

2019

Evaluation of Two Real Time Methods for Assessing THM Precursor Concentrations

Griffin Moriarty
University of Massachusetts Amherst

Follow this and additional works at: https://scholarworks.umass.edu/cee_ewre



Part of the [Environmental Engineering Commons](#)

Moriarty, Griffin, "Evaluation of Two Real Time Methods for Assessing THM Precursor Concentrations" (2019). *Environmental & Water Resources Engineering Masters Projects*. 100.
Retrieved from https://scholarworks.umass.edu/cee_ewre/100

This Article is brought to you for free and open access by the Civil and Environmental Engineering at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Environmental & Water Resources Engineering Masters Projects by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

Evaluation of Two Real Time Methods for Assessing THM Precursor Concentrations

Griffin Moriarty

Submitted to the Department of Civil and Environmental Engineering of the University of
Massachusetts in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CIVIL ENGINEERING

May 2019

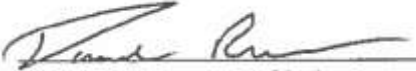
Evaluation of Two Real Time Methods for Assessing THM Precursor Concentrations

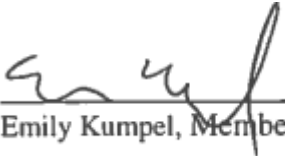
A Masters Project Presented


by

Griffin Moriarty

Approved as to style and content by:


Dr. David Reckhow, Chairperson


Emily Kumpel, Member



Civil and Environmental Engineering Department

Table of Contents

Table of Figures	3
Abstract.....	4
Introduction.....	5
Methods.....	8
Sample and Data Collection.....	8
Sample Preparation	9
Results and Discussion	10
Conclusions and Future Work	24
Watershed Behavior: Increased flow events and responses in TOC	24
THM Method Correlations: TOC, UV254, and chlorine demand, and Accelerated Methods ..	24
Acknowledgements.....	26
References.....	27
Appendix A: Compilation of Data.....	28
Appendix B: Standard and Accelerated Lab Method Sample Preparation Details	30
Appendix C: (A) A map of the sampling site and (B) An image of the pump system used for sampling.....	31

Table of Figures

Figure 1. Experimental Setup: (A) – NextSand Microturb Filter; (B) – Aquametrology Systems THM-100; (C) – RealTech UV254; (D) – Mantech PeCOD (not enough available data); (E) – Suez GE Portable TOC Series M5310C; (F) – Water distribution manifold.	9
Figure 2. (Left) Standard lab method sample incubation storage. (Right) Accelerated lab method incubation sample storage.....	10
Figure 3. Mill River flow and TOC from July 2018 to March 2019 with data points representing dates that samples were taken	12
Figure 4. Seasonal variability in time between peak flows during rain events and peak TOC and subsequent THM concentrations: (A) Early Summer Rain Event; (B) Late Summer Rain Event; (C) Fall Rain Event; (D) Winter Rain Event	14
Figure 5. Raw data collected from Mill River (Hadley, MA) samples over three sampling events: (A) September 24 th to October 2 nd , 2018; (B) October 16 th to November 18 th , 2018; (C) December 3 rd to December 13 th , 2018	15
Figure 6. Concentration of THMs produced by chlorinated Mill River samples according to quantification method across three sampling events: (A) September 24 th to October 2 nd , 2018; (B) October 16 th to November 18 th , 2018; (C) December 3 rd to December 13 th , 2018	16
Figure 7. Direct comparison of the accelerated methods against the standard lab method. (A) Accelerated Lab vs. Standard Lab;(B) Accelerated Lab vs. AMS; (C) AMS vs. Standard Lab ..	19

Figure 8. Direct comparisons of (A) AMS THM vs. Standard Lab THM; (B) TOC vs. Standard Lab THM; (C) UV254 vs. Standard Lab THM; (D) Standard Lab Chlorine Demand vs. Standard Lab THM; (E) Accelerated Lab Chlorine Demand vs. Standard Lab THM; (F) TOC * UV254 vs. Standard Lab THM 20

Figure 9. (A) Logarithmic regression of TOC * UV vs. Standard Lab THM; (B) Linear regression of a multivariate analysis performed by JMP to predict Standard Lab THM using equation 1 vs. Standard Lab THM; (C) Linear regression of a multivariate analysis performed by Sigmaplot to predict Standard Lab THM using equation 2 vs. Standard Lab THM 21

Figure 10. Predictive abilities of a multivariate analysis of TOC and UV254 as well as the accelerated methods with absolute errors compared to the measured standard lab method values for each sample. 22

Abstract

Conventional drinking water treatment generally requires maintenance of a disinfectant residual, most commonly free or combined chlorine. Since the discovery of disinfection byproducts (DBPs), utilities have relied on a broad range of water quality parameters to help them achieve compliance with DBP regulations. Most notably, dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV254) have been used to assess DBP precursor levels in near-real time. These are often compared to actual system DBP concentrations or to results from laboratory DBP precursor tests resulting in a site-specific precursor-DBP model. The DOC or UV254 models are often inaccurate, requiring re-calibration, especially in the face of changing water quality. For this reason, there is an interest in developing better real-time precursor monitoring strategies and these new methods will be compared against a DOC and UV254 predictive model from the same water source.

This project focuses on two new near real-time technologies that are intended to allow better prediction of the conventional 72-hour lab based THM precursor test. The first non-conventional methodology, the AMS method, is integrated with a commercially-available THM monitoring instrument. This instrument automatically chlorinates a sample of river water and incubates the sample at an elevated temperature for approximately one hour before using a purge and trap method to collect the THMs followed by a colorimetric method to quantify and analyze THM concentrations. The second technology, the accelerated lab method, employs a reaction vessel modified for temperature fluctuations in which sample and chlorine are added. The sample

is then incubated at an elevated temperature for one hour. Next, the sample is sent to a gas chromatograph for THM analysis and residual chlorine is measured.

The accelerated lab method was the most successful in predicting THM concentrations formed by the standard lab method with an average absolute error of 11 ppb and a median absolute error of 9 ppb. The second most successful method of predicting standard THM formation potential was an equation that resulted from a multivariate analysis of TOC and UV254 values taken for the Mill River in Hadley, MA. This equation predicted concentrations produced by the standard lab method with an average absolute error of 15 ppb and a median absolute error of 10 ppb. The third best method of predicting standard method THM concentrations was another multivariate analysis, this time using the log of standard lab chlorine demand and UV254 measurements. This method predicted standard lab THM concentrations with an average absolute error of 15 ppb and a median absolute error of 11 ppb. The fourth most successful method for predicting standard THM concentrations was the AMS THM-100 with an average absolute error of 20 ppb and a median absolute error of 19 ppb. Each of these methods had a sample size of 34 data points and the data points used were identical across the methods to mitigate sample bias. While the absolute errors between the methods may indicate a clear choice of methodology in terms of accuracy, each method has certain aspects that are beneficial in unique ways.

Introduction

Natural organic matter (NOM) is a broad term for the heterogenous mixture of a greatly diverse set organic compounds that is found in all surface water bodies. There are thousands of organic compounds with varying properties that are all classified as NOM. NOM has material is both the particulate and dissolved phases but the vast majority, approximately 90%, is in the dissolved phase. This property makes NOM highly mobile within a body of water, so NOM is considered omnipresent in surface waters. Due to the fact that NOM is formed from a plethora of sources which are all affected by climate, land cover, and organisms surrounding the water body, the qualities and concentrations of NOM greatly vary between raw water sources. An understanding of the mechanisms that control the transport pathways and fluxes of NOM, particularly dissolved NOM, or dissolved organic carbon (DOC), is imperative to sustaining aquatic ecosystem health (Bormann et al. 1969; Gomi et al. 2002; Rabalais et al. 2002; Bernhardt

et al. 2005; Raymond and Saiers, 2010). The knowledge and understanding of DOC fluxes and transport mechanisms is equally as impactful to the overall efficiency of drinking water treatment (Garvey and Tobiason 2003; Sharp et al. 2004) and the concentration and speciation of DOC can lead to vastly differing concentrations of potentially harmful disinfection byproducts (Singer 1994; Chow et al. 2008).

Due to the increasing awareness and regulatory standards for disinfection byproducts (DBPs), the reactions between NOM and common disinfectants are of great interest to drinking water quality operators. Currently, the standard method of quantifying DBPs requires a reaction time between 72 hours and 1 week for a significant portion of the NOM to react with the disinfectant and form DBPs (W APHA, and AWW AEEF, 2010). Unfortunately, by the time utility managers receive the results from this standard lab method, that aliquot of water is in the distribution system and on its way to the consumer.

Water treatment plant operators would greatly benefit from a method to predict or quantify DBP formation much closer to real-time in order to keep pace with increasingly stringent drinking water standards. Currently Trihalomethanes (THMs) and Haloacetic Acids (HAAs) are the only DBPs regulated by the EPA at 80 and 60 ug/L respectively. With increasingly prominent and persistent levels of DBP precursors and subsequent DBPs, those regulations are sure to become stricter. DBPs have been linked to a variety of health issues including bladder cancer, developmental effects, and kidney disorders (US EPA), thus it is extremely important for operators to know what they are providing to the consumers.

Many recent studies have been focused largely on the characterization of NOM in order to better predict the formation of DBPs during and after treatment (Hua et al., 2015, Hu et al., 2014, Li et al., 2014, Rosario-Ortiz et al., 2004). While the information brought to light by these studies may be useful for determining the source of DBP formation, the methods are still quite involved and the results convoluted, requiring more research on many fronts:

Further studies using size characterization and chemical functional group analysis, such as Fourier transform infrared (FTIR) and solid-state nuclear magnetic resonance (NMR)

spectroscopy, are needed to confirm which NOM functional groups are interacting with the SPE sorbents. Further development and analysis of NOM probes and also of natural NOM samples from different origins will also shed light on the nature of interaction between specific functionalities and the SPE materials. In addition, variations of this technique to include the sequential characterization of NOM need to be performed and compared to existing methods. Sequential fractionation using SPE cartridges will yield information on how NOM is changed and which specific fractions are subject to change. (Rosario-Ortiz et al., 2004)

Again, while useful in some ways, the PRAM method and other methods to characterize DOC do not yet shorten the time taken to quantify or predict DBP formation.

This project aims to utilize and compare two non-conventional accelerated methods with the standard 72-hour laboratory method, hereinafter referred to as the standard lab method, developed by the Environmental Protection Agency (EPA) and predictive methods using more basic water quality parameters like total organic carbon (TOC), ultraviolet absorbance (UV) and chlorine demand. The first non-conventional method involves a commercially-available THM monitoring instrument and will be referred to as the AMS method. This instrument directly chlorinates an aliquot of raw water and raises the temperature of the chlorinated sample to accelerate the formation of THMs. After a set reaction time, the instrument uses a purge and trap methodology to collect THMs and then uses a colorimetric method to measure THMs. The entire process utilized by this instrument takes about 4 hours, a significant decrease from 72 hours. The second non-conventional method is very similar to the standard 72-hour lab method and will be referred to as the accelerated lab method. This method involves the chlorination of a sample followed by immediate incubation at an elevated temperature. Incubation is followed by solid phase extraction and the samples are then analyzed for DBPs by a gas chromatograph. Since the correlation between many water quality parameters including UV254 and DOC and the resulting THMFP has been shown to vary largely between sources (Chow et al, 2008), it is the hope that utilizing these accelerated methods will create a more efficient and standardized way to quantify THMs, eliminating the need for utilities to operate conservatively and reduce avoidable financial and environmental costs.

Methods

Sample and Data Collection

All samples collected during the course of this project were taken from the Mill River in Hadley, Massachusetts. See Appendix C at the end of the report for more details on the location of sampling and the pump system used. Mill River water was pumped from the river to the Water and Energy Technology Center at the University of Massachusetts Amherst where it was filtered down to five microns by a NextSand Microturb filter. The Mill River water was then sent through a pipe manifold where it was distributed to analyze total organic carbon (TOC) (GE Suez Portable TOC M5310C), UV absorbance at the wavelength of 254 nm (UV254) (RealTech UV254), photoelectric chemical oxygen demand (PeCOD) (Mantech PeCOD, limited data), and THMs (Aqua Metrology Systems THM-100). TOC was recorded every two minutes, UV254 took a measurement every few seconds, and the PeCOD instrument takes a measurement every hour. These instruments and the manifold can be seen in Figure 1. Samples intended for laboratory analysis were taken from the effluent of the instrument manifold and stored in 500 mL Nalgene bottles with as little headspace as possible. These bottles were then stored in a constant temperature room of 4 °C until they were analyzed.

Aqua Metrology Systems THM-100 is a fully automated, self-calibrating device designed to operate unattended with little to no maintenance. The instrument, during the course of this project, operated in online mode taking samples and producing and quantifying THMs every four hours. The analyzer directly chlorinates a sample of water and sends the sample to a holding vessel where it is heated to a temperature selected by the operator, in the case of this project the temperature was 50 degrees Celsius. After approximately ninety minutes, the analyzer uses the purge and trap sampling method and then desorbs the THMs into a chemical mixture which generates a colored solution and time-resolved spectrophotometric analysis for the detection and determination of speciated THM levels. The analyzer then reports the largest of either chloroform or bromoform as well as the total THMs produced (Aqua Metrology Systems, 2016).



Figure 1. Experimental Setup: (A) – NextSand Microturb Filter; (B) – Aquametrology Systems THM-100; (C) – RealTech UV254; (D) – Mantech PeCOD (not enough available data); (E) – Suez GE Portable TOC Series M5310C; (F) – Water distribution manifold.

Sample Preparation

The 72-hour lab method follows the procedure developed by EPA (W APHA, and AWW AEEF, 2010). The accelerated 1-hour lab method very closely follows the same EPA method but with slight differences. These methods were carried out simultaneously and from the same sample of water to mitigate errors and discrepancies but can be carried out independently of one another. Four hundred fifty milliliters of the five hundred milliliter Mill River sample were dosed with chlorine with the intention of leaving a chlorine residual so as to mimic the uniform formation conditions developed by Summers et al. in 1996 as closely as possible. The sample was then split into two vessels: a 300mL BOD bottle which was capped and sealed with Parafilm, and a 100 mL Pyrex wide mouth sample bottle with an alteration to allow for expansion of water under temperature changes. These vessels can be seen in Figure 2, below. The 300 mL BOD bottle was placed in a constant temperature environment of 20 °C and left to react for 72 hours. The 100 mL sample bottle was placed in a constant temperature bath of 50 °C and left to react for 1 hour.



Figure 2. (Left) Standard lab method sample incubation storage. (Right) Accelerated lab method incubation sample storage.

After the allotted reaction time, chlorine residual was measured for each sample to ensure adequate chlorine was dosed and the maximum DBP formation potential was reached. Sample preparation for THM analysis was carried out via the method developed by Scott Summers and, once prepared, the samples were analyzed using an Agilent 6890N Gas Chromatograph. Additional details on sample preparation can be found in Appendix B at the end of the report.

Results and Discussion

Over seven months, July 2018 – February 2019, fifty-one samples from the Mill River were collected and analyzed for THM formation potential. The data collected have been summarized in Appendix A at the end of the report. In the interest of examining the impacts of flow on concentrations of TOC and THM formation potential, samples were taken surrounding rain events whenever possible. Figure 3 displays the discharge of the Mill River at the site of sampling as well as the dates that samples were taken and the available corresponding TOC concentrations recorded by the GE Suez Portable TOC M5310C from July 1, 2018 to March 6, 2019. According to this data an increase in river discharge, no matter how small, is always followed by an increase in TOC. The TOC concentrations following an increase in flow in warmer weather, mainly the summer months and into the early fall, tend to be substantially

higher than similar events in the winter. Examples of this observation include the events from August 8th to August 11th , September 18th to September 19th , and September 26th to September 28th. This is most likely a result of higher water temperatures in the summer that persist into the early fall; this correlation of higher water temperatures leading to higher DOC influxes has been observed by Raymond and Saiers in 2010. A second possible explanation for this observed phenomenon is that plant life is far more active in the summer months leading to higher TOC productivity and higher overall TOC levels surrounding the water source. Another interesting observation that can be seen in Figure 3 and drawn from Raymond and Saiers is that consecutive rain events lead to severe increases in TOC concentrations: August 8th to August 11th ; September 18th to September 19th ; September 26th to September 28th ; January 24th to January 26th ; and February 7th to February 8th. However, it seems that this observation has its limitations. Two nearly consecutive increases in flow cause the drastic increase in TOC that was observed by Raymond and Saiers, but each increase in flow following the first two seem to have diminishing effects. There are certainly still increases in TOC following the subsequent events, but the rises in TOC are not as substantial as the first sharp increase. This could be due to an accumulation of organic material being washed into the river from the first two surges in flow. The three rain events in September 2018 are a great example of the diminishing effects of flow on TOC and DOC influx. Another good example are the four rain events in early August.

Mill River Flow and TOC over Period of Sampling

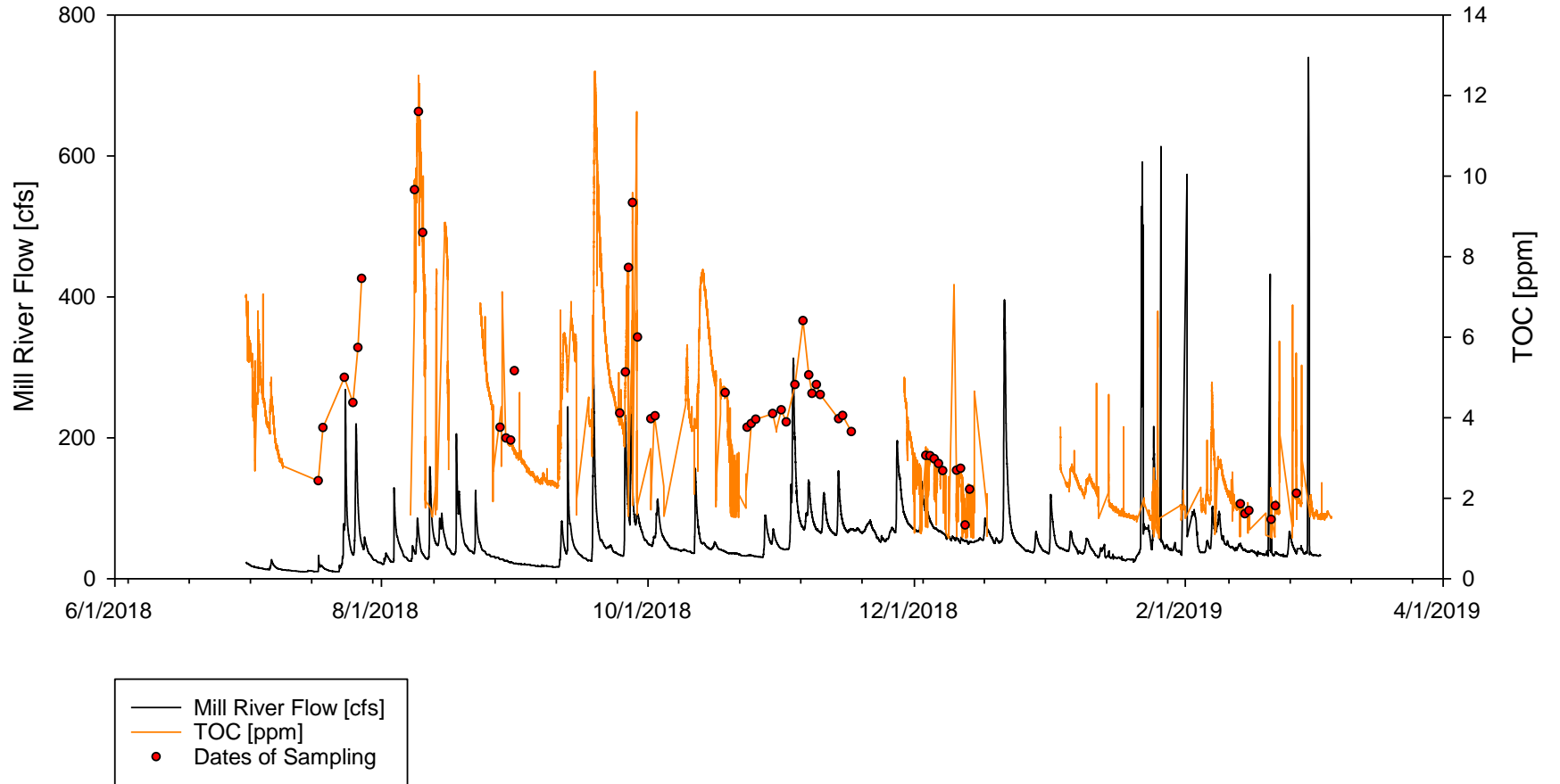


Figure 3. Mill River flow and TOC from July 2018 to March 2019 with data points representing dates that samples were taken

A third interesting phenomenon was observed in the timing of TOC and THM concentration peaks with respect to peaks in flow. A closer look at this phenomenon can be observed in Figure 4. In the early summer, the peak TOC concentration occurs about 6 hours after the peak flow. In the late summer, the peaks in TOC and THM concentrations occur almost simultaneously to the peak in flow, lagging only two hours behind. In the fall, the TOC and THM concentration peaks begin to lag even more with a separation of approximately 14 hours between the peaks. In the winter, the lag time is far more drastic with nearly a full day between the initial increase in flow and the peak TOC and subsequent THM concentrations. The severe lag time observed in the winter could be due to the river embankments being frozen and delaying the influx of TOC. This phenomenon has yet to be observed elsewhere but should certainly be looked into as a potential early warning system for drinking water operators.

These fifty-one samples from the Mill River were analyzed for THM formation potential using the standard method, TOC, UV254, and chlorine demand, and two accelerated methods. The raw data and the results of THM analysis for three events of increased flow are summarized in Figure 5 and Figure 6 respectively. Figure 5 shows strong trends between TOC, UV254, and the chlorine demand for both the standard lab method as well as the accelerated lab method. TOC, chlorine demand, and, to a lesser extent, UV254 all increase and decrease respectively. Upon further analysis of the relation between TOC, UV254, chlorine demand and standard lab THM formation, the correlation is not as strong as the correlations shown between the accelerated methods and standard lab THM formation.

Figure 6 shows strong trends between each of the three methods used to quantify THMs: the standard lab method, the accelerated lab method, and the AMS method, again over three events of increased flow. Typically, as one method increases or decreases, the others do as well. Figure 6 also shows that, compared to the standard lab method, the accelerated lab method tends to underproduce THMs while the AMS method tends to overproduce THMs. On average, the accelerated lab method only produced 83% of the THMs produced by the standard lab method whereas the AMS method produced approximately 168% of the THMs produced by the standard lab method.

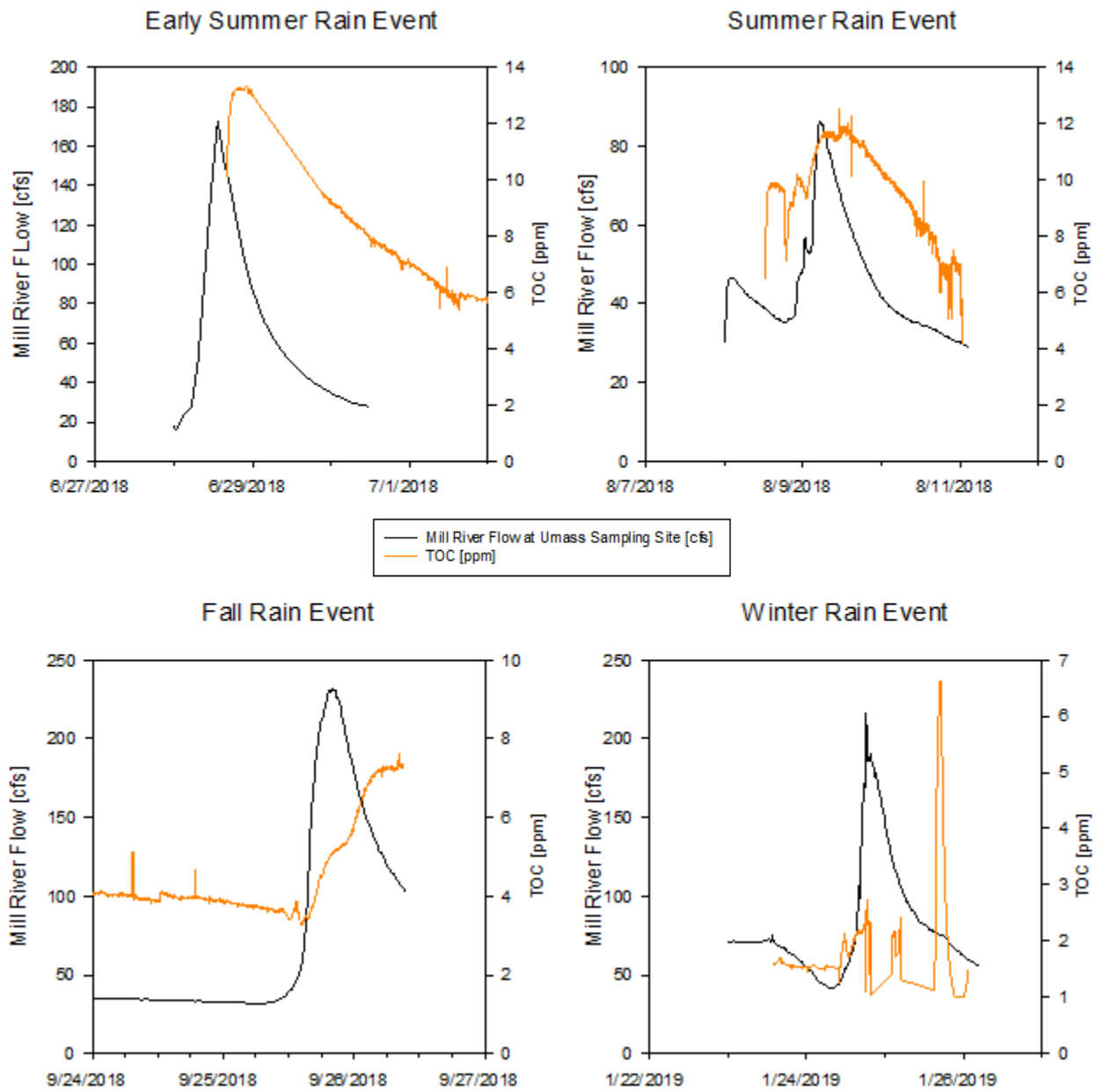
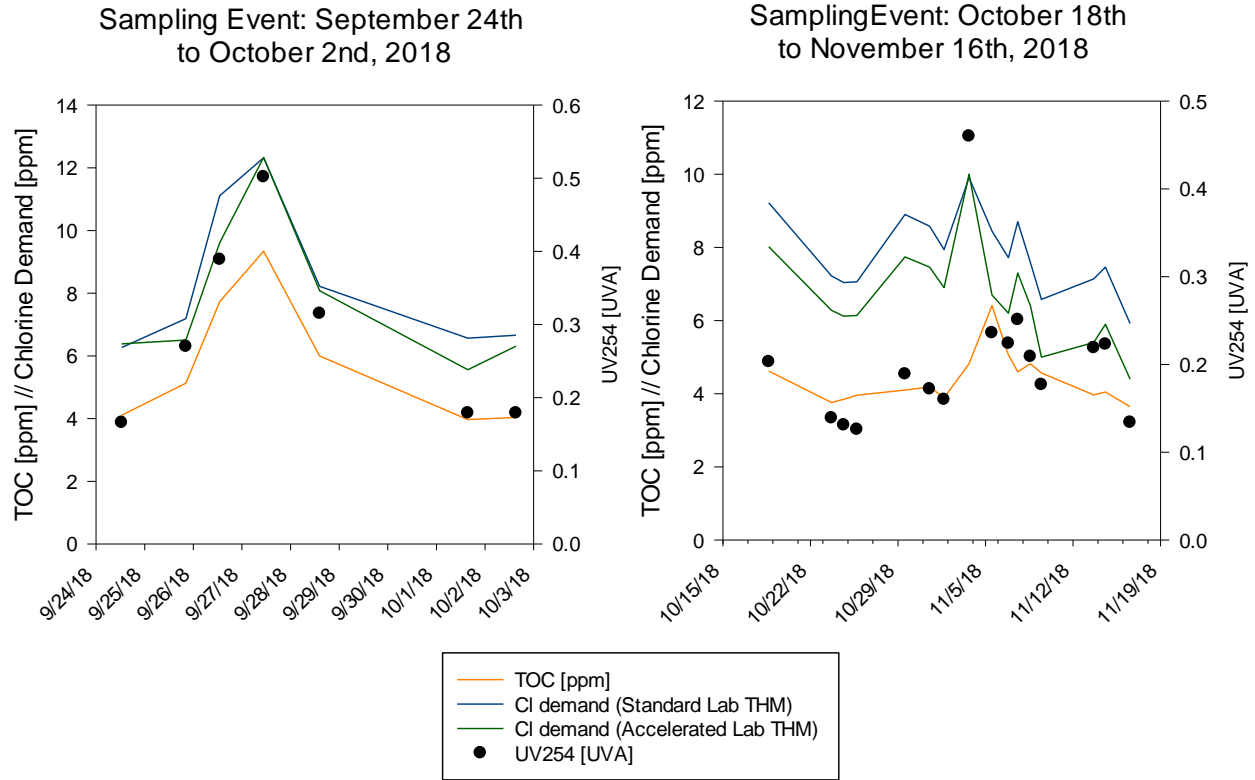


Figure 4. Seasonal variability in time between peak flows during rain events and peak TOC and subsequent THM concentrations: (A) Early Summer Rain Event; (B) Late Summer Rain Event; (C) Fall Rain Event; (D) Winter Rain Event



Sampling Event: December 3rd to December 13th, 2018

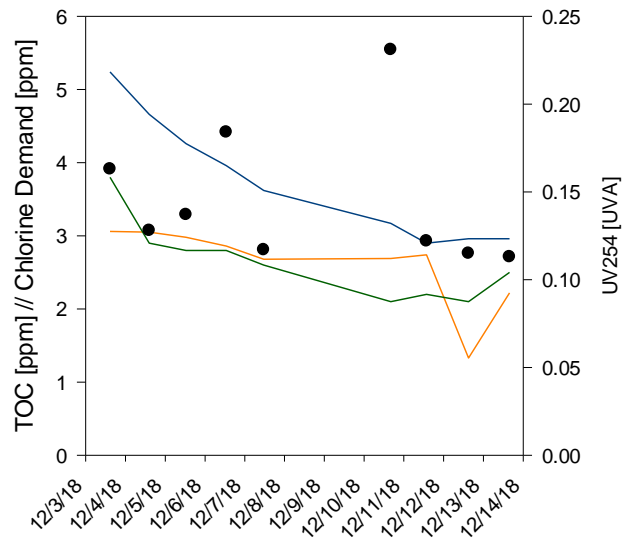


Figure 5. Raw data collected from Mill River (Hadley, MA) samples over three sampling events: (A) September 24th to October 2nd, 2018; (B) October 16th to November 18th, 2018; (C) December 3rd to December 13th, 2018

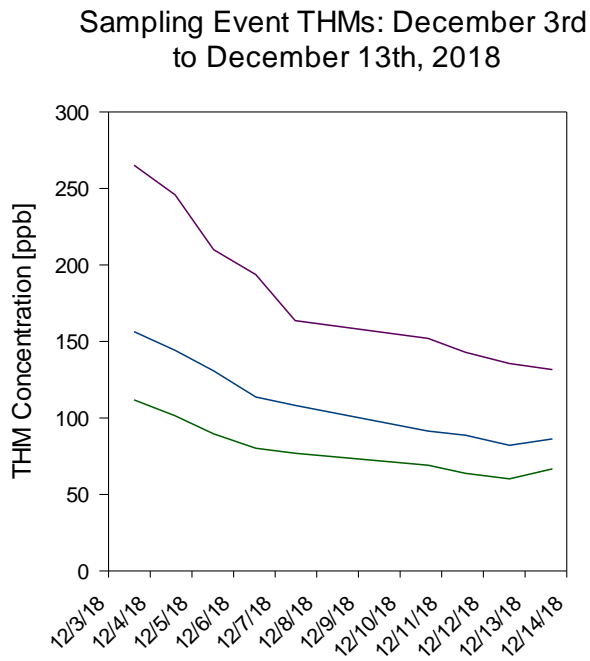
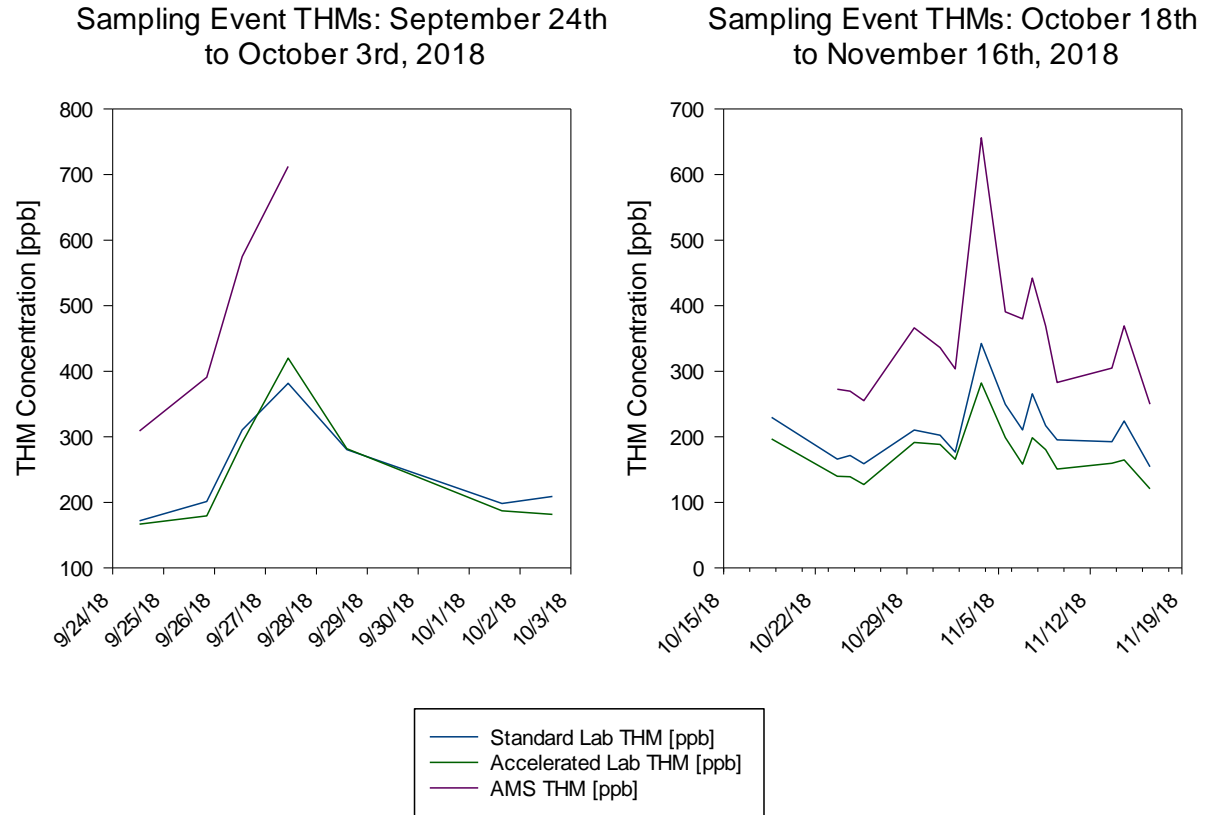


Figure 6. Concentration of THMs produced by chlorinated Mill River samples according to quantification method across three sampling events: (A) September 24th to October 2nd, 2018; (B) October 16th to November 18th, 2018; (C) December 3rd to December 13th, 2018

To determine which of the two accelerated methods were more correlated with respect to the standard lab method, a direct comparison of each data set was performed. Figure 7A displays the correlation between the accelerated lab method and the standard lab method. These two methods have the same analysis technique (gas chromatography), yet differ in reaction time and temperature. Of the three THM method comparisons the accelerated lab method compared with the standard lab method has the highest R^2 value at 0.967. Figure 7B displays the direct comparison of the accelerated lab method against the AMS method. These two methods share very similar reaction times and temperatures, yet differ in the methods of THM quantification (gas chromatography vs. Fujiwara chemistry). For this direct comparison, the R^2 is slightly lower at 0.963. The third direct comparison, Figure 7C, displays the standard lab method against the AMS method which differ in both THM analysis method and reaction time and temperature. This direct comparison has the lowest R^2 value of the three at 0.960. It appears that differing THM analysis methods affect correlation more than differing reaction times and temperatures, but both differences certainly affect correlation. Despite the slight discrepancy between the two comparisons of the accelerated methods, both of them have a better correlation with the standard lab method than any combination of the commonly used predictive methods of using TOC, UV254, and chlorine demand measurements that were attempted in this report.

Several attempts to establish the strongest predictive method between combinations of TOC, UV254, and chlorine demand and THM formation were made and are reported in Figures 8 and 9. Many linear regressions using water quality parameters are reported in Figure 8 with a linear regression comparing AMS THM and standard lab THM ($R^2 = 0.961$) for perspective on how well the parameters correlate to standard lab THM concentrations. The next strongest correlation ($R^2 = 0.930$) comes from comparing the chlorine demand of the standard lab THM tests with the standard lab THM concentrations. TOC and standard lab THM concentration have the third highest correlation ($R^2 = 0.900$). These two parameters having the best two correlations with standard THM concentrations is to be expected as TOC and chlorine react to form THMs, mainly chloroform, the THM with three chloride molecules attached to methane. Since TOC, a surrogate measurement for NOM or DOC, has such a wide range of potential compounds and configurations, a lesser correlation compared to chlorine is expected. The correlations drop sharply with the remaining comparisons of UV254, accelerated lab chlorine demand, and TOC *

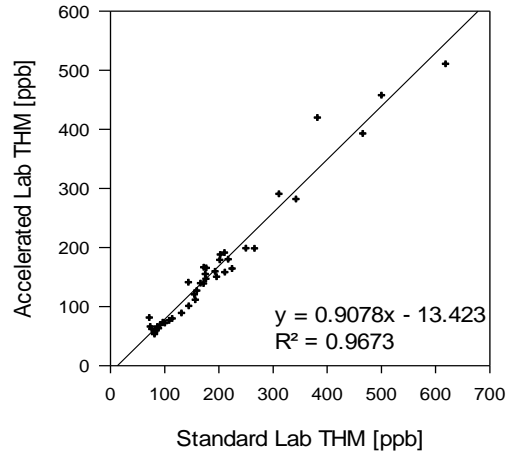
UV254. A poor correlation between UV254 and standard lab method THM concentrations is reasonable because, like TOC, UV254 attempts to measure organic compounds in water. As the name suggests, UV254 uses ultraviolet light to make a measurement which is a much more sensitive method of measurement to particles or other substances that should not be incorporated into the measurement. Accelerated lab method chlorine demand correlated poorly to standard lab method THM concentrations because the accelerated lab method already under predicts the formation of standard lab THM concentrations. Therefore, using a measurement from the accelerated lab method will not be as accurate as using the standard lab method chlorine demand. The linear regression of TOC * UV254 has a low R² value because a linear regression is not the correct method of analysis. The data seemed to represent more of a logarithmic regression which is represented in Figure 9A. Even the logarithmic regression was not nearly as correlated as the accelerated method comparisons. Figures 9B and 9C show predicted values from two multivariate regressions performed with TOC, UV254, and a log of chlorine demand. Figure 9B shows predicted standard lab THM concentrations using TOC and UV254 in the form of eq. 1

$$\text{Equation 1. Standard Lab THM [ppb]} = 2.33 + (27.72 * \text{TOC [ppm]}) + (358 * \text{UV254 [UVA]})$$

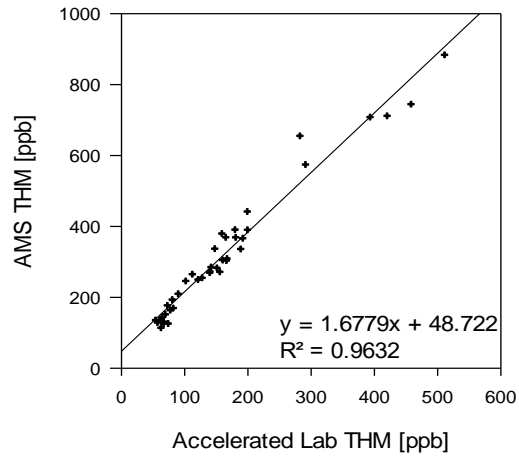
$$\text{Equation 2. Standard Lab THM [ppb]} = -71.862 + (216.506 * \text{LOG \{Standard Lab Chlorine Demand [ppm]\}}) + (461.142 * \text{UV254 [UVA]})$$

compared with measured standard lab THM concentrations. The multivariate model is much more correlated to the standard lab THM concentrations than both the linear and logarithmic regressions. Another multivariate predictive model is displayed in Figure 9C and uses eq. 2 to predict standard lab method THM concentrations. Figures 9B and 9C has R² values of 0.89 and 0.91 respectively, but as is shown in Figure 10, correlation does not prove accuracy.

Standard Lab Method THM vs. Accelerated Lab Method THM



Accelerated Lab Method THM vs. AMS Method THM



Standard Lab Method THM vs. AMS Method THM

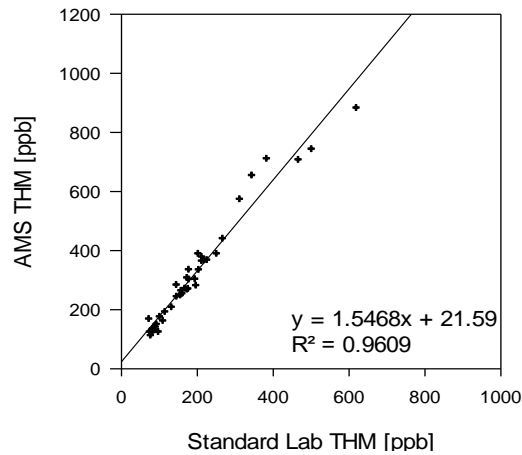


Figure 7. Direct comparison of the accelerated methods against the standard lab method. (A) Accelerated Lab vs. Standard Lab; (B) Accelerated Lab vs. AMS; (C) AMS vs. Standard Lab

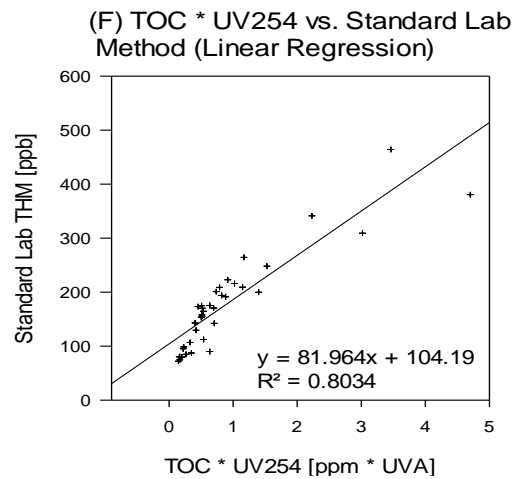
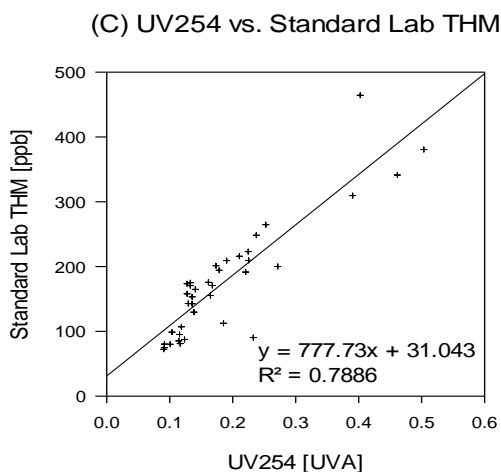
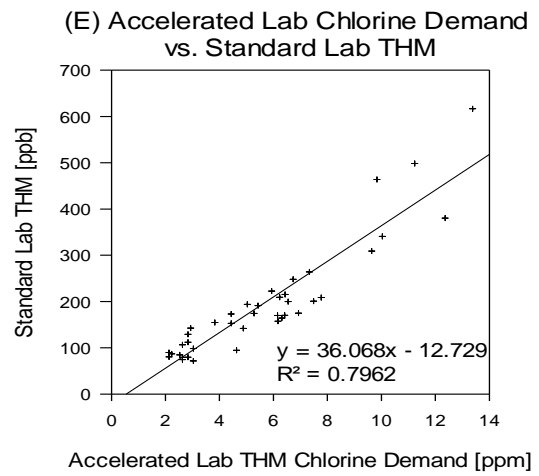
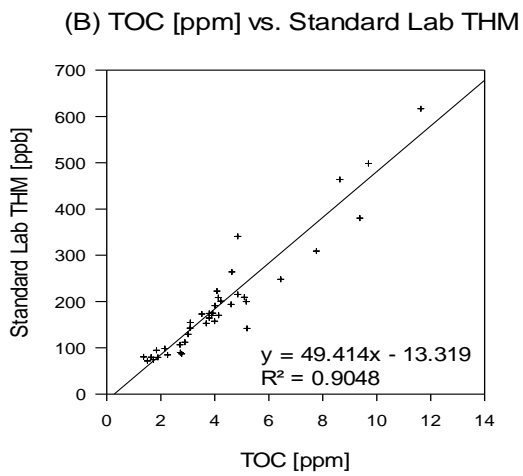
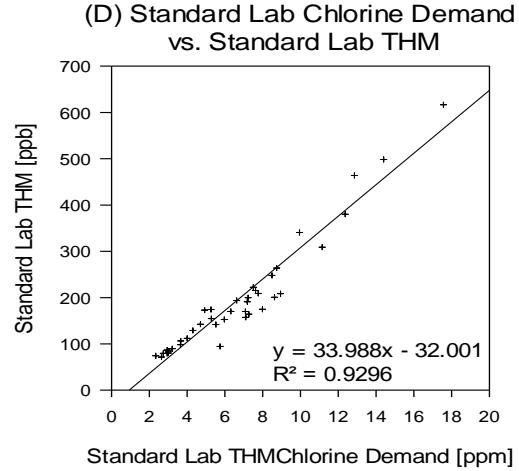
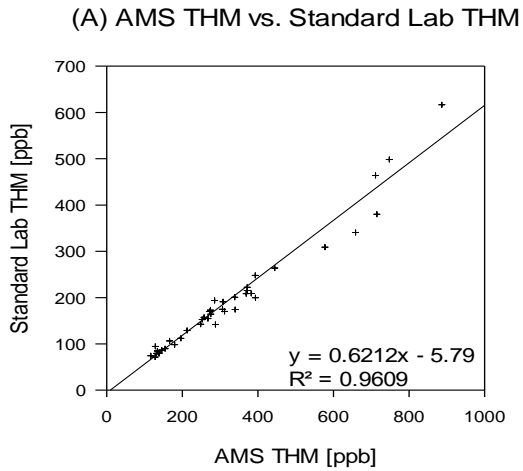
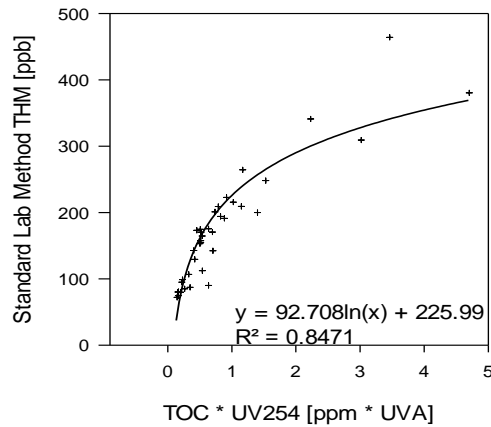
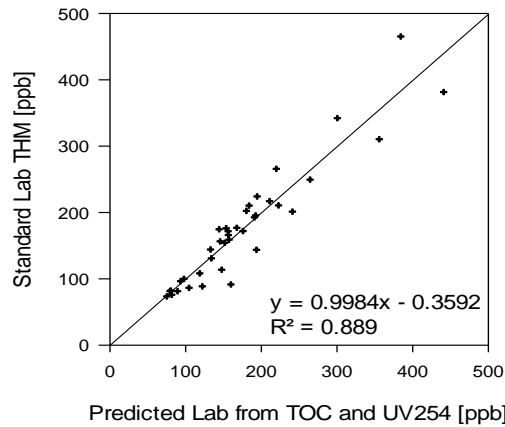


Figure 8. Direct comparisons of (A) AMS THM vs. Standard Lab THM; (B) TOC vs. Standard Lab THM; (C) UV254 vs. Standard Lab THM; (D) Standard Lab Chlorine Demand vs. Standard Lab THM; (E) Accelerated Lab Chlorine Demand vs. Standard Lab THM; (F) TOC * UV254 vs. Standard Lab THM

TOC * UV254 vs. Standard Lab Method (Logarithmic Regression)



Predicted Standard Lab Concentration from TOC and UV254
 (Using multivariate analysis from JMP)



Predicted Standard Lab THM Concentration from UV254 and
 LOG of Standard Lab Chlorine Demand
 (Using Multivariate analysis from Sigmaplot)

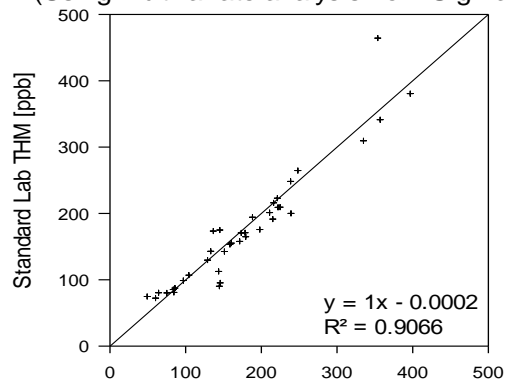


Figure 9. (A) Logarithmic regression of TOC * UV vs. Standard Lab THM; (B) Linear regression of a multivariate analysis performed by JMP to predict Standard Lab THM using equation 1 vs. Standard Lab THM; (C) Linear regression of a multivariate analysis performed by Sigmaplot to predict Standard Lab THM using equation 2 vs. Standard Lab THM

Predictive Abilities of Accelerated Methods and TOC and UV

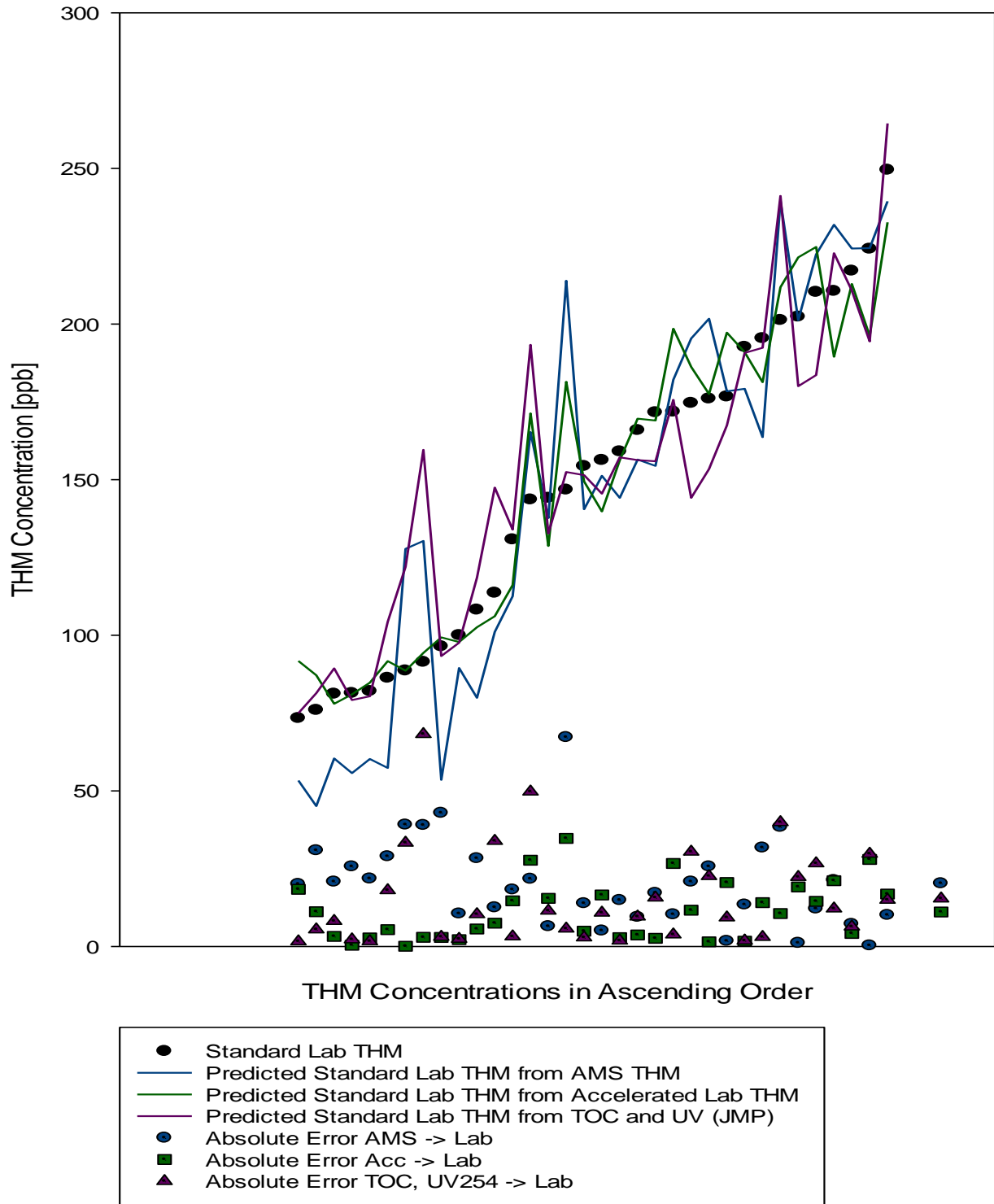


Figure 10. Predictive abilities of a multivariate analysis of TOC and UV254 as well as the accelerated methods with absolute errors compared to the measured standard lab method values for each sample.

No matter how strong the correlations are between the predictive methods and the standard method, correlation will struggle to help drinking water treatment plant operators as quickly and effectively as absolute errors. The predictive abilities of each method must be examined for accuracy if they are truly to assist operators in DBP quantification. Figure 10 displays the measured standard lab THM concentrations as well as the predicted THM concentrations from each of the three predictive methods and the absolute errors associated with each data point for each method. For THM concentrations in the range of 70 ppb to 250 ppb, the accelerated lab method has an average absolute error of just 11 ppb with a median error of 9 ppb while the AMS method has an average absolute error of 20 ppb and a median error of 19 ppb. Predicting standard lab THM formation using TOC and UV254 fell in between the two accelerated methods with an average absolute error of 15 ppb and a median error of 10 ppb. Using UV254 and the log of standard lab chlorine demand to predict standard lab THM concentrations resulted in a mean error of 17 ppb and a median error of 12 ppb which is more accurate than the AMS method, yet less accurate than using TOC and UV254 or the accelerated lab method. With an EPA set THM regulation of 80 ppb, these errors are still quite significant and the accelerated methodology could benefit from refinement. Table 1 below summarizes important metrics from the four methods examined in detail in this project, including the error found by each method for the three standard lab method THM concentrations closest to the maximum contaminant level of 80 ppb (81.19, 81.39, and 82.01).

Table 1. Summary of important metrics across the four most accurate methods examined.

Method	R ²	Mean Absolute Error [ppb]	Median Absolute Error [ppb]	Absolute Error at MCL (80 ppb)
Accelerated Lab	0.967	11	9	2
Aqua Metrology Systems	0.960	20	19	23
TOC and UV254	0.889	15	10	4
LOG Cl Demand and UV254	0.907	15	11	9

Conclusions and Future Work

Watershed Behavior: Increased flow events and responses in TOC

A precipitation event, or any other cause of increased flow is always followed by an increase in TOC concentration. Higher water temperatures, which can be observed in the summer months and persist into the early fall, result in substantially higher TOC influx after an increase in flow, as was predicted by Raymond and Saiers. Two consecutive events of increased flow also lead to a significantly higher influx of TOC. However, if additional events occur shortly after the first two, this significant increase in TOC becomes lesser with each subsequent event. Peak flows, peak TOC concentrations, and peak THM concentrations do not necessarily happen simultaneously. There is a certain level of seasonal variation observed in the timing of the separate peaks. In the summer, peak flow is nearly simultaneous with the increase in TOC and THM formation; In the fall and into the winter, the TOC and THM formation peaks occur further and further after the peak in flow. In the early summer, the time-shift between the peak in TOC and the peak in flow appears to mimic that of a fall rain event, suggesting that the peaks begin to occur closer together through the spring. The tracking of further rain events with these parameters in mind would be a great addition to future works on this topic. It is entirely possible that operators would be able to use an increase in flow to predict an increase in TOC and DBP formation potential a few hours or even a day in advance but they would need to know when they can use this tactic and when they should expect to see simultaneous peaks.

THM Method Correlations: TOC, UV254, and chlorine demand, and Accelerated Methods

TOC, UV254, and chlorine demand are not as correlated yet are nearly as accurate as the accelerated lab method when predicting standard lab THM concentrations. The problem with using TOC and UV254 as predictive measurements remains that the measurements are largely variable from source to source. This requires the collection of these data sets for a prolonged period of time for each individual water source followed by analysis to see if they are accurate predictors of THM concentrations for that source. There may be unexplored water qualities that are even better suited for predicting DBP formation than TOC, UV254, and chlorine demand or some combination of these measurements. Future works should certainly explore these parameters to observe the potential connection to DBP formation. Parameters that should be explored include PeCOD and the full UV spectrum.

Using the accelerated lab method and obtaining THM concentrations within 10 ppb in as little as 3 hours can be very helpful to drinking water operators. This work verifies that accelerated methods can be more efficient than the standard lab methods without sacrificing too much accuracy. Both the AMS method and the accelerated lab method show a very strong correlation with the standard lab method and maintain accuracy within one standard deviation of the measurement. They successfully shorten the amount of time required to quantify THMs without sacrificing significant accuracy. The accelerated lab method is the best predictor in the relevant range of THM concentrations, yet still requires the use of laboratory equipment and reagents. It is also entirely possible that the THM production ratio between the accelerated method and the standard lab method would require site specific calibration just like water quality parameters. Further analysis across different sources of water would be needed to test this hypothesis.

The AMS method is fully automated and very convenient for obtaining an estimate of the standard lab THM concentrations if a lab is not available but does not appear to be as accurate in the lower ranges that would be crucial for drinking water operators to successfully mitigate THMs. This conclusion was drawn from testing filtered river water, however, so the AMS THM-100 could be more accurate when testing water at different points in a treatment system for formation potential but again, further work would be required. Another drawback of the AMS system as it has been tested is that there is limited information of the speciation of THMs produced and the instrument is designed to quantify only THMs. The AMS THM-100 shows the user the higher concentration between bromoform or chloroform as well as the summation of the THMs detected. A significant benefit of the accelerated lab method is that, since it requires the use of a gas chromatograph, a full speciation breakdown can be recorded not only for THMs but for other DBPs including haloacetic acids, as well. An interesting project would be to examine one method that could account for different DBP sets. If a method could be found, this would be highly beneficial and should be looked into in the future.

Acknowledgements

I would like to very sincerely thank Dr. David Reckhow and Patrick Wittbold for the opportunity to perform this research. I would also like to thank Yue Sun for greatly assisting me with nearly all of the solid phase extractions impertinent to the standard and the accelerated lab methods. Thank you to Michael West and Aqua Metrology Systems for allowing me to collect and analyze data from their instrument, the THM-100.

References

- Aqua Metrology Systems. (2016). THM-100 Online THM Monitor [Brochure]. Author. Retrieved from <http://www.aquametrologysystems.com/wp-content/uploads/2014/12/AMS027-thm100-brochure-WEB.pdf>
- Bernhardt ES, Likens GE et al (2005) Can't see the forest for the stream? In-stream processing and terrestrial nitrogen exports. *Bioscience* 55:219–230
- Bormann FH, Likens GE et al (1969) Biotic regulation of particulate and solution losses from a forest ecosystem. *Bioscience* 19:600–610
- Chow AT, Dahlgren RA et al (2008) Relationships between specific ultraviolet absorbance and trihalomethane precursors of different carbon sources. *J Water Supply Res Technol Aqua* 57:471–480. doi:10.2166/aqua.2008.064
- EPA Environmental Protection Agency (2009). *MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY* (EPA Document # EPA 815-B-09-009). Retrieved from <https://nepis.epa.gov/Exe/ZyPDF.cgi/P100J75C.PDF?Dockey=P100J75C.PDF>
- Garvey EA, Tobiason JE (2003) Relationships between measures of NOM in Quabbin Watershed. *J Am Water Works Assoc* 95:73–84
- Gomi T, Sidle RC et al (2002) Understanding processes and downstream linkages of headwater systems. *Bioscience* 52:905–916
- Hu, C., Zhu, H., Lin, Y., Zhang, T., Zhang, F., & Xu, B. (2014). Dissolved organic matter fractions and disinfection by-product formation potential from major raw waters in the water-receiving areas of south-to-north water diversion project, China. *Desalination and Water Treatment*, 56(6), 1689-1697. doi:10.1080/19443994.2014.953211
- Hua, G., Reckhow, D. A., & Abusallout, I. (2015). Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. *Chemosphere*, 130, 82-89. doi:10.1016/j.chemosphere.2015.03.039
- Li, A., Zhao, X., Mao, R., Liu, H., & Qu, J. (2014). Characterization of dissolved organic matter from surface waters with low to high dissolved organic carbon and the related disinfection byproduct formation potential. *Journal of Hazardous Materials*, 271, 228-235. doi:10.1016/j.jhazmat.2014.02.009
- Rabalais NN, Turner RE et al (2002) Gulf of Mexico hypoxia, aka “The dead zone”. *Annu Rev Ecol Syst* 33:235–263. doi:10.1146/annurev.ecolsys.33.010802.150513
- Raymond, P. A., & Saiers, J. E. (2010). Event controlled DOC export from forested watersheds. *Biogeochemistry*, 100(1-3), 197-209. doi:10.1007/s10533-010-9416-7
- Reckhow, " PRAM: Polarity Rapid Assessment Method," University of Massachusetts;, vol. 1, 2012.
- Reckhow, "Analysis of Trihalomethanes and Related Pentane-Extractable Organic Halides," University of Massachusetts, vol. 1, 2012.
- Reckhow, D.A., P.L. Rees, K. Nusselin, G. Makdissy, G. Devine, T. Conneely, A. Boutin, and D. Bryan. 2007. Long-term Variability of BDOM and NOM as Precursors in Watershed Sources. AWWARF Report 91186, Denver, CO.
- Rosario-Ortiz, F., Kozawa, K., Al-Samarrai, H., Geringer, F., Gabelich, C., & Suffet, I. (2004). Characterization of the changes in polarity of natural organic matter using solid-phase extraction: Introducing the NOM polarity rapid assessment method (NOM-PRAM). *Water Science and Technology: Water Supply*, 4(4), 11-18. doi:10.2166/ws.2004.0055
- Sharp EL, Parsons SA et al (2004) The effects of changing NOM composition and characteristics on coagulation performance, optimisation and control. In: 3rd international conference on natural organic material research, Victor Harbor, South Africa
- Singer PC (1994) Control of disinfection by-products in drinking water. *J Environ Eng ASCE* 120:727–744
- Summers, R. S., Hooper, S. M., Shukairy, H. M., Solarik, G., & Owen, D. (1996). Assessing DBP yield: Uniform formation conditions. *Journal - American Water Works Association*, 88(6), 80-93. doi:10.1002/j.1551-8833.1996.tb06573.x
- Thurman, E.M., and R.L. Malcolm. 1981. Preparative Isolation of Aquatic Humic Substances. *Environmental Science & Technology* 15:463-466.
- W APHA, and AWW AEEF. 2010. Standard Methods for the Examination of Water and Wastewater, 21th Edition: Section 5710 Disinfection By-Products Precursors.

Appendix A: Compilation of Data

Date Collected	Online TOC [ppm]	UV254 [UVA]	Cl demand [ppm] (Standard Lab)	Cl demand [ppm] (Accelerated Lab)	Standard Lab THM [ppb]	Accelerated Lab THM [ppb]	AMS THM [ppb]	Mill River Flow [cfs]
7/17/2018 13:00	2.43		3.78		149.37		271.42	13.22
7/18/2018 14:30	3.75		5.06		157.88		364.08	16.24
7/23/2018 12:30	5.00		7.04		291.97		493.21	72.74
7/25/2018 10:45	4.37		6.55		330.45		490.63	34.20
7/26/2018 14:15	5.74		8.84		462.01		581.71	113.11
7/27/2018 10:30	7.46		9.89		565.78		728.09	50.33
8/8/2018 13:30	9.66		14.36	11.2	500.02	458.04	744.95	37.99
8/9/2018 11:00	11.6		17.52	13.35	618.31	511.00	884.10	69.03
8/10/2018 10:20	8.6	0.401	12.81	9.8	465.46	393.17	708.5	35.34
8/28/2018 3:00	3.76	0.131	5.22	5.25	176.05	147.22	336.9	27.98
8/29/2018 11:40	3.49	0.126	4.88	4.4	174.61	155.38	327.9	25.43
8/30/2018 13:50	3.44	0.153	5.11	4.2	146.76	150.91	354.3	23.62
8/31/2018 10:20	5.16	0.134	5.48	4.85	143.60	141.37	285.1	21.54
9/24/2018 12:40	4.11	0.166	6.27	6.39	171.87	166.90	309.05	34.10
9/25/2018 20:20	5.13	0.27	7.19	6.51	201.29	179.43	390.85	230.26
9/26/2018 13:00	7.73	0.389	11.11	9.61	310.62	291.18	575.04	91.81
9/27/2018 10:40	9.34	0.502	12.32	12.33	381.77	420.09	712.31	131.90
9/28/2018 14:20	6.00	0.315	8.22	8.08	280.45	281.86		91.81
10/1/2018 15:30	3.97	0.179	6.57	5.56	198.36	187.11		47.54
10/2/2018 15:15	4.04	0.179	6.66	6.31	209.05	181.70		59.38
10/18/2018 16:10	4.62	0.203	9.22	8.02	229.66	196.92		38.47
10/23/2018 16:30	3.76	0.139	7.22	6.28	165.91	139.77	272.55	32.83
10/24/2018 16:00	3.85	0.131	7.04	6.12	171.61	139.21	269.65	33.05
10/25/2018 17:15	3.96	0.126	7.06	6.14	159.06	127.23	255.06	31.89

Date Collected	Online TOC [ppm]	UV254 [UVA]	Cl demand [ppm] (Standard Lab)	Cl demand [ppm] (Accelerated Lab)	Standard Lab THM [ppb]	Accelerated Lab THM [ppb]	AMS THM [ppb]	Mill River Flow [cfs]
10/29/2018 13:30	4.1	0.189	8.9	7.74	210.30	191.56	366.32	60.97
10/31/2018 13:00	4.19	0.172	8.58	7.46	202.34	188.40	336.21	43.10
11/1/2018 16:30	3.89	0.16	7.94	6.90	176.70	165.70	303.78	41.73
11/3/2018 16:30	4.82	0.46	9.91	10	342.43	282.22	655.99	193.11
11/5/2018 12:30	6.41	0.236	8.45	6.7	249.54	198.99	390.63	72.19
11/6/2018 20:10	5.06	0.224	7.72	6.2	210.63	158.42	379.88	133.49
11/7/2018 14:00	4.6	0.251	8.7	7.3	265.62	198.74	441.97	90.13
11/8/2018 14:15	4.82	0.209	7.58	6.4	217.10	180.41	369.01	70.34
11/9/2018 11:20	4.57	0.177	6.58	5	195.42	150.79	282.82	65.24
11/13/2018 16:00	3.97	0.219	7.14	5.4	192.65	159.81	304.91	151.46
11/14/2018 14:10	4.05	0.223	7.46	5.9	224.18	164.73	369.21	81.18
11/16/2018 13:30	3.65	0.134	5.92	4.4	154.34	120.84	249.82	70.53
12/3/2018 14:40	3.06	0.163	5.24	3.8	156.31	111.78	265.12	92.98
12/4/2018 14:20	3.05	0.128	4.66	2.9	144.13	101.34	245.8	83.46
12/5/2018 12:30	2.98	0.137	4.26	2.8	130.78	89.56	210	72.19
12/6/2018 12:45	2.86	0.184	3.96	2.8	113.61	80.18	193.7	67.72
12/7/2018 11:30	2.68	0.117	3.62	2.6	108.18	76.86	163.57	65.05
12/10/2018 16:10	2.69	0.231	3.17	2.1	91.38	69.09	151.91	57.78
12/11/2018 13:40	2.74	0.122	2.9	2.2	88.64	63.73	142.81	54.52
12/12/2018 15:00	1.33	0.115	2.96	2.1	82.01	60.13	135.6	53.90
12/13/2018 15:45	2.22	0.113	2.96	2.5	86.28	66.64	131.51	52.86
2/13/2019 14:30	1.86	0.099	2.9	2.6	81.19	53.76	135.87	49.48
2/14/2019 15:50	1.61	0.09	2.7	2.8	81.39	56.62	129.17	41.50
2/15/2019 13:30	1.69	0.09	2.3	2.6	75.97	62.36	114.11	38.47
2/20/2019 15:30	1.47	0.089	2.6	3	73.35	66.66	125.77	37.76
2/21/2019 14:30	1.81	0.114	5.7	4.6	96.4	73.78	126.07	36.80
2/26/2019 10:45	2.12	0.102	3.6	3	100	72.39	177.19	35.34

Appendix B: Standard and Accelerated Lab Method Sample Preparation Details

Table 1. THM Extraction Summary

1. Prepare calibration standards. (table 2)
2. Place twenty milliliters of sample or standard to be analyzed into vial.
3. Add 250 microliters of 0.1N sodium arsenite solution into the vials containing the 20 milliliters of sample to quench residual chlorine.
4. Add 4 milliliters of pre-mixed Pentane1 + internal standard. (table 4)
5. Add approximately 15g of Na₂SO₄
6. Shake well for 15 minutes.
7. Transfer organic layer into autosampler vials
8. Freeze to remove water and analyze on GC.

Table 2. Standards Preparation

1. Prepare Stock Solution II:
 - a. Obtain 10 milliliter volumetric flask that contains acetone
 - b. Add 100 microliters of 551A commercial mix
 - c. Add 20 microliters of 551B commercial mix
2. Prepare calibration standards:
 - a. Add 20 milliliters of Super-Q to 8 vials.
 - b. Add 0, 5, 10, 20, 30, 50, 80 and 100 microliters of stock II to the respective vials
 - i. Volumes of stock addition may be adjusted based on expected THM concentration range and speciation.

Table 3. Internal Standard Preparation

1. Place a 10 milliliter volumetric flask partially filled with MtBE in an analytical balance
2. Zero the balance
3. Add 6-7 drops of 1,2-dibromopropane and record the weight
4. Fill to the mark with MTBE
5. The concentration of the Internal Standard Stock solution is determined by:
 - a. $CIS_{stock} = (\text{weight IS (g)} / 10 \text{ ml}) * (1000 \text{ mg/g})$
 - b. The concentration should be around 10 mg/mL.
6. Place the unused portion of this solution in a heavy-walled extract vial (Supelco #3-3293),
7. Label the vial with the IS concentration and store it in a refrigerator.

Table 4. Preparation of Pentane with Internal Standard

1. Rinse a dry on liter volumetric flask with THM-grade or HPLC-grade Pentane (1x).
 - a. Dispose of this rinse solution into a waste bottle
2. Fill the flask to about 2/3rd capacity with THM-grade pentane
3. Calculate the amount of 1,2-dibromopropane stock necessary to prepare a 300 µg/L solution:
 $(\text{"x"} \text{ mL} / 1000 \text{ mL}) * (CIS_{stock} \text{ mg/mL}) * (1000 \text{ mL/L}) * (1000 \text{ µg/mg}) = 300 \text{ µg/L}$
4. Add appropriate amount of the standard solution to the pentane
5. Place this into a bottle labeled THM + IS
6. The total volume should be 1000 milliliters

Appendix C: (A) A map of the sampling site and (B) An image of the pump system used for sampling



(A)



(B)