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Supplemental Information for Environmental Science: Water Research & Technology

Article: *De facto* Reuse and Disinfection By-Products in Drinking Water Systems in the Shenandoah River Watershed

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Example models showing estimated THM4 formation based on a range of realistic conditions that might be found in the Shenandoah River watershed.

Equation [1] is an example of a model developed by researchers[1] that is based on low to moderate chlorine doses applied to raw/untreated water. As shown in Equation [1], water quality parameters such as total organic carbon (TOC), bromide (Br), pH, and temperature, as well as applied chlorine (Cl2) dose and reaction time, are used to model THM4 formation. Based on this equation, the water quality parameters having the most to least effect are as follows: pH>TOC>temperature>time>Cl2>Br.

$$THM4 = (0.0412 \times TOC)^{1.098} \times (Cl2\ Dose)^{0.152} \times (Br)^{0.068} \times (temp)^{0.609} \times (pH)^{1.601} \times (time)^{0.263} \quad [1]$$

Where:
THM4 is in µg/L;
TOC is for source water, in mg/L;
Cl2 dose is the applied chlorine dose, in mg/L;
Br is the concentrations of source water bromide, in µg/L;
Temp is the water temperature, in ^{o}C;
pH is the water pH, on a numeric scale used to specify the acidity or basicity of an aqueous solution; and
time is that amount for reaction with the applied chlorine dose, in hours.

Table 1 shows a range of estimated values of THM4 concentrations based on the use of Equation 1 and varying ranges of TOC, Br, and temperature. As this table shows, the concentration of THM4 would increase by about 7 mg/L when comparing a third quarter temperature (22 ^{o}C) versus an annual average temperature (11 ^{o}C) at a TOC = 1 mg/L and Br = 20 µg/L. With a TOC concentration of 2 mg/L and Br = 20 µg/L, which closely represents the values expected with *de facto* reuse, the concentration of THM4 would increase by about 16 mg/L when comparing a third quarter temperature (22 ^{o}C) and an annual average temperature (11 ^{o}C). At a higher bromide concentration (Br = 50 µg/L) and a TOC of 2 mg/L, the concentration of THM4 would increase by about 17 mg/L when comparing a third quarter temperature (22 ^{o}C) and an annual average temperature (11 ^{o}C).

Table 1. Estimated values of THM4 concentrations based on the use of Equation 1

TOC (mg/L)	Cl2 (mg/L)	Br (μg/L)	Temp (^{o}C)	pH	time (hrs)	Estimated Concentration of THM4 (μg/L)
1	4	20	11	7	24	14.0
1	4	20	22	7	24	21.3
2	4	20	11	7	24	29.9
2	4	20	22	7	24	45.6
2	4	50	11	7	24	31.8
2	4	50	22	7	24	48.5

Equation [2] is another example of a model, developed by the U.S. Environmental Protection Agency (USEPA)[2], and is based on a study that examined chlorination of treated (i.e., finished) water. Like Equation [1], Equation [2] also indicates that these types of parameters have a relatively strong influence on THM4 formation.

$$THM4 = 23.9(TOC \times UVA)^{0.403} \times (Cl2\ Dose)^{0.225} \times (Br)^{0.141} \times 1.027^{(temp-20)} \times 1.156^{(pH-7.5)} \times (time)^{0.264} \quad [2]$$

Where:
THM4 is in μg/L;
TOC is for treated water, in mg/L;
UVA (ultraviolet light absorbance) is the treated water UVA, in 1/cm
Cl2 dose is the applied chlorine dose, in mg/L;
Br is the concentration of treated water bromide, in μg/L;
Temp is the water temperature, in ^{o}C;
pH is the treated water pH, on a numeric scale used to specify the acidity or basicity of an aqueous solution; and
time is that amount for reaction with the applied chlorine dose, in hours.

Table 2 shows a range of estimated values of THM4 concentrations based on the use of Equation [2] and varying ranges of TOC, Br, and temperature. As the table shows, the concentration of THM4 would increase by about 11 mg/L when comparing a third quarter temperature (22 ^{o}C) and an annual average temperature (11 ^{o}C) at concentrations of TOC = 1 mg/L and Br = 20 µg/L.

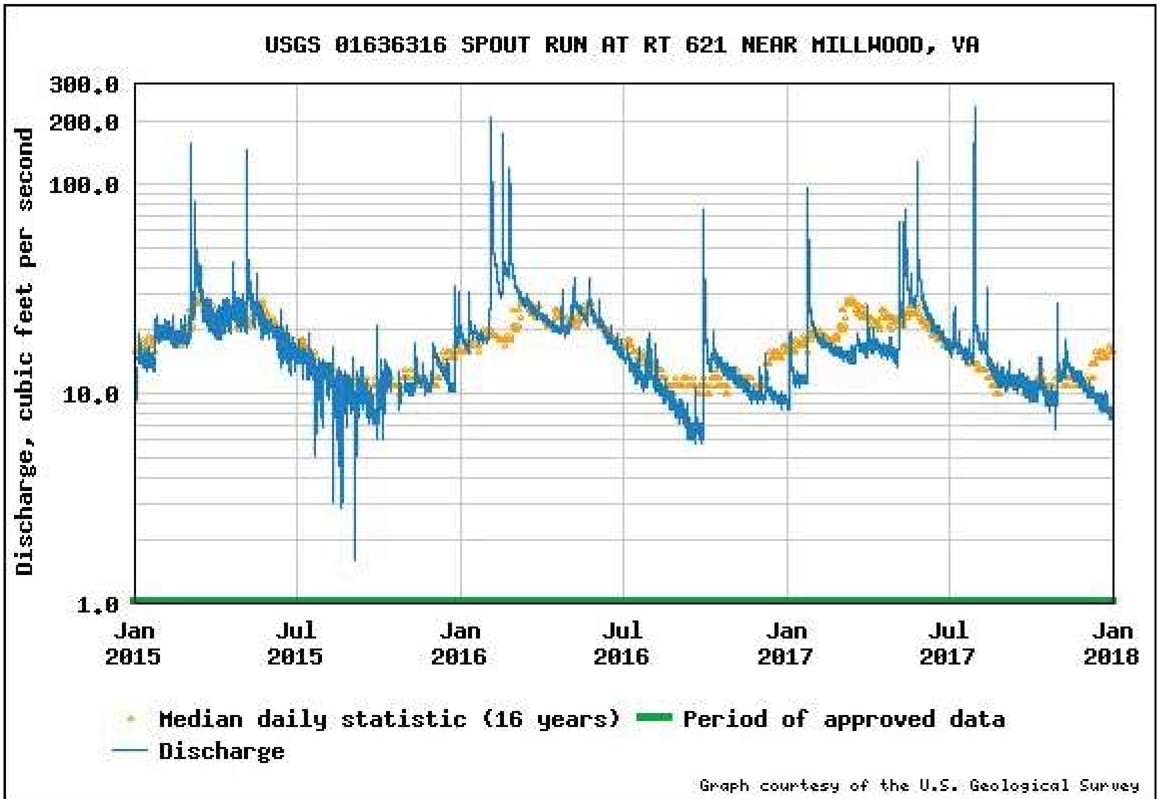
Table 2. Estimated values of THM4 concentrations based on the use of Equation 2

TOC (mg/L)	UVA	Cl2 (mg/L)	Br (µg/L)	Temp (^{o}C)	pH	time (hrs)	Estimated Concentration of THM4 (µg/L)
1	0.1	4	20	11	7	24	33.3
1	0.1	4	20	22	7	24	44.7
2	0.1	4	20	11	7	24	44.1
2	0.1	4	20	22	7	24	59.1
2	0.1	4	50	11	7	24	50.2
2	0.1	4	50	22	7	24	67.3

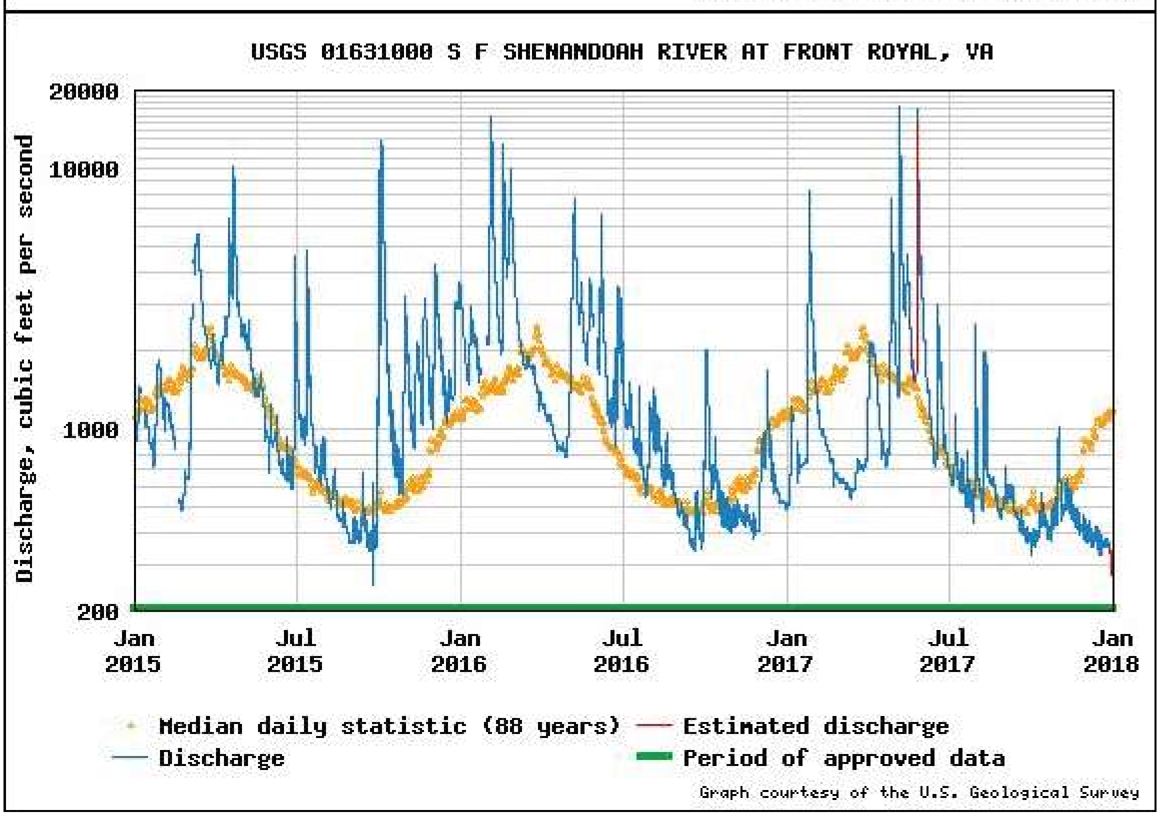
Several studies have shown a wastewater TOC in the range of 8 to 15 mg/L[3, 4], suggesting that 10 mg/L could be a reasonable value. Such an increase in TOC may not be associated with a substantial impact on THM4 or HAA5. The authors note that the results from this study of the Shenandoah River watershed indicate a modest correlation (with r values for THM4 of 0.61 and 0.64 for annual average and third quarter conditions, respectively), which may derive from the relatively small increase in TOC and Br from wastewater.

Preliminary Evaluation of Additional Stream Gages in the Shenandoah River Watershed

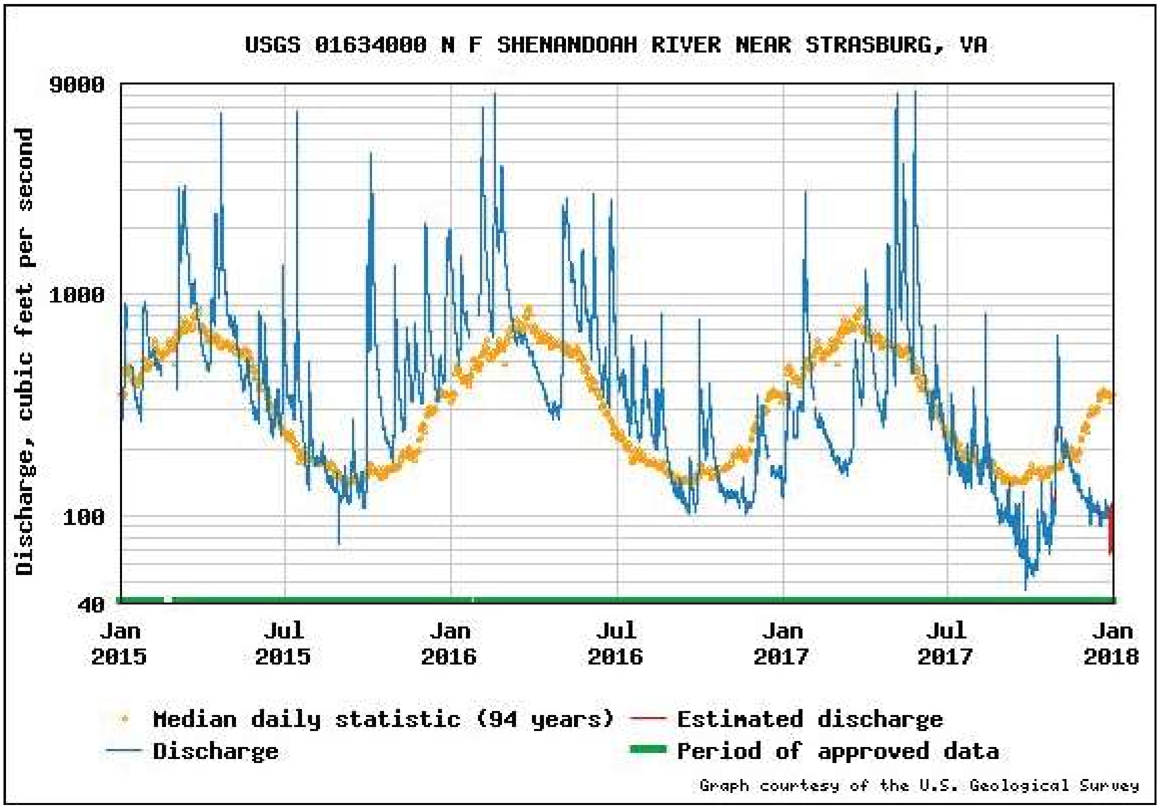
Stream gages in the Shenandoah River watershed over a 3-year period (from January 2015 to December 2017) showed that flows tended to be higher in the winter and spring, and lower in the summer and fall seasons[5].



USGS 01636316 SPOUT RUN AT RT 621 NEAR MILLWOOD, VA
Discharge, cubic feet per second
300.0
200.0
100.0
10.0
1.0
Jan 2015
Jul 2015
Jan 2016
Jul 2016
Jan 2017
Jul 2017
Jan 2018
Median daily statistic (16 years)
Period of approved data
Discharge
Graph courtesy of the U.S. Geological Survey



USGS 01631000 S F SHENANDOAH RIVER AT FRONT ROYAL, VA
Discharge, cubic feet per second
20000
10000
1000
200
Jan 2015
Jul 2015
Jan 2016
Jul 2016
Jan 2017
Jul 2017
Jan 2018
Median daily statistic (88 years)
Estimated discharge
Discharge
Period of approved data
Graph courtesy of the U.S. Geological Survey



Pre-Stage 2 versus Post-Stage 2 D/DBPR for Annual Average THM4 Concentrations

Table 3. Comparison of Annual Average THM4 Concentrations [6] Before and After Stage 2 D/DBPR Compliance Deadlines

PWS	Yearly Average - Pre-Stage 2 (2002 – 2012)	Yearly Average - Post-Stage 2 (2013 – 2016)
A	64.5	41.6
B	42.5	66.8
D	32.0	34.9
F	42.3	54.7
G	64.6	59.9
H	15.5	17.0
I	30.0	37.8
J	36.6	43.2
K	33.9	40.7
L	15.4	22.8
Average	**37.7**	**41.9**

Based on linear modeling using R [7], this comparison had a p-value of 0.018, thus showing we did not find substantial differences in annual average values across the PWSs in this study, however, differences were observed at individual PWSs.

References:

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3. Dobbs, R. A, R. H. Wise, R.B. Dean, 1972, "The Use of Ultra-Violet Absorbance for Monitoring the Total Organic Carbon Content of Water and Wastewater", Water Research, Vol. 6, pgs. 1173-1180.
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7. R Core Team, 2018, "R: A Language and Environment for Statistical Computing", R Foundation 560 for Statistical Computing, Vienna, Austria.

Additional information: