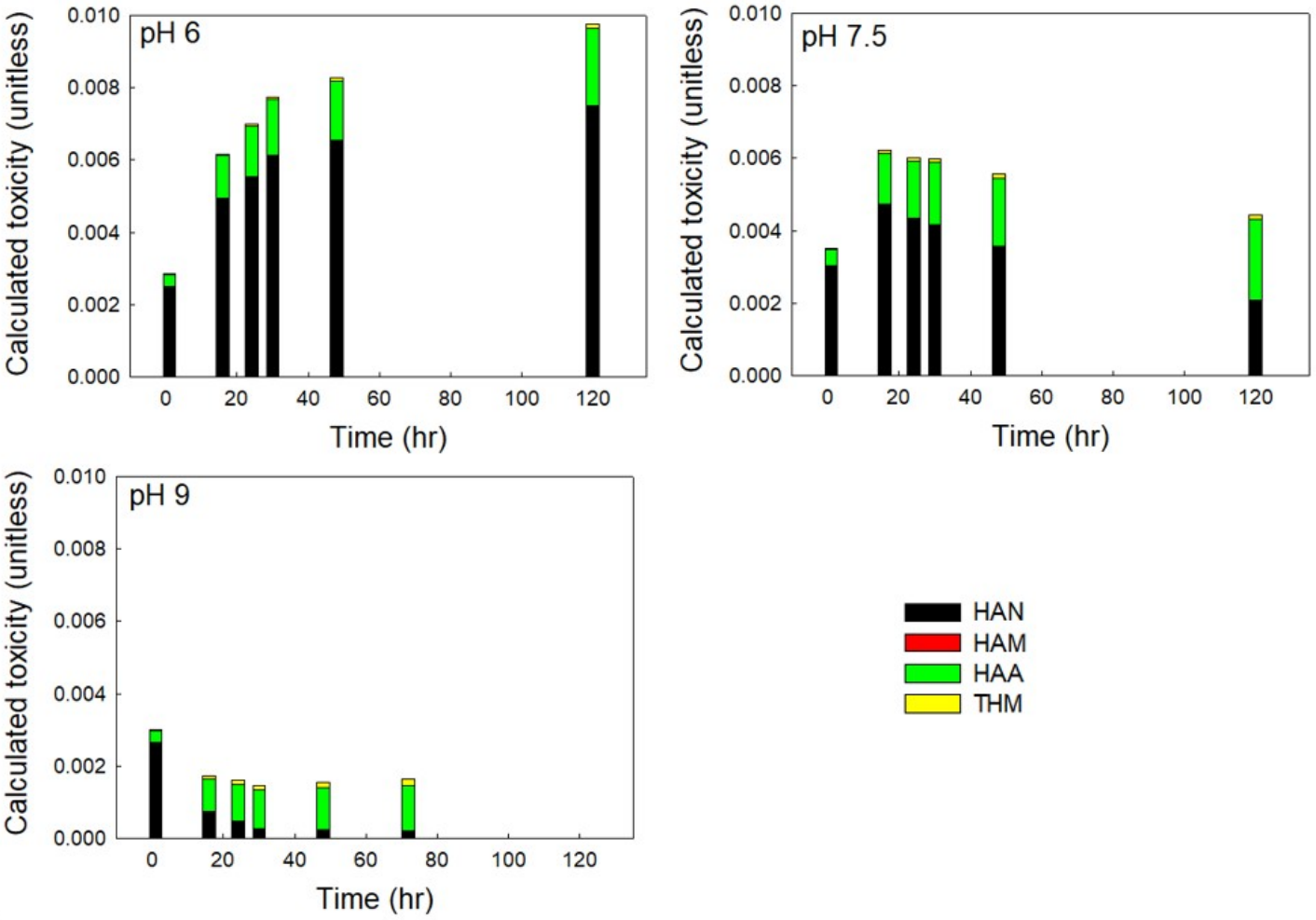

Figure SI-5: Toxicity contribution of each DBP class for Suwannee River NOM at pH 6, 7.5, and 9.

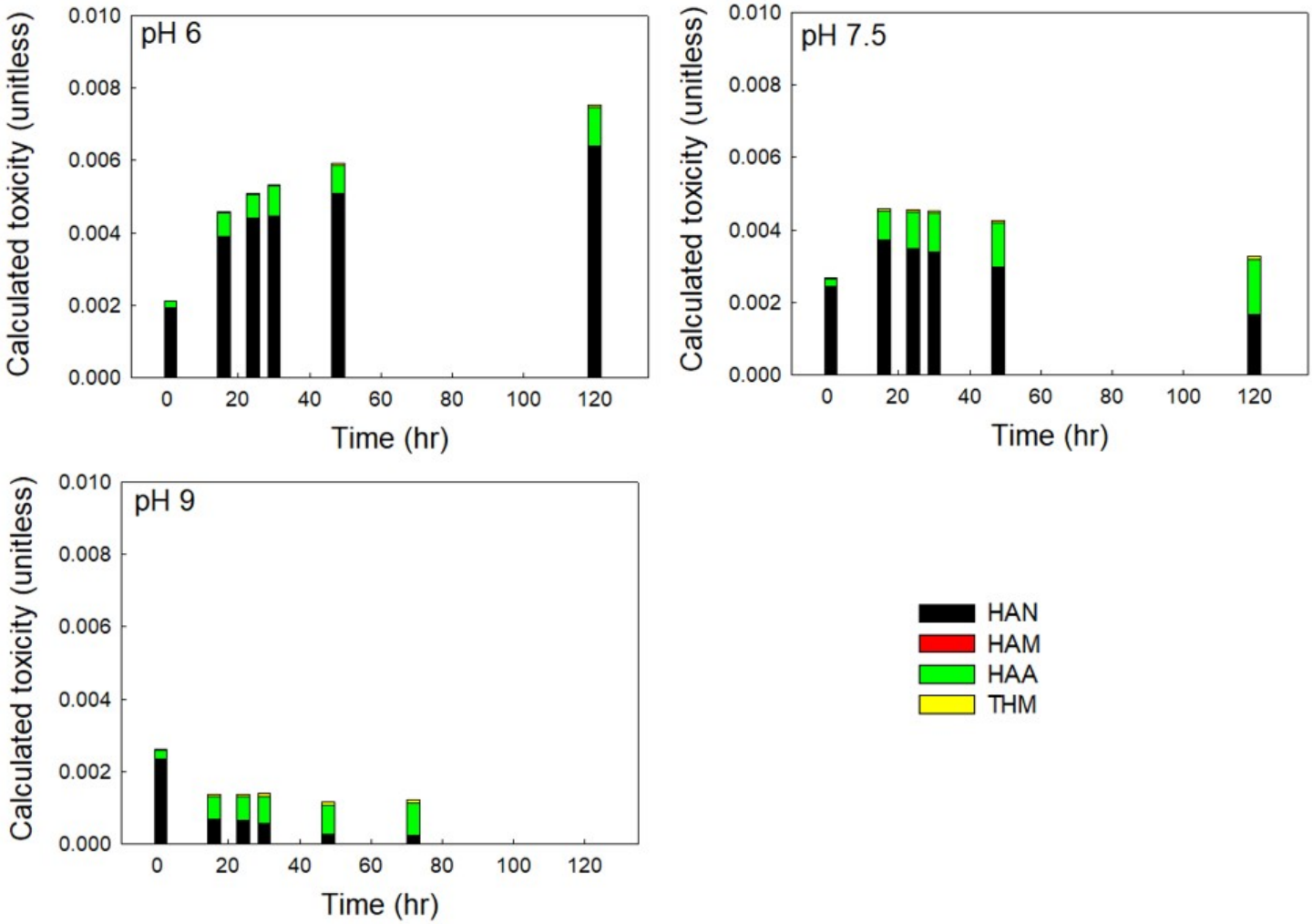

Figure SI-6: Toxicity contribution of each DBP class for Upper Mississippi River NOM at pH 6, 7.5, and 9.