

University of Rhode Island

DigitalCommons@URI

---

Civil & Environmental Engineering Faculty  
Publications

Civil & Environmental Engineering

---

2018

## Quantifying and contextualizing disinfection byproducts during the Flint Water Crisis: a case study, and framework for broader application

Joseph E. Goodwill

*University of Rhode Island, goodwill@uri.edu*

Mark W. Hagemann

Marc A. Edwards

David A. Reckhow

Follow this and additional works at: [https://digitalcommons.uri.edu/cve\\_facpubs](https://digitalcommons.uri.edu/cve_facpubs)

---

### Citation/Publisher Attribution

Goodwill, J. E., Hagemann, M. W., Edwards, M. A., & Reckhow, D. A. (2018). Quantifying and contextualizing disinfection byproducts during the Flint Water Crisis: a case study, and framework for broader application. *Journal of Water Supply: Research and Technology-Aqua*, 67(7), 648-658. doi: 10.2166/aqua.2018.075  
Available at: <https://doi.org/10.2166/aqua.2018.075>

This Article is brought to you by the University of Rhode Island. It has been accepted for inclusion in Civil & Environmental Engineering Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact [digitalcommons-group@uri.edu](mailto:digitalcommons-group@uri.edu). For permission to reuse copyrighted content, contact the author directly.

---

## Quantifying and contextualizing disinfection byproducts during the Flint Water Crisis: a case study, and framework for broader application

The University of Rhode Island Faculty have made this article openly available.  
Please let us know how Open Access to this research benefits you.

This is a pre-publication author manuscript of the final, published article.

### Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

1 **Quantifying and contextualizing disinfection byproducts during the Flint**  
2 **Water Crisis: A case study, and framework for broader application**

3  
4 Joseph E. Goodwill<sup>1\*</sup>, Mark W. Hagemann<sup>2</sup>, Marc A. Edwards<sup>3</sup>, David A. Reckhow<sup>2</sup>

5  
6 <sup>1</sup>Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, RI,  
7 USA; <sup>2</sup>Department of Civil and Environmental Engineering, University of Massachusetts,  
8 Amherst, MA, USA; <sup>3</sup>Department of Civil and Environmental Engineering, Virginia Tech,  
9 Blacksburg, VA, USA. \*Corresponding author Email: goodwill@uri.edu

10

11 **SHORT TITLE:** Quantifying and contextualizing disinfection byproducts, Flint Water Crisis

12

13 **ABSTRACT**

14 Total trihalomethanes (TTHMs) and other disinfection byproducts (DBPs) have been a concern  
15 in Flint, Michigan, in both delivered water and water from home water heaters. Historical TTHM  
16 data and DBP sampling results from Flint were combined with models for predicting hot water  
17 TTHMs to assess the probability of certain DBP concentrations. Results were compared with hot  
18 and cold water DBPs from a water system in Florida. Flint results were used to estimate cancer  
19 risk resulting from chronic exposure to hot water TTHMs, and compared to similar risk  
20 assessments in other water systems. Results indicate TTHM concentrations decreased in Flint  
21 following a return to water from the Detroit Water and Sewerage Department, and were very  
22 near the mean value for public drinking water systems in the United States. Measurement of  
23 other unregulated DBPs also indicated levels within the typical ranges. Monte Carlo simulations

24 coupled with modeling of hot water TTHMs indicated a low probability of TTHMs exceeding 80  
25  $\mu\text{g/L}$  in Flint in 2016. The estimated cancer risk from exposure to TTHMs in Flint is similar to  
26 other areas. The methods used in this work can apply broadly to other water systems to de-  
27 escalate perceptions of risk following a water crisis.

28  
29 **KEYWORDS** | disinfection byproducts; water heaters; trihalomethanes; risk; modeling

## 30 31 **INTRODUCTION**

32 The City of Flint, Michigan (Flint) has experienced a well-documented water crisis (Schwake *et*  
33 *al.* 2016; Pieper *et al.* 2017). In April of 2014, Flint switched from using finished water from the  
34 Lake Huron Water Treatment Plant of the Detroit Water and Sewerage Department (DWSD) to  
35 water from the Flint River, treated in the City's Water Treatment Plant (Flint WTP). Differences  
36 in raw water chemistry and failure to add corrosion control chemicals caused extensive  
37 corrosion, and released lead (Pb) into consumers' water. The Flint water system also experienced  
38 elevated levels of total trihalomethanes (TTHMs), which exceeded United States Environmental  
39 Protection Agency (USEPA) regulations (State of Michigan Department of Environmental  
40 Quality 2014). Corrective action was recommended to address these water quality problems,  
41 although the response was delayed (Masten *et al.* 2017). On October 16, 2015, the Flint water  
42 system resumed using DWSD water in an effort to abate the public health crises. Public  
43 confidence in the water supply and government agencies was severely weakened.

44 Following the return to DWSD water, an advocacy group began measuring  
45 trihalomethanes (THMs) and other compounds in delivered and heated tap water in Flint homes,  
46 and publicly announced that "dangerous" levels of chloroform and other THMs were present

47 (Water Defense 2016). However, this group's sampling methods were unorthodox, and results  
48 were not peer reviewed. The accuracy and value of these results are indeterminable.  
49 Nevertheless, the findings were broadcasted by media outlets, with the implication that water in  
50 Flint was unsafe for bathing and other basic hygiene practices, and many consumers stopped  
51 bathing as a result. Simultaneously, outbreaks of preventable communicable disease such as  
52 Shigellosis appeared in Flint, which were possibly due to a decrease in hygiene behaviors arising  
53 out of the escalating fear (Hauser 2016; Roy 2017).

54 The results were difficult to assess for another reason: domestic hot water quality is not  
55 regulated, and data on DBP in heated water is scant. The possible risk from exposure to THMs in  
56 cold and especially hot water required further study. Published approaches exist for predicting  
57 hot water DBPs based on water quality parameters in the cold water (Chowdhury, Rodriguez,  
58 Sadiq, & Serodes 2011). Likewise, methods exist for estimating potential health risk posed by  
59 DBP concentrations (W. Wang, Ye, Yang, Li, & Wang 2007; Chowdhury, Rodriguez, & Sadiq  
60 2011; Y. Wang, Small, & VanBriesen 2016). These modeling and risk approximation methods  
61 were combined to help provide an informed estimation of risk from hot water DBPs, despite  
62 limited data. Also, sampling results of cold and hot water DBPs from a surface water system in  
63 Florida were directly compared with Flint measurements to provide additional contextualization.

64 The overarching goal of this study was to enable more informed water usage decisions by  
65 providing defensible measurements and context to Flint DBP results. To that end, the specific  
66 objectives of this study were to: (1) measure THMs and other DBPs in Flint, allowing direct  
67 comparison with previously reported results; (2) compile, integrate, and review historical data for  
68 TTHMs and other DBPs from Flint, DWSD and prior national THM surveys; (3) use Monte  
69 Carlo simulations coupled with previously developed hot water TTHM predictive models to

70 develop probable hot and cold water TTHM ranges experienced by Flint water consumers from  
71 2014–2016; and (4) contextualize probable hot-water THM risk levels against prior published  
72 cancer risk approximations in Flint following the return to DWSD. While applied to Flint here,  
73 the approach in this work may be useful as a framework for perceived risk management in other  
74 systems with limited DBP data and increasing customer concern.

75

## 76 **MATERIALS AND METHODS**

### 77 **Sampling and measurement of cold and hot water disinfection byproducts**

78 All DBP sampling and analysis for this study was executed using established methodology  
79 (Stevens & Symons 1976; Symons, Krasner, Simms, & Scilimenti 1993; APHA 2012). Both hot  
80 and cold water samples were collected from four sites selected based on previously known issues  
81 with elevated DBPs. Sampling was conducted on two dates in May 2016. Samples were  
82 collected from each site and analyzed for regulated and unregulated DBPs. Reporting focused on  
83 TTHMs and other volatiles since these were the constituents of interest in work by other groups.  
84 Compliance data show the City of Flint did not have a haloacetic acid (HAA) violation in 2014,  
85 2015, or 2016 (City of Flint 2016), including during the peak of the water crisis. As such, they  
86 were not the focus of this study.

87         Samples were collected from bathtub taps in three residential locations and from a sink in  
88 a separate commercial location. Samples were drawn in the middle of the day without prior  
89 consideration of water age. Water had previously been used at the sampling fixture in each  
90 location prior to the moment of sampling, and fixtures were not further flushed prior to drawing  
91 samples. Cold water samples were drawn first, directly from the respective water fixture with the  
92 hot water tap completely shut. Hot water samples were drawn immediately following cold water

93 by fully shutting the cold water valve and fully opening the hot water valve. Temperature was  
94 monitored until it reached a stable, maximum value (approximately 10–20 seconds) and then a  
95 hot sample was collected.

96 One sample for each family of DBPs (e.g., HAAs, THMs, etc.) was collected at each  
97 location in 3-litre acid-washed and chlorine demand free borosilicate glass bottles. Preservatives  
98 were added to each bottle prior to filling for the purpose of quenching residual chlorine and  
99 stabilizing the analytes. Sample bottles were filled completely without headspace, sealed  
100 securely, and kept cold ( $\sim 4^{\circ}\text{C}$ ) and in the dark during transport. Hot water was sampled in  
101 variable-volume, headspace-free bottles developed specifically for the sampling of DBPs in hot  
102 water (Liu & Reckhow 2013). In short, these variable-volume bottles contain a piston that  
103 contracts as the water cools thereby stopping the development of negative pressure inside the  
104 bottle which would increase the likelihood of air intrusion and the loss of volatile analytes.

105 Analytes in this study included four chlorine- and bromine-containing THMs (e.g.,  
106 summed to comprise TTHMs), three dihaloacetonitriles (DHANs; dichloro-, bromochloro-, and  
107 dibromoacetonitriles), two haloketones (HKs; dichloropropanone (DCP) and trichloropropanone  
108 (TCP)), and chloropicrin (CP). The four THMs comprising TTHMs are chloroform ( $\text{CHCl}_3$ ),  
109 bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ ).  
110 Arsenite was used as the quenching agent for all analytes. These compounds were measured by  
111 liquid/liquid extraction (LLE) with pentane followed by gas chromatography (GC) with electron  
112 capture detection (ECD). All analytical steps conformed to USEPA Method 551.1 (USEPA,  
113 1995). DBP samples from the independent sampling event in Florida were treated in the same  
114 manner as the Flint DBP samples. Samples were analyzed in duplicate (e.g. two sub-samples  
115 from one bottle collected, as previously described) with two injections per sub-sample. Sampling

116 in Flint and Florida included a travel blank for each site, consisting of deionized (DI) water only.  
117 The DI water was transferred on site to a DBP sampling bottle at the time other samples were  
118 collected. TTHM concentrations in the travel blanks ranged from 1.0% to 1.4% of the TTHM  
119 concentrations found in the domestic water samples. All other DBPs in the travel blanks were  
120 below detection limits.

121 Chlorine was measured using an adapted DPD (N,N-diethyl-p-phenylenediamine  
122 colorimetric method (APHA, 2012). Temperature and pH were measured using a calibrated field  
123 pH meter and probe with automatic temperature correction.

124

## 125 **Modeling methods**

126 Published models for predicting hot water DBPs based on other water quality parameters were  
127 adopted (Chowdhury et al. 2011b) including a main factors linear (MFL) model, and a log-linear  
128 (LL) model. These two models were chosen based on previously assessed performance. The  
129 MFL and LL models were found to have the best performance by Chowdhury et al. (2011b) in  
130 terms of correlation coefficient, with respective values of 0.89 and 0.86. The inputs for the MFL  
131 model were: free chlorine residual in distributed water ( $Cl_{2Free}$ ); cold water THMs as measured in  
132 the distribution system ( $THM_{WDS}$ ); and cold water pH, shown in Equation (1). The LL model  
133 also has inputs of  $Cl_{2Free}$  and  $TWH_{WDS}$ , shown in Equation (2). Model coefficients developed by  
134 Chowdhury et al. (2011b) were utilized in this study without modification; however, they were  
135 originally developed using water from multiple water sources with varying water quality (i.e.  
136 raw water TOC ranged from 1.2 to 12.6 mg/L). Thus, the models are at least somewhat site  
137 independent.

138



139 
$$THM_{HWT} = \beta_0 + \beta_1 THM_{WDS} + \beta_2 Cl_{2Free} + \beta_3 pH$$
 (1)

140

141 where  $THM_{HWT}$  = hot water tank THMs,  $\beta_0 = 307.1$ ,  $\beta_1 = 1.073$ ,  $\beta_2 = 48.91$ ,  $\beta_3 = -40.4$ ,  $Cl_{2Free}$  =  
142 distribution system free chlorine,  $THM_{WDS}$  = distribution system THMs.

143

144 
$$THM_{HWT} = Exp(\beta_0 + \beta_1 Ln(Cl_{2Free}) + \beta_2 Ln(THM_{WDS}))$$
 (2)

145

146 where  $\beta_0 = 2.367$ ,  $\beta_1 = 0.431$ , and  $\beta_2 = 0.588$ .

147

148 Models were used to predict  $THM_{HWT}$  for each year from 2014 through mid-2016, a time  
149 period over which significant changes in water source, treatment operation and water quality  
150 occurred (Masten et al. 2017). Model inputs were generated from a distribution having the mean  
151 and variance equal to that of each year's measured data (see Supplementary Information, Table  
152 SI-1). For 2014 and 2015, data for  $THM_{WDS}$  were obtained from Flint's DBP monitoring  
153 program (City of Flint 2015), while pH and  $Cl_{2Free}$  values were taken from the Flint WTP  
154 Monthly Operation Reports (MORs) (City of Flint 2016). Model inputs for 2016 came from  
155 USEPA data produced by monthly sampling from January 2016 through June 2016 (24 sites,  
156 sampled monthly) (USEPA 2016a).

157 Monte Carlo sampling was used to assess the probability distribution of THM exposure  
158 from hot-water tanks. Similar approaches have been used successfully to inform DBP regulations  
159 (USEPA 1997) and to assess the effect of increasing bromide concentrations on THM risk  
160 (Wang et al. 2016). The sample mean and standard deviation for the data from each year were  
161 used to generate a random sample of size 10000 for pH,  $Cl_{2Free}$ , and  $THM_{WDS}$ . A log-normal

162 distribution was assumed for  $\text{Cl}_{2\text{Free}}$  and  $\text{THM}_{\text{WDS}}$ , and a normal distribution was used for pH.  
163 These samples were used to simulate a distribution of predicted  $\text{THM}_{\text{HWT}}$  via Equations (1) and  
164 (2). Model residual error was included in the MFL and LL predictions, based on the RMSE  
165 reported in Chowdhury et al. (2011b).

## 167 **Risk assessment**

168 Cancer risk from TTHMs was estimated using a published model that calculates a risk (lifetime  
169 cancer risk based on exposure) for each regulated THM species including  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  
170  $\text{CHClBr}_2$  and  $\text{CHBr}_3$ , and for each potential exposure pathway (oral, inhalation, and dermal),  
171 including cold water and heated water used for showering (Chowdhury, Rodriguez, & Sadiq  
172 2011). This additive approach has also been used to assess the cancer risk associated with  
173 increasing bromine in drinking water sources (Wang et al. 2016). The specific cancer risks were  
174 based on the slope factors for each THM ( $\text{mg kg}^{-1} \text{day}^{-1}$ ), which were taken from the Integrated  
175 Risk Information System (IRIS) (USEPA 2016b) and Risk Assessment Information System  
176 (RAIS) (US Department of Energy 2016). A slope factor for  $\text{CHCl}_3$  is not available from IRIS as  
177 its classification is under reassessment, thus it has not been included in this calculation, an  
178 approach taken in similar risk assessments (Chowdhury 2016). Inhalation exposure slope factors  
179 for  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$  have not been determined and were taken to equal the oral exposure  
180 slope factors, an imperfect but necessary assumption. Many other assumptions went into the  
181 calculation of specific risk (e.g. body mass, bathroom ventilation) and these values may vary  
182 significantly across the Flint population. Values from these variables were taken from several  
183 sources (McKone 1987; United States Environmental Protection Agency 1998; Chowdhury &  
184 Champagne 2009). However, no model will be able to perfectly capture all of this variation, and

185 slope factors extrapolated from rodent studies of single contaminants carry additional limitations.  
186 For specific cancer risks, the three regulated THMs were multiplied by the hot water THMs  
187 measured in the May 2016 sampling event when calculating thermal exposure during showering,  
188 an inherently conservative approach compared with other studies attempting to calculate a blend  
189 of cold and hot water THMs. Cold water THMs measured in this study were assumed for the  
190 injection exposure pathway. The risk assessment did not consider haloacetic acids (HAAs) as  
191 there was no violation of HAA maximum contaminant levels at any point during the crisis. Also,  
192 HAAs are non-volatile and thus unlikely to pose significant risk through the inhalation pathway  
193 as opposed to TTHMs. The risk assessment did also not consider adjustment factors for potential  
194 early life exposure.

195

## 196 **RESULTS AND DISCUSSION**

### 197 **Historical trihalomethanes**

198 Results from THM sampling conducted by the City of Flint (May 2014 – October 2015) and the  
199 EPA (February 2016 – May 2016) are summarized in the Supplementary Information in Figure  
200 SI-1. TTHMs in the summer of 2014 were elevated. For August 2014, the lowest TTHM result in  
201 the system was above the locational running annual average (LRAA) regulatory limit of 80 µg/L.  
202 The maximum result approached 200 µg/L, and the median was 134 µg/L. This led to  
203 recommendations for corrective action including system flushing to reduce water age, and the  
204 cessation of filter prechlorination (Masten et al. 2017). Sampling in May and August of 2015  
205 showed significant improvement, with median TTHMs of approximately 57 and 63 µg/L,  
206 respectively.

207 Figure SI-1 also includes the DWSD average highest LRAA, which was calculated from  
208 averaging the reporting highest LRAA from DWSD consumer confidence reports from 2006  
209 through 2015 (City of Detroit 2016). Over the last 10 years, the highest LRAA of the DWSD  
210 system was approximately 35 µg/L, 55% less than the regulatory limit. The TTHM sampling  
211 results from 2016 again showed marked improvement over the results from 2015. The most  
212 recent data available for Flint shows a median TTHM concentration of 35 µg/L, 60% less than  
213 the median from May of 2014 (USEPA 2016a). A subsequent, independent study of one cold  
214 water site in Flint noted a TTHM concentration of 38.4 ±3.6 µg/L (Allen et al. 2017). A 2014  
215 survey of TTHMs in 394 larger (> 100,000 customers) public water systems in the United States  
216 found upper and lower quartile limits of approximately 43 and 17 µg/L, respectively (Seidel,  
217 Samson, Bartrand, Ergul, & Summers 2017).

218

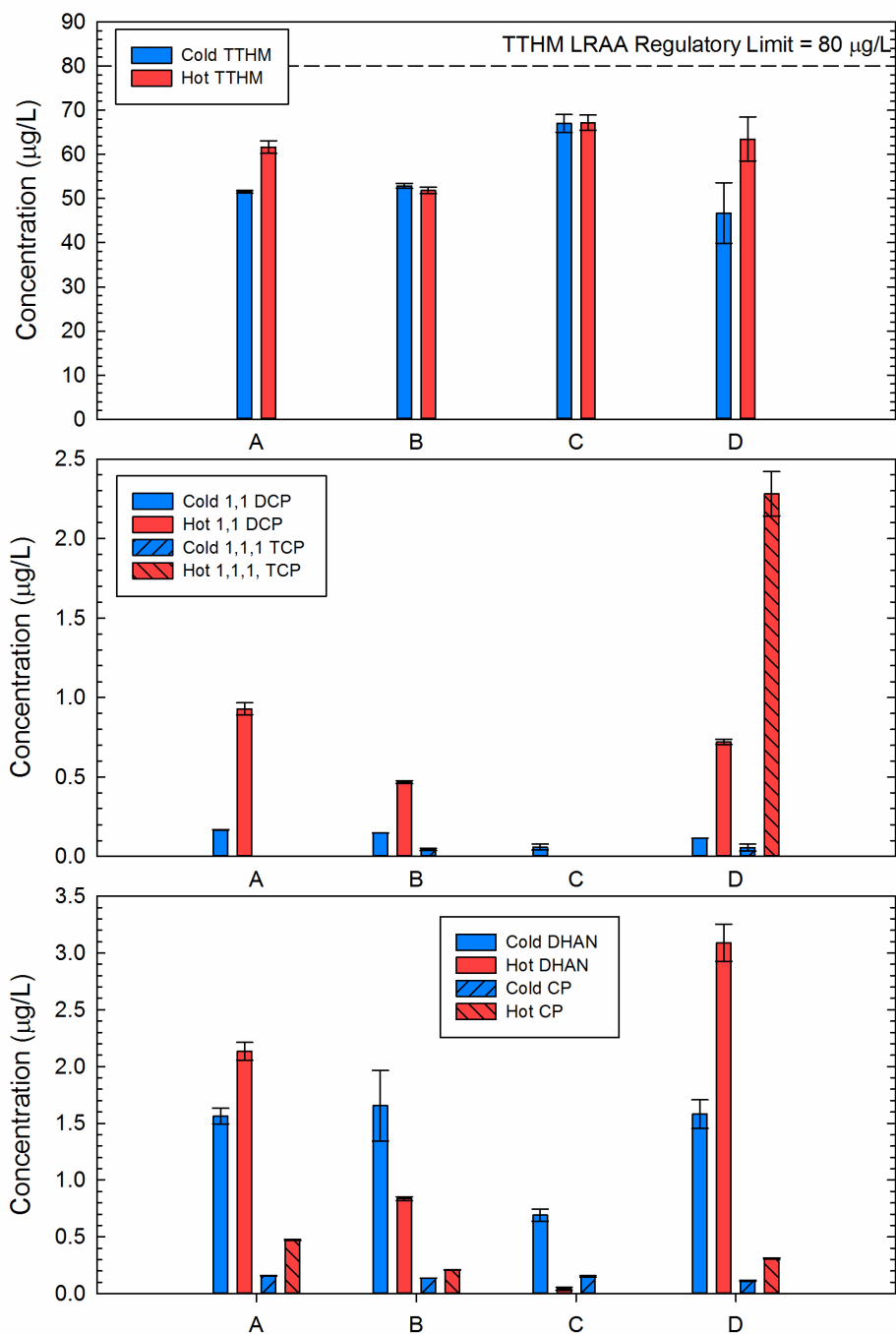
### 219 **Field measurements of disinfection byproducts and water-quality parameters**

220 Figure SI-2 (Supplementary Information) includes results of pH, free chlorine residual, and  
221 temperature for the four sites sampled as part of this study in May 2016. For each sampling  
222 location, the cold water had higher concentrations of free chlorine than hot water. Sample  
223 location A had the largest decrease in Cl<sub>2</sub> residual between the hot and cold water, followed by  
224 location D. Location D was the only site with significant remaining Cl<sub>2</sub> residual in the hot water,  
225 suggesting relatively low water age in the water heater. Location D also had the lowest hot water  
226 temperature.

227 The hot and cold concentrations of multiple DBPs in each location is presented in  
228 Figure 1. Cold water TTHMs ranged from 50 to 63 µg/L with hot water TTHMs falling in the  
229 same range. All measured hot and cold water TTHMs were below the LRAA TTHM regulatory

230 limit. Two of the four sample sites, A and D, had significant differences between cold and hot  
231 water TTHM. For locations A and D, hot water TTHMs were 19.6% and 35.8% higher,  
232 respectively, than in cold water. An increase in hot water TTHMs has been noted previously,  
233 including up to 120% increase in TTHMs in a surface water-supplied drinking water system in  
234 Massachusetts (Liu & Reckhow 2015). Chloroform was also found to increase over 100% as a  
235 result of heating in bench-scale studies at pH 7, in waters with an age of less than 72 hours (Liu  
236 & Reckhow 2013). Other investigators comparing a single cold and hot water sample from the  
237 same tap in Flint from a similar time as this study reported a 105% increase in TTHMs (38.4 to  
238 78.8  $\mu\text{g/L}$ ) (Allen et al. 2017). The exact mechanism resulting in TTHM increase is unclear, but  
239 it may be due to accelerated reactions between chlorine and precursors as well as accelerated  
240 hydrolysis of the immediate halogenated precursors (Liu & Reckhow 2013). The increase in  
241 TTHMs was also directly proportional to the magnitude of loss in residual chlorine due to  
242 heating, which was also noted in eleven additional study sites in Florida (see Figure 2).

243



244

245 Figure 1. Cold and hot water concentrations of total trihalomethanes (TTHM, top), 1,1-  
 246 dichloropropanone and 1,1,1-trichloropropanone (DCP, TCP, middle), and dihaloacetonitriles  
 247 and chloropicrin (DHAN, CP, bottom) at four sites sampled in May 2016 from the Flint

248 distribution system. Error bars represent two standard deviations. (LRAA = location running  
249 annual average)

250

251 The presence of halopropanones (i.e., DCP and TCP) in hot water was noted in a previous study  
252 of DBPs in home heating systems (Liu & Reckhow 2015). 1,1-DCP was found to increase in  
253 Locations A, D and, to a lesser extent, B in the hot water samples. Following heating, 1,1-DCP  
254 increased between 300% and 700%. The increase in 1,1-DCP was also noted in a bench-scale  
255 study where heating increased DBPs of up to 500% at neutral or slightly acidic pH, regardless of  
256 water age (Liu & Reckhow 2013). Location D had a significant increase in TCP between the hot  
257 and cold sample, increasing from 0.1 to 2.3 µg/L. This increase was unexpected, as heating to  
258 55°C has been previously shown to degrade TCP to non-detectable levels after 3 hours (Liu &  
259 Reckhow, 2013), ultimately undergoing hydrolysis reactions and forming chloroform (Reckhow  
260 & Singer 1985). However, location D was found to have both the lowest hot water temperature  
261 (41°C) and the highest hot water chlorine residual, suggesting a short residence time in the hot  
262 water tank. Therefore, increased TCP could be explained by active formation at elevated  
263 temperature, with hydrolysis rates below those observed at 55°C. A prior DBP survey reported  
264 median quarterly values of 0.6 to 2.8 µg/L for TCP in chlorinated, surface water systems  
265 (McGuire, McLain, & Obolensky 2002). All cold and hot water samples from this study fall  
266 within this range.

267 Chloropicrin concentrations followed a similar pattern to DCP, but cold-water  
268 concentrations were all less, ranging from 0.16 to 0.11 µg/L, leading to larger percent increase  
269 for locations A and D. Liu and Reckhow (2013) also noted a similar change in CP concentration  
270 with heating for waters with ages less than 48 hours. Krasner et al. (1989) reported a first quarter

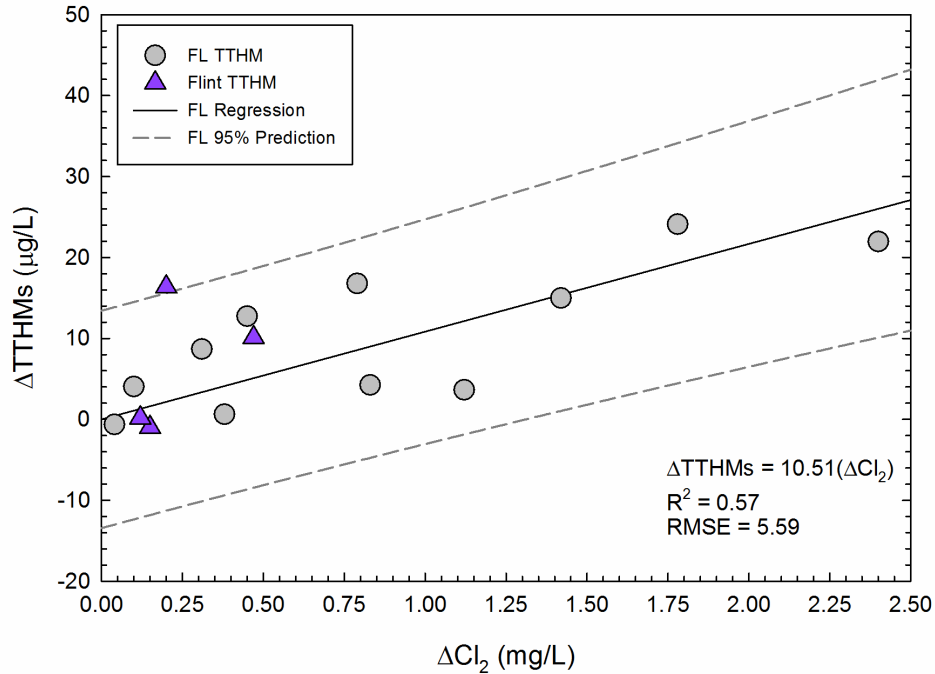
271 (e.g., spring) median chloropicrin concentration of 0.16 µg/L in their survey of DBPs in US  
272 drinking water.

273 DHANs increased between the cold water and the hot water in locations A and D. In  
274 location A, DHAN increased from 1.5 to 2.1 µg/L, or 36.5%. At location D, DHAN increased  
275 from 1.5 to 3.1, or 95.4%. While this increase is significant, the DHAN levels in the hot water  
276 samples were still within the range typically encountered in public drinking water distribution  
277 systems in the United States. A 2002 survey noted a mean DHANs values of 2.21 µg/L for  
278 surface water-sourced distribution systems (Chiu 2004). Krasner et al. (1989) reported quarterly  
279 median DHAN values ranging from 2.5 to 4.0 µg/L. DHANs decreased in locations B and C,  
280 which may be attributed to the presumed older water age in those locations. DCAN levels have  
281 been noted to drop with increasing time in hot water tanks with temperature above 35°C in a  
282 residential system (Lui & Reckhow, 2015).

283



284  
285



286

287 Figure 2. Change ( $\Delta$ ) in total trihalomethanes (TTHMs) as a function of free chlorine ( $\text{Cl}_2$ )  
288 residual loss across hot water heaters in both Flint, Michigan, and eleven sites in Florida (FL).

289

290 Figure 2 includes data from two sources: one from Flint and one from a surface-sourced  
291 chlorinated public drinking-water system in Florida. A positive correlation between the two  
292 parameters for both water systems is shown. This indicates that water heaters tend to drive  
293 reactions between free chlorine and DPB precursors to completion, which has also been noted in  
294 bench-scale simulations (Liu & Reckhow 2013).

295

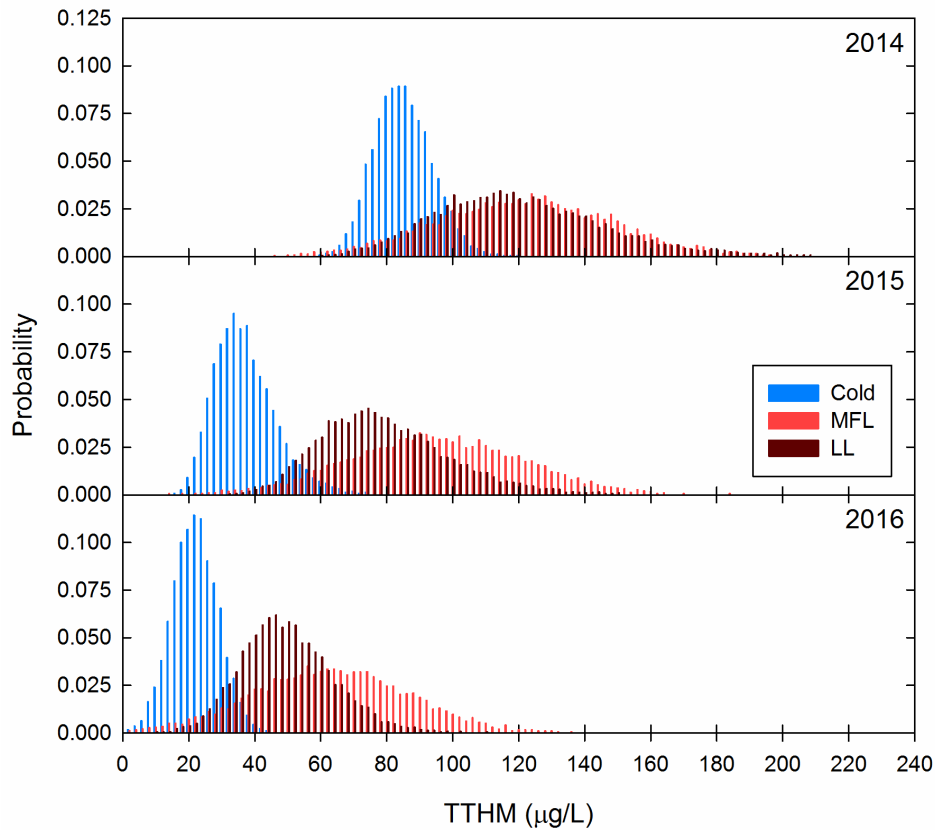
296 Figure 2 contains a linear regression of the Florida data. The linear model shows a  
297 potential stoichiometry of 10.5  $\mu\text{g/L}$  TTHM produced per 1 mg/L of  $\text{Cl}_2$  lost during heating. All  
Flint data fall within or nearly within the 95% prediction interval of the linear regression which

298 indicate that there is no strong evidence that Flint hot water TTHMs have a different relationship  
299 with changes in free chlorine as a result of water heating than those in the Florida water system.  
300 In other words, measured hot water TTHMs from Flint would have been predicted based on the  
301 Florida results. In this way, there was nothing exceptional about the changes in DBPs due to  
302 water heating in Flint in the context of the Florida results. Other factors may affect changes in  
303 TTHMs as a result of heating that are not captured in the linear regression model ( $R^2 = 0.57$ ).  
304 Examples could include heating time, heating temperature, and the nature of natural organic  
305 material (NOM). It was not possible to quantify the nature of the Flint water NOM within the  
306 scope of field sampling. This intersystem linear regression model comparison technique may  
307 assist other investigators exploring the exceptionality of changes to DBPs as a result of heating.

308

### 309 **Modeling of probable trihalomethane concentrations**

310 Figure 3 shows a drastic decrease in simulated cold and hot water TTHMs from May 2014 to  
311 May of 2016. For 2014, both models suggested a high probability ( $p > 0.9$ ) of hot water TTHMs  
312 being above 80  $\mu\text{g/L}$ . The MFL results for 2016 suggested a probability of 0.77 for hot water  
313 TTHMs falling below 80  $\mu\text{g/L}$ , with the LL producing a corresponding probability of 0.97.  
314 Independent of sampling of Flint hot water DBPs at two locations in July 2016 noted hot water  
315 TTHMs of  $78.8 \pm 3.6$  and  $69.5 \pm 1.4$   $\mu\text{g/L}$  (Allen *et al.* 2017). Hot water TTHMs for all model  
316 years were directly proportional to cold water TTHMs, as shown in Equations (1) and (2).



317

318 Figure 3. Results of Monte Carlo simulation (ten thousand iterations) of probable cold and hot  
 319 water total trihalomethanes concentrations in delivered Flint water in 2014, 2015 and January–  
 320 May 2016. (MFL = hot water TTHMs from main factors linear model; LL = hot water TTHMs  
 321 from log-linear model). 80 µg/L is the current USEPA TTHM LRAA regulatory limit for  
 322 delivered water.

323

324 While this study generated samples of  $Cl_{2Free}$ , pH and  $THM_{WDS}$  independently of one another  
 325 when conducting the Monte Carlo simulation, a more accurate account of  $THM_{HWT}$  distribution  
 326 would have considered the covariance structure between these quantities. Unfortunately,  
 327 available data did not allow covariance to be quantified as, with very few exceptions, the  
 328 measurements of different water quality parameters were not concurrent, and instead came from

329 different water samples at different times and/or locations. Therefore, the assumption that all  
330 model input variables are independent was necessary. If the predictor variables were positively  
331 correlated then the true variance could have been larger, resulting in a higher probability of  
332 THM<sub>HWT</sub> exceeding 80 µg/L.

333

### 334 **Risk comparison**

335 While TTHMs are regulated in aggregate, there are individual health considerations for each  
336 compound. Results from DBP field sampling from the USEPA and this study for each regulated  
337 THM are shown in Figure SI-3 (Supplementary Information). The average bromide  
338 incorporation factor (BIF) (Obolensky & Singer 2005) for all USEPA cold water results was  
339 0.175. Siedel et al. (2017) reported an annual median BIF of THMs from 121 large drinking  
340 water systems in the United States ranging from of 0.13 to 0.21. In this study, the BIF was 0.131  
341 and 0.120 for cold and hot water samples, respectively, indicating bromide incorporation less  
342 than many large drinking water systems in the US.

343 The median estimated cancer risk for the Flint system was estimated at  $3.1 \times 10^{-5}$ , or 3.1  
344 per 100,000 (Chowdhury 2016). Based on the limitations of the estimation methods  
345 (extrapolation from rodent exposure studies, lack of slope factors for all pathways, etc.), it is  
346 anticipated that this result is more valuable when compared with the results of prior, similar risk  
347 assessments of other potable water systems, and not as a quantification of specific risk in Flint.  
348 Other investigators have reported similar risks from TTHMs, including a median average risk for  
349 the Providence of Ontario of 1.9 per 100,000 and a 90<sup>th</sup> percentile risk of 5.5 per 100,000  
350 (Chowdhury, Rodriguez, & Sadiq 2011). A study of THMs in Taiwanese cities reported median  
351 and 90<sup>th</sup> percentile cancer risk for the city of Kaohsiung of 6.4 and 19.3 per 100,000, respectively

352 (Wang, Ye et al. 2007). The estimated cancer risk in Flint falls between the median and 90<sup>th</sup>  
353 percentile risk assessed for Ontario, and less than the median risk for Kaohsiung. Cancer risk  
354 assessment from DBPs, both in cold and hot water, remains challenging; however, these  
355 assessments and comparison may prove helpful to water utilities when concerns over  
356 “dangerous” levels of DBPs emerge following a crisis.

357

### 358 **Broader hot water DBP concerns**

359 Concerns regarding hot water DBPs extend beyond Flint. These concerns persist partly because  
360 regulations do not cover heated water DBPs in premise plumbing. Yet, heated water represents a  
361 significant contribution to the overall exposure to THMs. Federal regulatory jurisdiction limits  
362 what can be done to protect the public from drinking water contaminants. Thus, there is an  
363 inherent, persistent gap between risk and regulatory protection. In this gap, perceived risk can  
364 expand leaving some to propose that a problematic level of unreasonable fear is becoming  
365 common among water consumers (Mercer 2017). While actual risk may not be possible to  
366 quantify exactly, the perception of risk from treated water can be de-escalated using the  
367 approaches described here. In this way, the response to hot water TTHMs in Flint can be seen as  
368 a broader framework for the contextualization and de-escalation of perceived risk following a  
369 water crisis, as shown in Figure 4.

370

371 Figure 4. Framework for de-escalation of perceived risk following water crisis event

372

373 Figure 4 contains all of the approaches contained in this study including a historical comparison  
374 (Figure SI-1), a geographical comparison (Figure 2, and literature references), defensible

375 measurements (Figure 1), hot water THM modeling and Monte Carlo Sampling (Figure 3), and  
376 risk comparison. Each step in this framework may serve to decrease a water quality knowledge  
377 gap, enabling more informed perceptions of risk and choices regarding personal water use.

378         Communication with the public is an important part of shifting perception (Fischhoff  
379 1995; Johnson 2003). Results in this study were disseminated to the public through several  
380 pathways including traditional media press conferences and social media. While examining  
381 specific communication techniques is not in the scope of this work, communication with water  
382 customers is an active field of applied research within the water industry (K. Smith 2016).  
383 Recently, former technical leadership at Water Defense retracted prior statements regarding  
384 dangerous disinfection byproducts in Flint citing several components of this study and  
385 framework (S. Smith 2018).

386

## 387 **CONCLUSIONS**

388 Results show TTHMs and other unregulated DBPs in Flint water were likely near median values  
389 for delivered drinking water from surface water treatment plants across the United States,  
390 following a return to DSDW. There were very few noteworthy or exceptional characteristics  
391 about the Flint DBP profile found in this study, or by the sampling of the USEPA and other  
392 investigators. The changes in Flint TTHM concentrations and speciation as a result of water  
393 heaters is also similar to those noted in a Florida surface water system. The approximated cancer  
394 risks from DBPs in Flint based on results in this study are similar to or less than those in other  
395 developed regions of North America and Asia.

396         Additionally, models and field measurements suggest it is unlikely that hot water TTHMs  
397 and some unregulated DBPs were elevated in the first half of 2016. These results are important,

398 as there has been persistent heightened consumer concern over TTHMs in Flint. This concern  
399 increased due to several factors, including credence given to DBP sampling by third parties using  
400 unproven methodology. This concern caused changes in hygiene practices requiring water such  
401 as handwashing, and a subsequent increase in Shigellosis cases in Flint. Results in this study  
402 suggest these changes in handwashing may not be supported by the estimated cancer risk posed  
403 by TTHM concentrations in Flint, especially the low risk contributed by the dermal exposure  
404 pathway.

405

406

#### 407 **ACKNOWLEDGEMENTS**

408 Funding for some of this work came from the USEPA. The views expressed here are exclusively  
409 those of the authors, and not the USEPA. The authors acknowledge the efforts of Xuyen Mai,  
410 Xian Ma, Yanjun Jiang, Sherrie Webb-Yagodzinski, and Charles Spellman Jr. in water sampling,  
411 sample analysis, and data compilation.

412

#### 413 **REFERENCES**

414 APHA 2012 *Standard Methods for the Examination of Water and Wastewater* American Water

415 *Works Association/American Public Works Association/Water Environment Federation.*

416 Chiu N. (USEPA) 2004 *Halogenated Acetonitriles in Drinking-Water: Background Document*

417 *for Development of WHO Guidelines for Drinkingwater Quality.* Retrieved from

418 [http://www.who.int/water\\_sanitation\\_health/water-](http://www.who.int/water_sanitation_health/water-)

419 [quality/guidelines/chemicals/halogenatedacetone.pdf](http://www.who.int/water_sanitation_health/water-quality/guidelines/chemicals/halogenatedacetone.pdf) (accessed 21 December 2016)

420 Chowdhury S. 2016 Effects of plumbing systems on human exposure to disinfection byproducts

421 in water: A case study. *Journal of Water and Health*, **14**(3), 489–503.  
422 <https://doi.org/10.2166/wh.2015.145>

423 Chowdhury S., Champagne P. 2009 Risk from exposure to trihalomethanes during shower:  
424 Probabilistic assessment and control. *Science of the Total Environment*, **407**(5), 1570–1578.  
425 <https://doi.org/10.1016/j.scitotenv.2008.11.025>

426 Chowdhury S., Rodriguez M. J., Sadiq R. 2011 Disinfection byproducts in Canadian provinces:  
427 Associated cancer risks and medical expenses. *Journal of Hazardous Materials*, **187**(1–3),  
428 574–584. <https://doi.org/10.1016/j.jhazmat.2011.01.085>

429 Chowdhury S., Rodriguez M. J., Sadiq R., Serodes J. 2011 Modeling DBPs formation in  
430 drinking water in residential plumbing pipes and hot water tanks. *Water Research*, **45**(1),  
431 337–347. <https://doi.org/10.1016/j.watres.2010.08.002>

432 City of Detroit 2016 Water Quality Reports. [http://www.detroitmi.gov/How-Do-I/Find/Water-](http://www.detroitmi.gov/How-Do-I/Find/Water-Quality-Reports)  
433 [Quality-Reports](http://www.detroitmi.gov/How-Do-I/Find/Water-Quality-Reports) (accessed 21 December 2016)

434 City of Flint 2015 *City of Flint Water Timeline*. Flint. Retrieved from  
435 <https://www.cityofflint.com/public-works/city-water-system-timeline/> (accessed 5 January  
436 2017)

437 City of Flint 2016 Water Treatment Plant. [https://www.cityofflint.com/public-](https://www.cityofflint.com/public-works/utilitieswater/water-treatment-plant/)  
438 [works/utilitieswater/water-treatment-plant/](https://www.cityofflint.com/public-works/utilitieswater/water-treatment-plant/) (accessed 4 March 2017)

439 Fischhoff B. 1995 Risk Perception and Communication Unplugged: Twenty Years of Process.  
440 *Risk Analysis*, **15**(2), 137–145. <https://doi.org/10.1111/j.1539-6924.1995.tb00308.x>

441 Hauser C. 2016, October 4 Flint Hit With Bacterial Illness as Residents Shun City Water. *New*  
442 *York Times*. New York, p. Retrieved from <http://nyti.ms/2dC4RXc> (accessed 5 January  
443 2017)



444 Johnson B. B. 2003 Do reports on drinking water quality affect customers' concerns?  
445 Experiments in report content. *Risk Analysis*, **23**(5), 985–998. <https://doi.org/10.1111/1539->  
446 [6924.00375](https://doi.org/10.1111/1539-6924.00375)

447 Liu B., Reckhow D. A. 2013 DBP formation in hot and cold water across a simulated  
448 distribution system: Effect of incubation time, heating time, pH, chlorine dose, and  
449 incubation temperature. *Environmental Science and Technology*, **47**(20), 11584–11591.  
450 <https://doi.org/10.1021/es402840g>

451 Liu B., Reckhow D. A. 2015 Impact of Water Heaters on the Formation of Disinfection By-  
452 products. *Journal - American Water Works Association*, **107**(6), E328–E338.  
453 <https://doi.org/10.5942/jawwa.2015.107.0080>

454 Masten S. J., Davies S. H., McElmurry S. 2017 Flint Water Crisis: What Happened and Why?  
455 *Journal - American Water Works Association*, **108**(12), 21–34.

456 McGuire M., McLain J., Obolensky A. 2002 *Information Collection Rule Data Analysis*. Denver,  
457 CO.

458 McKone T. E. 1987 Human Exposure to Volatile Organic Compounds in Household Tap Water:  
459 The Indoor Inhalation Pathway. *Environmental Science and Technology*, **21**(12), 1194–  
460 1201. <https://doi.org/10.1021/es00165a006>

461 Mercer K. L. 2017 Is Fear a CEC? *Journal (American Water Works Association)*, **109**(11), 2.

462 Obolensky A., Singer P. C. 2005 Halogen substitution patterns among disinfection byproducts in  
463 the information collection rule database. *Environmental Science and Technology*, **39**(8),  
464 2719–2730. <https://doi.org/10.1021/es0489339>

465 Pieper K. J., Tang M., Edwards M. A. 2017 Flint Water Crisis Caused By Interrupted Corrosion  
466 Control: Investigating 'Ground Zero' Home. *Environ. Sci. Technol.*, **51**(4), 2007–2014.

467 <https://doi.org/10.1021/acs.est.6b04034>

468 Reckhow D. A., Singer P. C. 1985 Mechanisms of organic halide formation and implications  
469 with respect to pre-ozonation. In: *Water Chlorination: Chemistry, Environmental Impact,*  
470 *and Health Impacts*, R. Jolley, R. Bull, W. Davis, & S. Katz (eds.). Chelsea, MI, pp. 1229–  
471 1257.

472 Roy S. 2017 The Hand-in-Hand Spread of Mistrust and Misinformation in Flint. *American*  
473 *Scientist*, **105**(1). <https://doi.org/10.1511/2017.124.22>

474 Schwake D., Garner E. D., Strom O. R., Pruden A., Edwards M. A. 2016 Legionella DNA  
475 markers in tap water coincident with spike in Legionnaires' disease in Flint, MI.  
476 *Environmental Science & Technology Letters*, **3**(9), 311–315.  
477 <https://doi.org/10.1021/acs.estlett.6b00192>

478 Seidel C., Samson C., Bartrand T., Ergul A., Summers R. S. 2017 Disinfection Byproduct  
479 Occurrence at Large Water Systems After Stage 2 DBPR. *Journal American Water Works*  
480 *Association*, **109**(7), 17–30.

481 Smith K. 2016 Lead Communication: Its not what you say but how you say it. *AWWA Opflow*,  
482 (April), 188–200. <https://doi.org/10.5991/OPF.2018.44.0038>

483 Smith S. 2018 Lessons I learned in Flint and clarifying the facts.  
484 <http://flintwaterstudy.org/2018/07/scott-smith-flint-guest-post/> (accessed 11 July 2018)

485 State of Michigan Department of Environmental Quality 2014 Violation Notice - Maximum  
486 Contaminant Level for Total Trihalomethanes. Lansing, p. 2. Retrieved from  
487 [https://www.cityofflint.com/wp-content/uploads/City-of-Flint-Violation-Notice-MCL-](https://www.cityofflint.com/wp-content/uploads/City-of-Flint-Violation-Notice-MCL-TTHM-12_16_14.pdf)  
488 [TTHM-12\\_16\\_14.pdf](https://www.cityofflint.com/wp-content/uploads/City-of-Flint-Violation-Notice-MCL-TTHM-12_16_14.pdf) (accessed 4 March 2017)

489 Stevens A. A., Symons J. M. 1976 Measurement of THM and precursor concentration changes.

490 *Journal - American Water Works Association*, **68**(10), 546–554.

491 Symons J. M., Krasner S. W., Simms L. A., Scilimenti M. 1993 Measurement of THM and  
492 precursor concentrations revisited: the effect of bromide ion. *Journal - American Water*  
493 *Works Association*, **85**(1), 51–62.

494 United States Environmental Protection Agency 1998 *Human Health Risk Assessment Protocol*.

495 US Department of Energy 2016 Risk Assessment Information System. <https://rais.ornl.gov/>  
496 (accessed 5 January 2017)

497 USEPA 1995 Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents and  
498 Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and  
499 Gas Chromatography With Electron-Capture Detection.

500 USEPA 1997 Exposure Factors Handbook. *Us Epa*, **I**(August 1997), 1193.  
501 [https://doi.org/EPA/600/P-95/002F a-c](https://doi.org/EPA/600/P-95/002F_a-c),

502 USEPA 2016a Flint Water Sampling Objectives. [https://www.epa.gov/flint/flint-water-sampling-](https://www.epa.gov/flint/flint-water-sampling-objectives)  
503 [objectives](https://www.epa.gov/flint/flint-water-sampling-objectives) (accessed 5 January 2017)

504 USEPA 2016b Integrated Risk Information System. <https://www.epa.gov/iris> (accessed 4  
505 January 2016)

506 Wang G.-S., Deng Y.-C., Lin T.-F. 2007 Cancer risk assessment from trihalomethanes in  
507 drinking water. *Science of The Total Environment*, **387**(1), 86–95.  
508 <https://doi.org/10.1016/j.scitotenv.2007.07.029>

509 Wang W., Ye B., Yang L., Li Y., Wang Y. 2007 Risk assessment on disinfection by-products of  
510 drinking water of different water sources and disinfection processes. *Environment*  
511 *International*, **33**(2), 219–225. <https://doi.org/10.1016/j.envint.2006.09.009>

512 Wang Y., Small M. J., VanBriesen J. M. 2016 Assessing the risk associated with increasing

513 bromide in drinking water sources in the Monongahela River, Pennsylvania. *Journal of*  
514 *Environmental Engineering*, **143**(Mcl), 1–10. [https://doi.org/10.1061/\(ASCE\)EE.1943-](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001175)  
515 [7870.0001175](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001175).

516 Water Defense 2016 Water Defense Finds Dangerous Chemicals in Bathtubs/Showers in Flint,  
517 MI. [https://waterdefense.org/content/water-defense-finds-dangerous-chemicals-](https://waterdefense.org/content/water-defense-finds-dangerous-chemicals-bathtubshowers-flint-mi)  
518 [bathtubshowers-flint-mi](https://waterdefense.org/content/water-defense-finds-dangerous-chemicals-bathtubshowers-flint-mi) (accessed 4 January 2017)

519

## 520 SUPPORTING INFORMATION

521 for

522 **Quantifying and contextualizing disinfection byproducts during the Flint Water Crisis: A**  
523 **case study, and framework for broader application**

524 **(JWSRTAQUA-D-18-00075)**

525

526 Joseph E. Goodwill<sup>1</sup>, Mark W. Hagemann<sup>2</sup>, Marc A. Edwards<sup>3</sup>, David A. Reckhow<sup>2</sup>

527

528 <sup>1</sup>Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, RI,  
529 USA; <sup>2</sup>Department of Civil and Environmental Engineering, University of Massachusetts,  
530 Amherst, MA, USA; <sup>3</sup>Department of Civil and Environmental Engineering, Virginia Tech,  
531 Blacksburg, VA, USA.

532

533

534 **This file (5 pages) includes:**

535 1 table and 3 figures addressing additional experimental data that are available for further  
536 information.

537

538

Accepted

539  
540

Table SI-1. Sources and basic statistical information for model inputs

Model Year	Model Variable	Source*	Mean	Units	SD	N
2014	THM <sub>WDS</sub>	A	93.1	µg/L	45.1	27
2014	Cl <sub>2Free</sub>	B	0.75	mg/L	0.54	938
2014	pH	B	7.6	na	0.30	363
2015	THM <sub>WDS</sub>	A	45.3	µg/L	22.3	27
2015	Cl <sub>2Free</sub>	B	0.87	mg/L	0.56	1000
2015	pH	B	7.57	na	0.27	365
2016	THM <sub>WDS</sub>	C	21.1	µg/L	7.0	96
2016	Cl <sub>2Free</sub>	C	0.59	mg/L	0.34	822
2016	pH	C	7.23	na	0.02	626

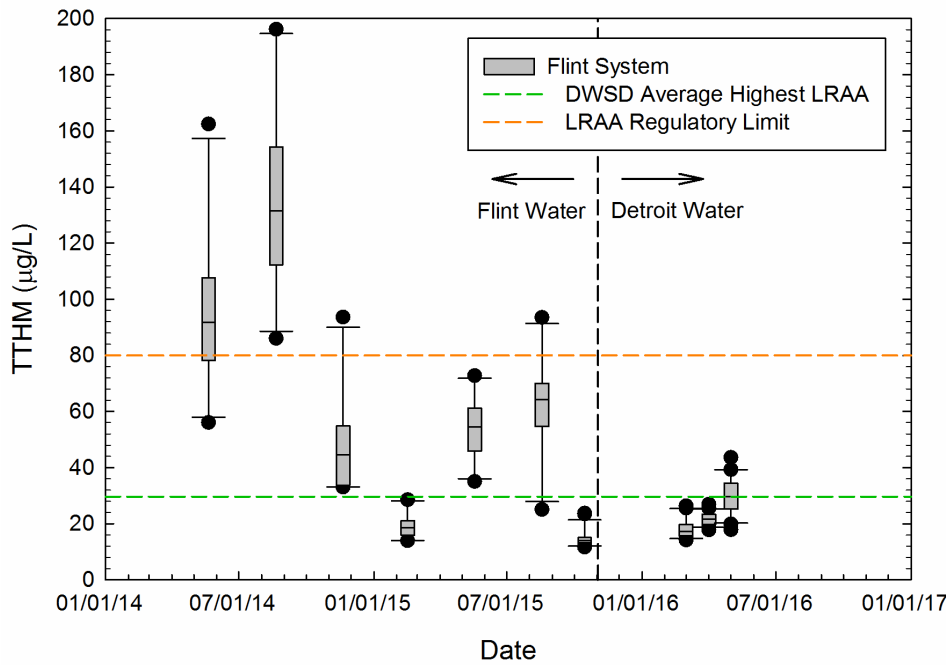
\*(A) City of Flint disinfection byproduct monitoring program

(B) City of Flint drinking water treatment plant monthly operating reports

(C) US Environmental Protection Agency Flint water quality monitoring

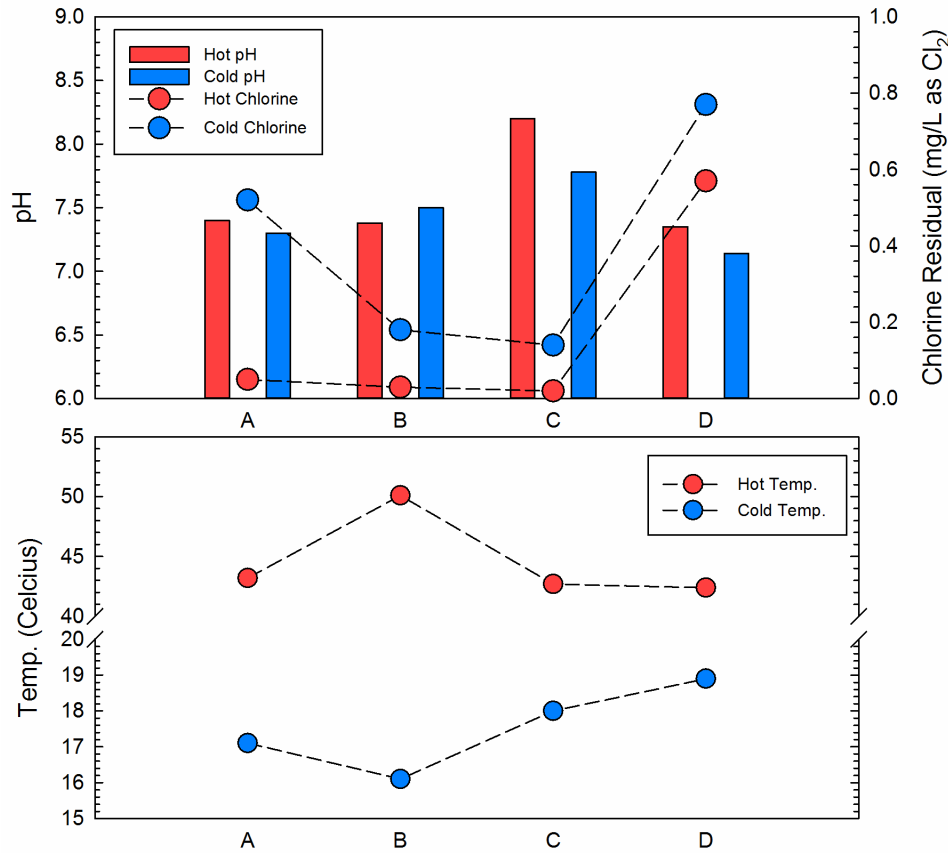
Notes: THM<sub>WDS</sub> = cold water trihalomethanes in distributed water (µg/L); Cl<sub>2Free</sub> = free chlorine residual in distributed water (mg/L); SD = standard deviation.

541  
542  
543

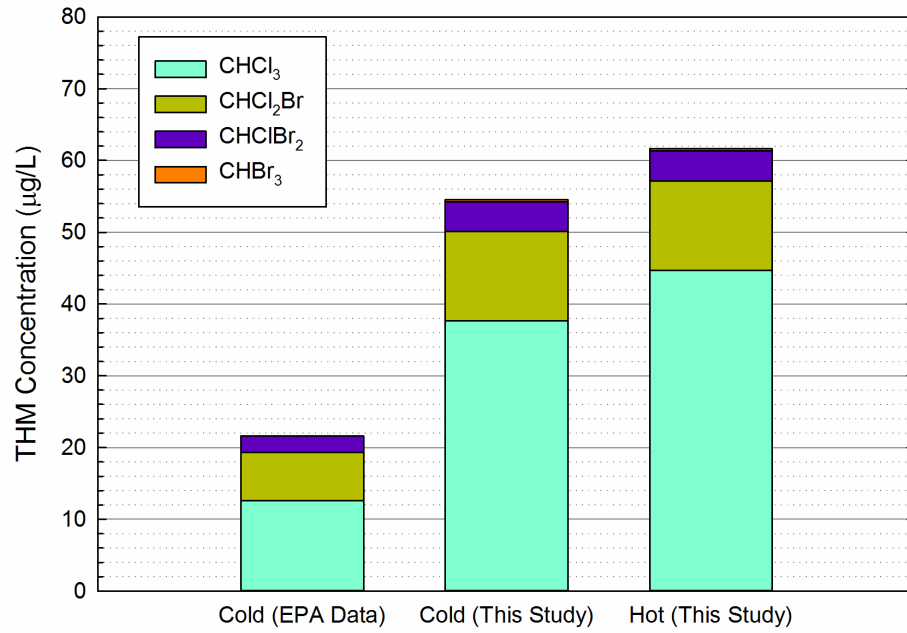


544

545 Figure SI-1. Total trihalomethanes results from May 2014 through May 2016 for the Flint  
 546 drinking water system. Publicly available data provided by City of Flint, and United States  
 547 Environmental Protection Agency. (DWSD = Detroit Water and Sewerage District; LRAA =  
 548 locational running annual average)



549  
 550 Figure SI-2. Differences in temperature, pH and chlorine residual at four studied sample  
 551 locations from the May 2016 sampling in Flint distribution system.  
 552



553

554 Figure SI-3. Speciation of trihalomethanes in Flint water in May 2016 from USEPA (N = 34)

555 collected data and this study (N = 4).

556

557

558