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Using Gas Chromatography to Investigate Volatile Organics in Drinking Water

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USING GAS CHROMATOGRAPHY TO INVESTIGATE VOLATILE ORGANICS IN DRINKING WATER

by

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Dedicated to:

My friends and family.

Without their help and support none

of this would have been possible.

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ABSTRACT

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Trihalomethanes (THMs) are a major class of disinfection by-products found in chlorinated drinking water. They are an unfortunate side effect of the chlorination process. Due to possible adverse health effects, the United States Environmental Protection Agency has set a maximum contaminant level of 0.080 milligrams per liter for Total Trihalomethanes in drinking water. Recently, the way in which utilities report their trihalomethane levels has changed. This has renewed interest in on-line, near real time monitoring of trihalomethane concentrations. The focus of this research was the development of a fully automated instrument capable of on-line near real time measurement of THMs concentrations in drinking water distribution systems and its application to real world problems. A commercial instrument that was shown to be both rugged and robust was developed. This instrument was used to collect unprecedented on-line THMs data in multiple distribution systems. This data was then used for treatment process optimization in a functioning water treatment plant. Comparison to empirical models showed that is possible to use on-line monitoring data to calibrate the models for a particular system. This is a possible alternative to the expensive process of developing an entirely new empirical model. Additional studies used the rate of formation for THMs to determine the time to the first tap for a particular treatment system. This determined amount of time was used with the rate of formation for haloacetic acids to distinguish between concentrations resulting from formation and those resulting from the use of bulk hypochlorite solution.

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LIST OF SYMBOLS AND ABBREVIATIONS

/	per (division)
<	less than
>	greater than
≤	less than or equal to
≥	greater than or equal to
±	plus or minus
~	approximately
x	multiplication
[A]	predicted concentration
$[A]_0$	initial concentration
ACS	American Chemical Society
AR	Arkansas
AWWA	American Water Works Association
BA	Bland-Altman
Br^-	bromide ion
BrO_2	bromine dioxide
°C	degrees Celsius (centigrade)
°C min^{-1}	degrees Celsius per minute
c_f	final concentration
c_i	initial concentration
$CHBr_3$	bromoform
$CHBrCl_2$	bromodichloromethane
$CHBr_2Cl$	dibromochloromethane
$CHCl_3$	chloroform
CI	confidence interval
Cl^-	chloride ion
Cl_2	chlorine

ClO_2	chlorine dioxide
cm	centimeters
CMS	capillary membrane sampler
CMS-GC	capillary membrane sampling gas chromatography
CMS-GC-ECD	capillary membrane sampling-gas chromatograph-electron capture detector
D	chlorine dose
DBPs	disinfection by-products
DELCD	dry electrolytic conductivity detector
DIA	direct aqueous injection
DOC	dissolved organic carbon
DPD	N,N-diethyl-p-phenyldiamine
ECD	electron capture detector
EFC	electronic flow controller
EPA	Environmental Protection Agency
FAC	free available chlorine
GC	gas chromatograph
GC-ECD	gas chromatography-electron capture detector
GEC	gas extraction cell
H^+	hydrogen ion
HAAs	haloacetic acids
HAA9	nine chlorinated and brominated haloacetic acids
HAAs/FAC	ratio of HAAs to FAC
HBr	hydrobromic acid
HCl	hydrochloric acid
H_2O	water

H_3O^+	hydronium ion
HOBr	hypobromous acid
HOCl	hypochlorous acid
HPLC	high performance liquid chromatography
HS	headspace
H_2SO_4	sulfuric acid
I^-	iodide ion
I_2	iodine
I_3^-	triiodide ion
ICP-MS	inductively coupled plasma-mass spectrometry
id	inner diameter
IL	Illinois
k	first order rate constant
kgs	kilograms
KI	potassium iodide
KIO_3	potassium iodate
KOH	potassium hydroxide
L	liters
lbs	pounds
LED	light emitting diode
LLE	liquid-liquid extraction
ln	natural log
LOQ	limit of quantitation
m	meters
mm	millimeters
µm	micrometers
MΩ cm	megaohm centimeters

MCL	maximum contaminant level
MDL	method detection limit
mg	milligrams
mg L^{-1}	milligrams per liter
µg	micrograms
µg L^{-1}	micrograms per liter
MGD	million gallons per day
min	minutes
mL	milliliters
mL min^{-1}	milliliters per minute
µL	microliters
MS	mass spectrometer
MT	moisture trap
MTBE	methyl tert-butyl ether
mV	millivolts
MVNL	multivariate nonlinear
N_2	nitrogen
$Na_2S_2O_3$	sodium thiosulfate
Na_2SO_4	sodium sulfate
NH_3	ammonia
^{63}Ni	nickel-63 isotope
NJ	New Jersey
nm	nanometers
NOM	natural organic matter
NY	New York
OBr^-	hypobromite ion
OCl^-	hypochlorite ion
OE	operator event

OK	Oklahoma
OPT-GC	on-line purge and trap gas chromatograph
OPTGC-DELCD	on-line purge and trap gas chromatograph-dry electrolytic conductivity detection
PAC	powdered activated carbon
PCR-IC	post-column reaction ion chromatography
PD-PID	pulsed discharge-photoionization detector
PEEK	polyetheretherketone
PID	photoionization detector
PP	peristaltic pump
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
RE	rainfall event
%RSD	percent relative standard deviation
SCADA	supervisory control and data acquisition
SCMS	supported capillary membrane sampler
SCMS-GC	supported capillary membrane sampling-gas chromatography
SCMS-GC-ECD	supported capillary membrane sampling-gas chromatography-electron capture detection
$S_2O_3^{-}$	thiosulfate ion
$S_4O_6^{2-}$	tetrathionate ion
SPME	solid phase microextraction
SUVA	specific ultraviolet absorbance
t	time
T	temperature

THAA3	total of three haloacetic acids found in hypochlorite solutions
THAA9	total of all nine haloacetic acids
THAAs/FAC	ratio of the total haloacetic acids to the FAC
THMs	trihalomethanes
THM4	the four regulated trihalomethanes
THM-RR	trihalomethane rapid-response
TN	Tennessee
TOC	total organic carbon
TTHMs	total trihalomethanes
TTHM4	total of four regulated trihalomethanes
TX	Texas
US	United States
USD	United States dollars
USEPA	United States Environmental Protection Agency
V1	3-way solenoid valve
V2	heated injection valve
WRF	Water Research Foundation
WTP	water treatment plant

CHAPTER 1

INTRODUCTION

Background

Chlorination as a Disinfection Process

Chlorination has been used to disinfect drinking water in the United States since 1908. This was one of the major reasons for the near elimination of water borne illnesses, and is considered one of the most important public health improvements. Chlorination is not only an extremely effective disinfectant but is also economically affordable for most water treatment facilities. These two factors have allowed it to be the most common drinking water disinfection method in the United States for over a century.

The most common methods of chlorination use chlorine gas, sodium hypochlorite solution, or calcium hypochlorite as a source of chlorine. Once introduced into the water source chlorine (Cl_2) will hydrolyze and form hypochlorous acid (HOCl), this can then further dissociate into hypochlorite ion (OCl^-), shown in Figure 1. These three species make up what is known as free available chlorine (FAC). The ratio of these species is dependent upon the pH of the solution. Most drinking water is maintained at a pH between 6.5 and 8 to prevent corrosion of the pipes. This results in HOCl and OCl^- making up the majority of FAC in drinking water systems. These two species are preferred as they are stronger oxidizers than Cl_2. In the presence of bromide ion, chlorine will quickly be replaced with bromine forming hypobromous acid (HOBr) and hypobromite ion (OBr^-).

$$Cl_2 + H_2O \rightleftarrows HOCl + Cl^- + H^+$$

$$HOCl + H_2O \rightleftarrows OCl^- + H_3O^+$$

$$HOCl + Br^- \rightleftarrows HOBr + Cl^-$$

$$OCl^- + Br^- \rightleftarrows OBr^- + Cl^-$$

Figure 1. Reaction of chlorine with water and the dissociation of hypochlorous acid in water. Formation of hypobromous acid and hypobromite ion.

Formation of Disinfection By-Products

One of the disadvantages to the chlorination process is the formation of disinfection by-products (DBPs). These are a result of the reaction of FAC with natural organic matter (NOM) that is present in the water. The presence of DBPs first began to appear in the literature around 1974 (Bellar et al., 1974 ; Rook, 1974). While there is no definitive mechanism for the formation of DBPs, humic acid is almost always considered to be the precursor. Humic acid is not a single compound but rather a class of acids that results from the decay of natural organic matter. It is the complex nature of these precursors that has made determining a mechanism difficult. A commonly suggested mechanism for the formation of DBPs is the reaction of FAC with the acetyl groups present in humic acid (Brush & Rice, 1994; Bunce, 1994; Oliver & Lawrence, 1979).

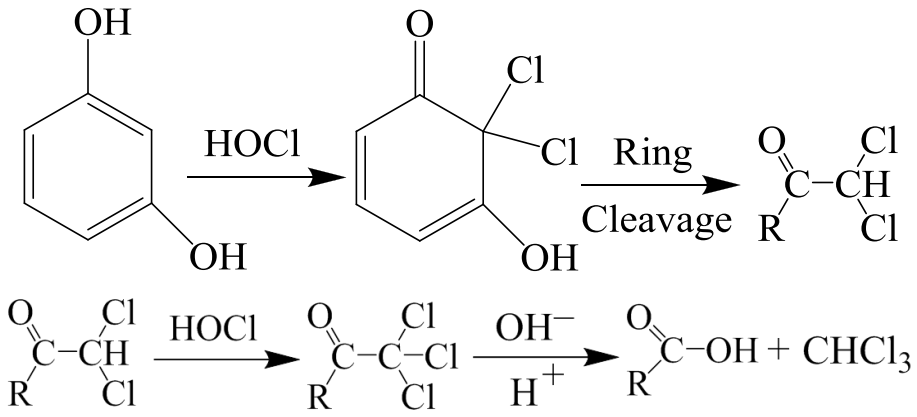


Figure 2. Formation of chloroform from the reaction of hypochlorous acid with 1,3-dihydroxybenzene.

This research has predominately focused on a single class of DBPs known as trihalomethanes (THMs). THMs are the most common class of DBPs found in chlorinated drinking water.

Regulations on Disinfection By-Products

Due to THMs being possible carcinogens the United States Environmental Protection Agency (USEPA) regulates the total THMs concentration in finished drinking water. The four THMs species that are regulated are chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). Collectively these are known as THM4. Regulation began with the 1974 Safe Drinking Water Act, however the current regulations have evolved through stage one and stage two of the Disinfectants and Disinfection By-products Rule of 1998 (USEPA, 1998). Stage two began coming into effect in 2012. This sets a maximum contaminant level (MCL) for Total THM4 at 0.080 mg L^{-1}.

During Stage 1 of this rule drinking water utilities were allowed to use a running annual average. This is done by taking quarterly monitoring levels for total THM4 from

several locations. These values are then averaged to get a final value for the utility. This allowed for utilities that may have certain sampling sites above the MCL, to remain in compliance as long as the final running annual average was below the MCL. Starting in 2012, Stage 2 began to be implemented (USEPA, 2006). This required several changes in the way that utilities report their total THM4 levels. The first change was the implementation of an initial distribution system evaluation. This was designed to identify areas within a distribution system that have the possibility of increased THM4 concentrations. The running annual average was replaced with the locational running annual average. This means that annual average at each individual sampling location must be reported. This eliminates situations in which higher levels at certain sampling sites are averaged out by low values at others. In essence, this means an increase in regulatory pressure, but also results in improved water quality.

USEPA Approved methods

There are currently three USEPA approved compliance monitoring methods for THM4: 502.2, 524.2 and 551.1 (USEPA, 1995a, 1995b, 1995c). All three methods use gas chromatography as a separation method, the major differences between them are in the sample handling and detection methods. All of these methods have been shown to have excellent method detection limits, mean percent recoveries, and percent relative standard deviations in relation to measuring THMs in drinking water samples.

Both 502.2 (USEPA, 1995a) and 524.2 (USEPA, 1995b) use a purge and trap system to remove the volatile species from the water sample and preconcentrate them on a trap. This trap is then heated to desorb the analyte species which are injected onto the column for separation. Purge and trap systems have the advantage of both removing the

analytes from the water sample while concurrently preconcentrating them. The difference in the methods begins after separation. Method 502.2 uses a photoionization detector (PID) in series with an electrolytic conductivity detector, commonly known as a Hall detector. The Hall detector works by reacting the halogenated species at ~850 ° C with hydrogen gas to form HCl or HBr. These species are introduced to a stream of n-propanol which passes through a conductivity cell. Method 524.2 replaces the PID-Hall detector with the use of a mass spectrometer. The mass spectrometer allows for easy verification of peaks and unknowns, while the PID-hall method relies on confirming THMs by the peaks showing up with both detectors. The PID-Hall method has no way of identifying unknown peaks other than retention times and whether or not they show up on an individual detector or both.

USEPA method 551.1 (USEPA, 1995c) uses a liquid-liquid extraction (LLE) method to remove volatile organic compounds from drinking water. This is done by first increasing the ionic strength of the water sample by adding a salt followed by extraction using either methyl-tert-butyl ether or pentane. This extract can then be injected onto a gas chromatograph for separation. Detection is done with the use of an electron capture detector (ECD). The ECD contains a ^{63}Ni foil that produces beta particles which ionize the nitrogen make-up gas. This forms electrons which results in a standing current within the detector. When electronegative compounds, such as THMs, enter the detector they capture some of these electrons which results in a decrease in the standing current. This process makes the ECD selective for electronegative compounds. The ECD electronics compensate for this decrease in current in attempt to maintain the original standing current. This is output as a voltage which can be amplified and then measured.

All of the approved USEPA methods are used for quarterly compliance monitoring. This only requires a small number of samples to be measured four times a year. Where they begin to fall short is when a more rigorous sampling schedule is needed, such as the hourly sampling rate shown in this research. All three methods are relatively expensive, complex, and require a certain level of operator skill level. For these reasons a large amount of research has been done into finding viable alternative methods for measuring THMs in drinking water.

Alternative Methods

While there has been a large amount of research into alternative methods, the majority of them still utilize gas chromatography. The major differences between them is the sampling method (Pavon et al., 2008). While there are also several different detection methods available, a mass spectrometer or electron capture detector are the most heavily utilized. Mass spectrometers are often used because they allow for confirmation of analytes without any extra analysis. Electron capture detectors are common because they are both sensitive and selective to halogenated compounds.

A variety of LLE extraction methods have been developed. Some of these are simply modifications to the current USEPA method 551.1 (Leivadara et al.,2008; Nikolaou et al., 2002; Nikolaou et al., 2005). Gonzalez Gago et al. have tried using a similar solvent, n-pentane coupled with newer detection methods such as inductively coupled plasma mass spectrometry (ICP-MS) (Gonzalez Gago et al., 2007). Others have experimented with the use of different solvents such as hexane (Buszewski & Ligor, 2001). All of these methods showed great method detection limits (less than 0.1 $\mu g\ L^{-1}$) and were shown to be viable methods for measuring THMs in water samples, but they are

still subject to the traditional problems associated with extraction methods. Extraction methods can become very time consuming depending on the number of samples being analyzed and they also require the use of a liquid solvent. With the move towards "greener" chemistry, reduction of solvent use is a large priority for many.

The move away from solvent based methods has increased interest in non-solvent based extraction methods such as headspace extraction (HS) and solid phase microextraction (SPME). Headspace techniques have seen an increase of use because the volatility of THMs makes them an ideal candidate for this method. One of the major advantages of headspace methods is that it allows volatile compounds to be analyzed without interference from complex matrices. The disadvantage of traditional HS techniques is sensitivity. The equilibrium that exists between the sample and the headspace means that not all of the analyte is available for extraction. The method detection limits obtained from these methods are still comparable to those from the standard USEPA methods (0.003 – 0.17 μg L^{-1})(Culea et al., 2006; Gallard & von Gunten, 2002; Golfinopoulus et al., 2001; Kuivinen & Johnsson, 1999; Nikolaou et al., 2002). Improvements in sensitivity have been seen when combining headspace techniques with cryotrapping (Kolb & Ettre, 2006). Solid phase microextraction is another technique that is often used in combination with HS methods. SPME methods are attractive because not only does it have the advantages of other HS methods but adds a level of preconcentration that helps compensate for the sensitivity issues normally seen with these methods.

Traditionally, injection of water onto a gas chromatograph is something that is avoided because it can cause damage to the column. However, advances in column

design have allowed for columns that are coated in an apolar liquid phase. This will cause water to elute before the analytes. This makes direct aqueous injection (DIA) methods possible. Using this method allows for the elimination of any sample preparation or solvent use. Due to the presence of other compounds in water samples it is necessary to use a guard column to help minimize contamination of the analytical column. With no preconcentration step the sensitivity of the method is completely dependent on the amount of sample that can be injected, this can be a major disadvantage depending on the column being used. Without additional steps this method has method detection limits that are several times higher than those of the USEPA approved methods (3-5 $\mu g\ L^{-1}$) (Golfinopoulos et al., 2001; Pyle & Gurka, 1994). If a cold on-column injection method is used then method detection limits on par with the USEPA methods can be achieved (Aeppli et al., 2008; Biziuk et al., 1996; Polkowska, 2004).

Previous Membrane Based Methods

In 2004, Emmert et al. published a report that reviewed methods that could be adapted to on-line monitoring of THMs in drinking water (Emmert et al., 2004a). Through this report they detailed several features than an "Ideal Method" would have. With these features in mind several different methods using membrane based sampling coupled with gas chromatography were developed.

Table 1. Features of an "Ideal Method"

Feature	Goal
Analysis rate	1 sample per hour
Method detection limit	0.5 – 5.0 μg L^{-1}
Mean % Recovery	95 – 105%
% RSD	< 10%
Total organic carbon interference	No effect from TOC < 20 mg L^{-1}
Portable	Transportable to sampling site
Operator skill level	Low
Evaluation in real world situations	Comparable to USEPA method
Automation	Full
Cost	<$20,000
Interface with communication network	e.g. FTP server

The first instrument in this series used a supported capillary membrane sampling device (SCMS). This sampling device consists of a probe around which a capillary silicone membrane is wrapped. This probe is inserted into either a calibration vessel or a fast loop/flow cell for on-line analysis. The THMs in the water will pervaporate across the silicone membrane into an inert gas stream. This stream can then be routed to an instrument for separation and detection. This method of sampling requires no sample preparation, no solvents, and is easily adaptable to a gas chromatograph. The first instrument this was coupled to was a "bench-top" gas chromatograph with an electron capture detector (SCMS-GC-ECD) (Cao, 2004; Duty, 2000; Emmert et al., 2004a, 2004b, 2007; Liao, 2001). During the initial development of this instrument several different configurations were tested including; silicone membrane versus Teflon AF membrane and electron capture detection versus flame ionization detection. It was determined that silicone membrane and electron capture detection gave the best results for measuring THMs in water samples (Duty, 2000). This instrument gave MDLs below 1 μg L^{-1} for all of the THM4 species except for bromoform which had an MDL of 6.1 μg L^{-1}. Acceptable

mean percent recovery and percent relative standard deviation values were reported as well.

The SCMS-GC-ECD instrument was altered two different times in attempt to conform more to the "ideal method" criteria. The first of these was a portable version of the original version. This consisted simply of connecting the existing sampling device to a smaller more portable GC instrument. An electron capture detector was still used for detection. This instrument reported MDLs around 1.0 μg L^{-1} for all four THM4 species. The major advantage of this instrument over the "bench-top" model was the ability to easily move the instrument to do on-line monitoring studies. A six day monitoring study was performed at the University of Memphis. Measurements were taken every hour, with a check standard every 12 hours. When compared to total THMs concentrations determined by USEPA 502.2, the method was found to have a bias of -0.8 μg L^{-1} for Total THM4 over the course of the study (Emmert et al., 2007).

The second adaptation of the SCMC-GC instrument was an attempt to make the smallest simplest instrument possible. This was done by replacing the traditional gas chromatography instrumentation with a heated injection valve and a column that was placed inside a heated valve enclosure. In place of an ECD, a pulsed discharge photoionization detector (PD-PID) was used. This instrument showed similar single μg L^{-1} MDL values for all four THM4 species as previous SCMS instruments (Emmert et al., 2006). However, this instrument also had several drawbacks. The complexity and instability of the PD-PID required a high level of operator skill and results in a high background noise. This was especially prevalent during attempts at on-line monitoring.

While this instrument was a great idea and worked to a certain degree, it was decided that it was not viable with the technology that was currently available.

The next advancement came not in the form of an instrument but in the sampling device itself. One of the issues with the SCMS device was that it required both a calibration vessel and an adaptor for on-line measurements. With this in mind, the capillary membrane sampler (CMS) was developed. This sampling device utilizes a tube within a tube design. The outer tube is made of a harder Tefzel plastic with a capillary silicone membrane threaded through the inside. This allows for nitrogen gas (acceptor stream) to be passed through the inside of the membrane while a water sample or standard solution(donor stream) is flown between the membrane and the outer Tefzel tubing in the opposite direction of the inner gas flow. The THMs can then pervaporate from the donor stream across the silicone membrane into the acceptor stream. The acceptor stream then passes into a sample loop on a heated injection valve. Once the sampling time is done the injection valve is rotated, allowing for the contents of the sample loop to be injected directly onto a GC column.

This new sampling device was then interfaced with a portable GC-ECD instrument. This setup, referred to as the CMS-GC-ECD, gave MDL values below 1 µg L^{-1} for all four THM4 species with excellent mean percent recovery and percent relative standard deviation values (Brown & Emmert, 2006; Emmert et al., 2007). Already, this is an improvement upon the original SCMS design. The CMS-GC-ECD instrument was used to perform three separate monitoring studies. Two of these took place in Memphis, TN, one during the winter and one during the summer. The third was done in Houston, TX. All three studies consisted of on-line measurements taken once every hour with a

check standard run every 12 hours. The Total THMs values obtained were compared to USEPA method 502.2. The first Memphis study took place during the winter and consisted of a total of 129 THM measurements. The average bias when compared to the USEPA method was found to be 0.1 µg L^{-1} for Total THM4 (Brown & Emmert, 2006; Emmert et al., 2007). The second Memphis study took place during the summer which saw an increase in the overall Total THM4 concentrations. This study consisted of 91 individual THMs measurements with an average bias of -2.8 µg L^{-1} Total THM4 when compared to USEPA 502.2 (Emmert et al., 2007). The final study took place in Houston and consisted of 97 THMs measurements. There was some signal drift that occurred during this study that most likely resulted from sample carryover. The check standard data was used to adjust for this. The average bias before the correction was 10 µg L^{-1} Total THM4, but after the correction it was 0.7 µg L^{-1} Total THM4 (Emmert et al., 2007). This research resulted in US patent #8,336,371 (Emmert & Brown, 2012).

With all of the improvements that were made by moving from the SCMS to the CMS device there were still several areas that could be improved upon. The CMS-GC-ECD instrument uses a linear calibration curve, however the linearity was found to very limited. Each THM4 species was only linear up to around 20-25 µg L^{-1}, with the exception of bromoform which maintained linearity up to approximately 35 µg L^{-1} (Brown & Emmert, 2006; Emmert et al., 2007). This could be an issue in certain distribution systems. If the overall Total THM4 concentration is high, for example 50 µg L^{-1}, but there is very little bromine presence in the source water then the majority of the Total THM4 concentration will be made up of chloroform. This could result in concentrations of a single THMs species that is outside of its linear range. Another issue

that is possible in these higher concentration ranges is carryover effects. This was seen in the Houston monitoring study in the form of an upwards drift in the Total THM4 concentrations (Emmert et al., 2007). While this can be corrected later with the use of check standard data, it would be a much more useful solution if it was possible to eliminate the carryover altogether.

During the same period that the CMS-GC-ECD instrument was being developed, another alternative instrument was also being tested. This instrument had several differences it used a sampling device known as a gas extraction cell (GEC), used a built in purge and trap system for preconcentration, and used a dry electrolytic conductivity detector (DELCD). This instrument was referred to as the on-line purge and trap gas chromatograph with a dry electrolytic conductivity detector (OPTGC-DELCD) (Brown et al., 2007). The GEC works similar to the CMS device. It consists of a hard outer metal shell with a capillary silicone membrane running through the inside. The water sample or standard (donor stream) is passed through the inside of the silicone membrane while nitrogen sweeping gas is passed over the outside of the membrane. The nitrogen sweep gas carries the THMs onto a Tenax trap. This results in preconcentration of the analytes. At the end of the sampling time, the trap is heated, desorbing the analytes which are then injected onto a GC column for separation. Detection was done using a DELCD. The DELCD works by reacting halogenated species at approximately 1200 °C to form ClO_2 and BrO_2 which is then detected by an electrode.

The OPTGC-DELCD instrument was shown to have MDL values below 1 µg L^{-1} for all four THM4 species with excellent mean percent recovery and percent relative standard deviation values as well. The OPTGC-DELCD instrument showed an improved

dynamic range in comparison to the CMS-GC-ECD instrument which is mostly the result of the use of quadratic calibration curves in place of the linear fits used previously. This allowed the OPTGC-DELCD to be calibrated over the range of 0.7 to 50 μg L^{-1} (Brown et al., 2007). Two on-line monitoring studies were performed using this instrument. For both studies measurements were taken once every hour with a check standard run every 12 hours. The first took place in Houston, TX and consisted of 41 THM4 measurements. The average bias in comparison to USEPA 502.2 was found to be -6.6 μg L^{-1} for Total THM4. The second study was performed in Memphis, TN and consisted of 83 individual THM4 measurements. The average bias for the study was found to be -0.1 μg L^{-1} for Total THM4 (Brown et al., 2007).

Although the OPTGC-DELCD instrument showed several improvements over the CMS-GC-ECD instrument, there were several issues associated with it as well. The most pressing issue was the stability of the DELCD. The operating temperature of approximately 1200 °C would cause the electrode to begin to bend under its own weight. This resulted in a change in the analytical signal. An attempt was made to reinforce the electrode with a metal rod. While this helped to stabilize it, it was still necessary to allow the instrument to equilibrate for a 24 hour period before use (Brown et al., 2007).

Statement and Purpose of Research

The ability to measure trihalomethanes on-line in near real time has been shown in previous research (Emmert et al., 2007). The main problem with these methods is the skill level required by the user for both instrument use and data processing. The main focus of this research has been in the development of a fully automated capillary membrane sampling gas chromatography method that is capable of on-line near real time monitoring and is also rugged and robust enough for extended on-line use. The goal was to develop an instrument that would work like a "THMs meter" and would allow utilities to monitor THMs concentrations in the same way as other water quality parameters. This type of data would allow for not only treatment process optimization but for quicker reaction times to changes within a system. Collection of long term data would allow for identification of patterns and trends in a system and access to large data sets could be used to system modeling.

Research Objectives

1. Fully automate the CMS-GC method to minimize analyst interaction from sampling through data processing.

2. Improve ruggedness and robustness of the CMS-GC instrument to allow for long term on-line monitoring with minimal maintenance.

3. Simplify skill level required to run the CMS-GC method to that of the average water treatment plant employee.

4. Perform long term on-line monitoring studies to both collect data and establish the performance of the improved instrumentation.

5. Develop methods to apply on-line near real time data to problems experienced with in actual water treatment systems.

Research Questions

1. Is it possible to both fully automate and simplify the CMS-GC method without reducing performance?

2. What is the maximum length monitoring study that can be performed and how can this time be increased?

3. How can on-line monitoring data be utilized by water treatment plants?

4. What other applications are there for these data sets?

5. How can this instrumentation be used to investigate THMs in previously unavailable ways?

Chapter 2

A DEVICE FOR THE FULLY AUTOMATED ON-SITE PROCESS MONITORING AND CONTROL OF TRIHALOMETHANE CONCENTRATIONS IN DRINKING WATER

Introduction

Water treatment plants routinely monitor a number of parameters including temperature, pH, turbidity, total organic carbon (TOC) and residual chlorine as part of their process control strategies. Years ago, it was common for these values to be measured daily, but today, such measurements are often done on-line and in near real-time. The results are available practically on demand. In this way, the on-line and on-site nature of process monitoring allows operators to observe changes in water quality and make adjustments to the treatment practices, if necessary. Such attention to detail has undoubtedly led to improved drinking water quality.

A major water quality concern for many water treatment plants (WTP) is the formation of potentially carcinogenic disinfection by-products (DBPs). The specific types of DBPs that form depends on many factors, but certainly the disinfectant used is of primary importance. In the Unites States where water chlorination is practiced by the majority of WTPs, the most common class of regulated DBPs are the trihalomethanes (THMs).

The THMs include four compounds: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). The United States Environmental Protection Agency (USEPA) has established a maximum

contaminant level (MCL) of 0.080 mg L^{-1} for the total concentration of the four THMs species (Total THMs) (USEPA, 1998). While this MCL value has not changed since 1998 (USEPA, 1998), there have been significant changes in how WTPs show compliance with THMs regulations. Prior to Stage 2 of the Disinfectant/Disinfection By-Product Rule (USEPA, 2013), WTPs were able to demonstrate MCL compliance by averaging sample concentrations from collection points spanning the entire distribution system, called the *running annual average*. Currently, WTPs are required to sample at specified locations in their distribution systems that exhibit the highest concentrations of DBPs. The running annual average at each location is subject to MCL compliance, and this is called the *locational running annual average.*

Is compliance with these regulations difficult for WTPs in the US? Consider Figure 3 which plots Total THMs MCL legal violations in 2007 using data drawn from the National Drinking Water Database (Environmental Working Group, 2014). For WTPs in the United States serving greater than 500 customers, there were 2796 legal violations for the Total THMs MCL out of 13,451 total legal violations reported in the database. Thus, about one in five of all MCL legal violations are Total THMs MCL violations. In fact, the total number of legal violations is likely even higher than indicated as the database is incomplete – THMs data is apparently not reported for six states (Colorado, Georgia, Kansas, Louisiana, Mississippi and Tennessee). But perhaps more importantly, the violations shown here occurred when MCL compliance was enforced using the less rigorous running annual average. Thus compliance with Total THMs violations is a serious problem for WTPs in the US that will likely become worse.

Figure 3. Total THMs Legal Violations in the United States for 2007. Adapted from (Environmental Working Group, 2014).

Unfortunately, controlling the concentrations of THMs in drinking water can be a difficult and an expensive task. Most models that have been developed for THMs control are empirical in nature (Bond et al., 2012; Brown et al., 2011a; Brown et al., 2011b; Chowdhury et al., 2009; Courtis et al., 2009; Di Christo et al., 2013; Platikanov et al., 2007). Many researchers report that THMs concentrations can vary in the short-term and this fine detail may be missed by empirical models. THMs concentrations have been shown to vary yearly, (Parvez et al., 2011), seasonally (Liu et al., 2011; Toroz & Uyak, 2005), monthly (Villanueva et al., 2005), daily (Chaib & Moschandreas, 2008) and even hourly (Pereira et al., 2004). The demands placed on a model that can accurately reflect the true, potentially dynamic, behavior of the system are strenuous in the least.

Large variations of Total THMs concentrations at the point of entry have been reported (Pereira et al., 2004), which may complicate the development of accurate

models that predict THMs concentrations in a distribution system. Routine grab samples may provide a snapshot of the behavior that occurs, but this snapshot may or may not be extrapolated to the behavior at other times. Even sampling on a weekly or daily schedule may give misleading results about exposure (Pereira et al., 2004) or just about the actual concentrations of Total THMs. If the goal is to mitigate THMs concentrations in the long term (USEPA, 2013), then the solution must start with monitoring and controlling THMs on a daily basis in the short term. From a treatment perspective, it is difficult to determine if a change in a treatment process has made a difference (good or bad) without knowing the THMs concentrations before, during, and after an operational change. Perhaps then, it is best to *measure* the THMs concentrations rather than *model* THMs concentrations. The ability to measure the concentrations of individual and Total THMs on-site eliminates reliance on complex empirical models or surrogates such a TOC and allows operators to base control decisions on real THMs measurements.

Unfortunately, the instrumentation and expertise required for monitoring individual and Total THMs is often perceived as being too expensive and technically demanding for on-site process control at WTPs. The USEPA methods for THMs (USEPA, 1999a, b, c) have low method detection limits (MDLs), good accuracy, precision and work well for compliance monitoring. However, none were designed for on-line and on-site process control. Most are complicated, expensive and all require a relatively high operator skill level. As such, most WTPs outsource compliance monitoring for THMs analysis to contract laboratories, but cannot use this data for process control strategies due to the turnaround times of 1-3 weeks for results.

In this chapter, an automated chemical analyzer capable of on-site, hourly monitoring of individual and Total THMs concentrations is reported. Specifically, the device is based on capillary membrane sampling-gas chromatography (Brown & Emmert, 2006; Emmert et al., 2007; Emmert & Brown, 2012), but offers significant improvements in performance and capabilities of the original device. The new instrument, called the THM-Rapid Response system (THM-RR), is subjected to rigorous MDL, accuracy and precision evaluations. Carryover issues from previous injections have been minimized relative to prior iterations of the device (Brown & Emmert, 2006; Emmert et al., 2007; Emmert & Brown, 2012). The device is packaged into a single portable unit that can be transported from place to place. Once calibrated, user intervention is essentially eliminated for weeks at a time. All data treatment and reporting is fully automated and is output in various file formats that are spreadsheet, database and SCADA compatible. Detailed MDL, accuracy, precision studies are reported. These concepts are extended to estimate detectable and quantifiable changes. The device is used in a WTP for monitoring individual and Total THMs concentrations and implementation of process optimizations strategies. Eventually, significant cost savings in water treatment chemicals were realized. Finally, additional aspects of device operation, ruggedness and robustness are examined.

Experimental

Chemicals and Reagents

All water used was deionized by a Barnstead E-pure four cartridge system (Thermo Scientific, Dubuque, IA, USA) to a resistivity of at least 18.2 MΩ cm. The

resulting reagent water does not contain any measurable organic or inorganic contaminants. All THM4 primary stock standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). Primary dilution standards were made from these stock standards by adding appropriate aliquots to 25.00 ml of methanol. Working standards were then made by diluting an appropriate volume of the primary dilution standard in reagent water using a 10-100 µL gastight syringe and 100.00 mL volumetric flasks.

Instrumentation

All THMs measurements were made using the THM-RR (Foundation Instruments, Collierville, TN, USA). The THM-RR (Figure 4) is an improved version of the capillary membrane sampling-gas chromatograph equipped with an nickel-63 (Ni-63) electron capture detector (ECD) and was demonstrated to agree with USEPA Method 502.2 to 0.1±0.1 µg L^{-1} for Total THMs (Brown & Emmert, 2006; Emmert et al., 2007).

The drinking water sample (the donor stream) flows through the capillary membrane sampling module and the THMs species pervaporate through the membrane from the donor stream into a stream of nitrogen (acceptor stream). The THM-RR is configured to sample for 15 minutes every hour with hourly sample analysis rates. The THMs are transported by the nitrogen to an automated sample injection valve held at 65° C and injected into the GC module of the device. During the chromatographic separation and in between sample analyses, a three-way solenoid valve (Model SV4102, Omega, Stamford, CT, USA) automatically allows the CMS device to be rinsed with reagent water to minimize carryover effects from previous samples (Brown & Emmert, 2006).

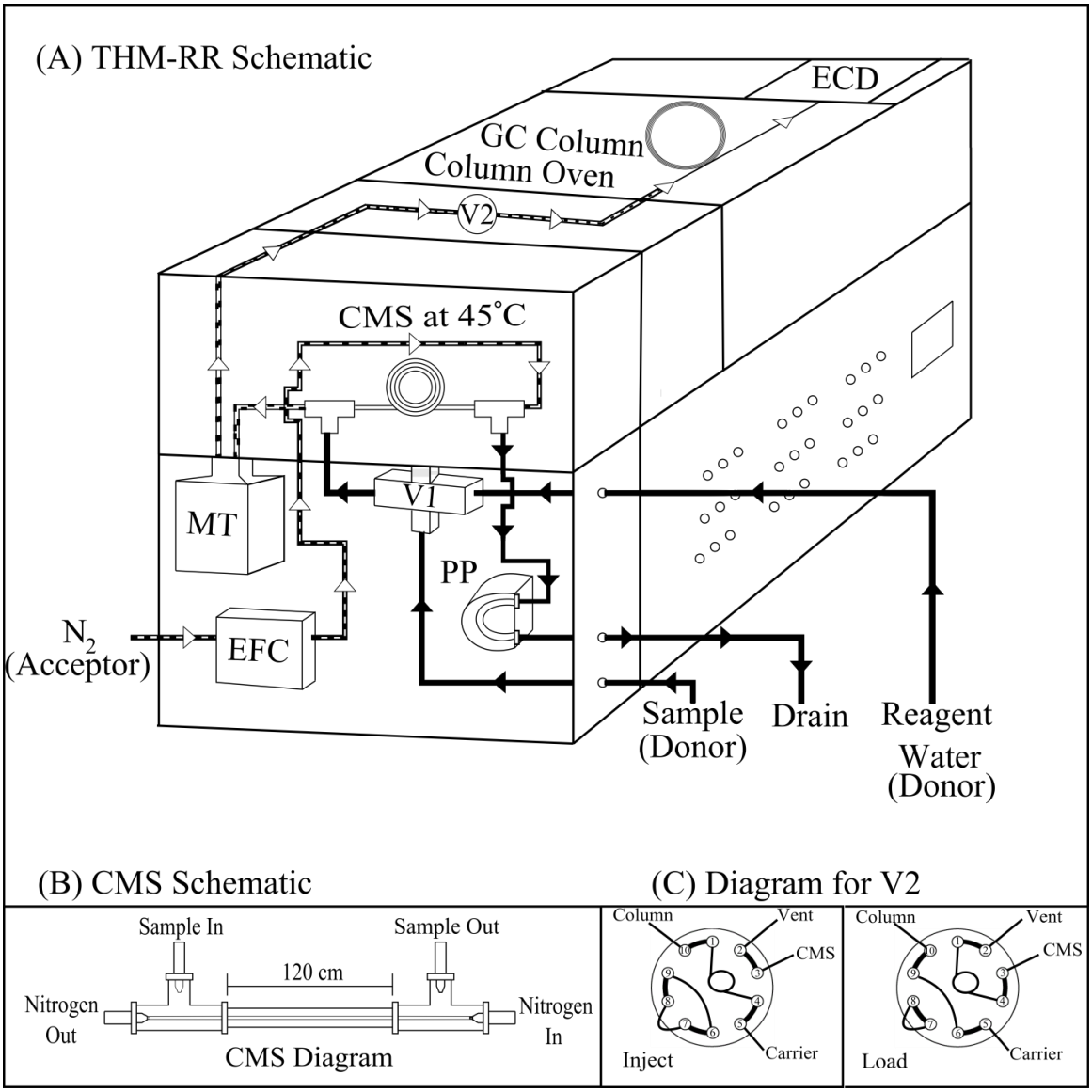


Figure 4. (A) THM-RR schematic showing analyte path from sample to detection: peristaltic pump (PP), 3 way solenoid valve (V1), moisture trap (MT), electronic flow controller (EFC), capillary membrane sampler (CMS), heated injection valve (V2), and electron capture detector (ECD). The solid flow lines represent donor stream flow (drinking water or reagent water), while the dashed lines represent the acceptor stream flow (nitrogen). (B) Detailed CMS schematic showing sample and gas flow. (C) Injection/load configuration for the 10-port heated injection valve (V2).

Chromatographic separation of the THMs species was accomplished using an MXT-502.2 (30 m x 0.52 mm i.d. x 3.00 µm film thickness) capillary column (Restek, Bellefonte, PA, USA). Nitrogen (typically zero grade/grade 5) was used as a carrier gas with a flow rate of 15.0 mL min^{-1}. The oven temperature was held at 40 °C for two minutes, increased at a rate of 15 °C min^{-1} to 150 °C where it was held at 150 °C for two minutes. The total chromatographic separation time was 11.3 minutes. The ECD was held constant at 250 °C and the ECD makeup gas was nitrogen at 40.0 mL min^{-1}.

The data treatment and reporting process for the THM-RR (Figure 5), once calibrated, is completely automated. The THM-RR is controlled using PeakSimple chromatography software (SRI instruments, Torrance, CA, USA) with customizable event files, which are provided with the device. The concentrations of individual THM species are calculated based on a calibration curve generated using external standards. The results from each sample analysis are calculated, stored, and can be output to multiple flatfile formats including Microsoft Excel and "comma separated values" text files that are readily imported into SCADA systems. During routine operation, the results are exported to Microsoft Excel where they are collected and displayed in real-time. The "dashboard" presents the individual and Total THMs concentrations from the last run in numeric format and also a continuously updated plot of the concentration of Total THMs as a function of time. Minimal user intervention is required.

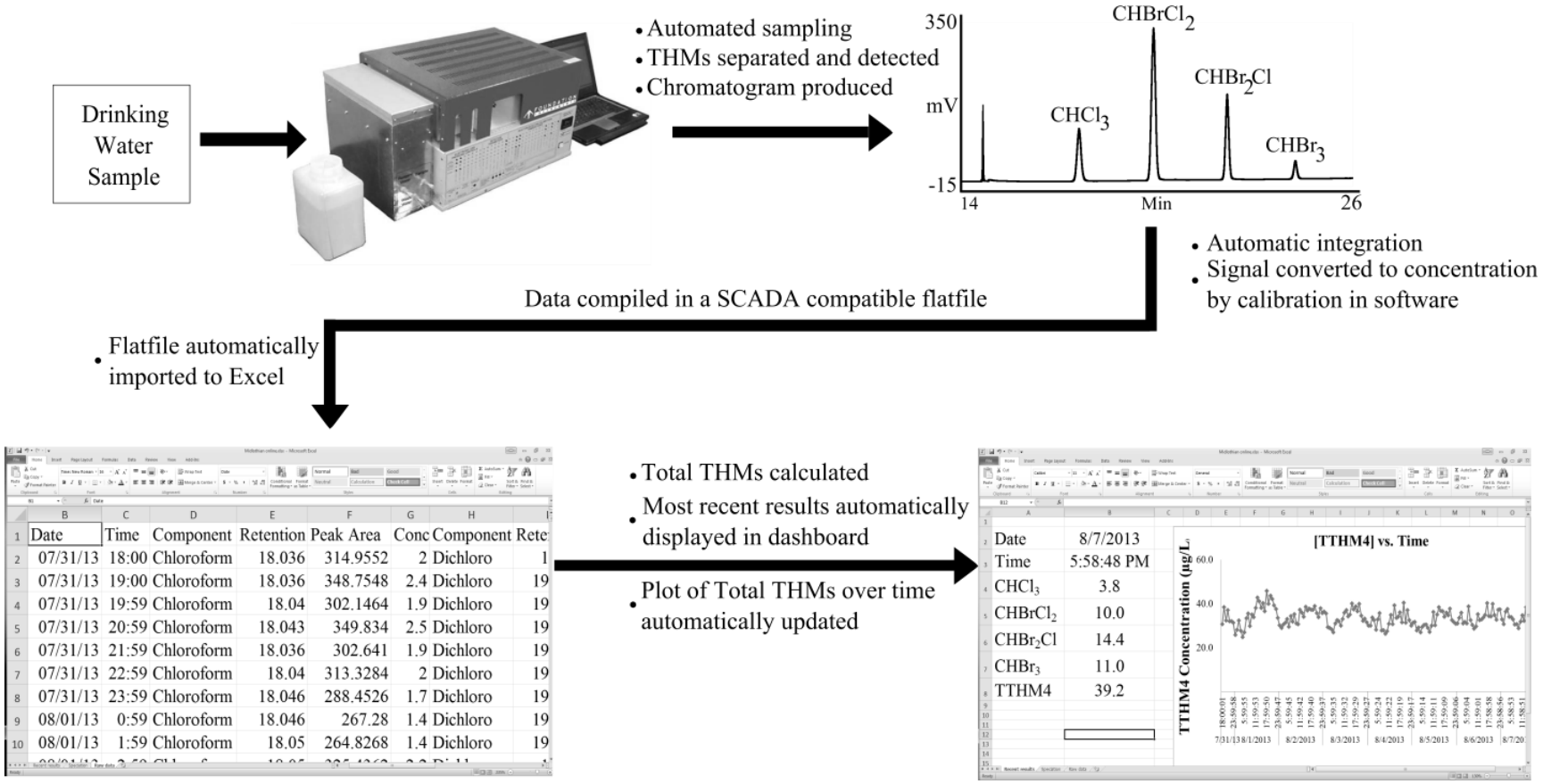


Figure 5. Overview of the Operation of the Automated THM-RR System. The drinking water sample enters into the THM-RR and is separated with each component being automatically quantified and summed to give Total THMs. The results are then logged and displayed on the dashboard of the controlling computer.

In practice, the THM-RR typically operates for up to three weeks on a single full sized cylinder of nitrogen (Airgas 300, Praxair type T, Nexair type 3). It can be connected to "house" nitrogen supplies or a nitrogen generator for continuous operation. At the time of submission, the THM-RR device used in this study has been in continuous operation for more than ten months with carrier gas resupply and two re-calibrations being the only necessary maintenance.

On-line THM-RR Setup

The THM-RR is designed to operate in one of two sampling configurations. It can be used in its "on-line" configuration to sample directly from the chosen sampling site continuously or it can be used in its "batch" configuration for the analysis of individual grab samples. Switching between the two configurations involves changing a single quick connect fitting. The THM-RR connects directly to most water taps using a sample loop comprised of a length of standard Tygon® tubing for the on-line sampling configuration. A length of PEEK tubing (1/16" (0.75 mm i.d.) is inserted directly through the wall of the Tygon® tubing to sample from this loop. A PEEK union connects a length of 1/16" PTFE tubing leading directly to the instrument.

Utility Description

The Lebanon, Tennessee WTP is a 12 million gallon per day (MGD) conventional facility located in Wilson County, Tennessee, USA. Water is drawn from the adjacent Cumberland River and powdered activated carbon (PAC), specifically Norit Hydrodarco O, is added to control taste and odor and reduce DBPs precursors. The water then enters a mixing tank where a polyaluminum chloride coagulant is added before transferring to flocculation chambers. The water is passed through tube settlers before being filtered

through dual media gravity filters. A small amount of chlorine is added on top of the filters to control bacteriological growth in the filter media. The filtered water is then disinfected with gaseous chlorine and blended phosphates are added as a corrosion inhibitor. After meeting required contact time, the finished drinking water is pumped to sanitized reservoirs, water storage tanks, and to the customer's tap. The utility maintains an active laboratory where common drinking water parameters are measured and logged with each shift including: water temperature, residual chlorine, alkalinity, hardness, manganese, iron, phosphate, turbidity, pH, fluoride, coliform, dissolved oxygen, total dissolved solids, and total organic carbon.

Study Details

The data presented in this study was measured over the time period April 2013 through January 2014. The individual THM concentrations were measured in the finished drinking water using the THM-RR and these results summed to provide Total THMs. Measurements were taken once an hour except for instances in which minor instrument maintenance was being performed, such as check standard analysis, calibration, or changing of the gas cylinder. The THM-RR was set up in the on-line configuration in a laboratory within the treatment plant sampling from the same point source used to make finished drinking water measurements for all other "in plant" water quality parameters. This site is the point of entry into the distribution system.

Results and Discussion

Method detection limit, accuracy, precision, detectable and quantifiable changes

Detailed MDL, accuracy and precision studies were performed for each THM4 species. The MDL for Total THMs was calculated by taking the square root of the sum of the squared MDL values for the individual THMs species. The THM-RR was calibrated using five standards ranging in concentration from 0.1-50 µg L^{-1} of each THM4 species. A separate check standard solution (0.3 µg L^{-1} of each THM4 species) was analyzed seven consecutive times. This check standard was not used in fitting the calibration curve. The results of these check standard analyses were used to determine MDL, accuracy and precision values (Table 2).

Table 2. Detailed MDL, accuracy, and precision studies for the THM-RR.

THM4 species	Abs. Error (µg L^{-1})	Rel. Error (%)	MDL (µg L^{-1})				Mean % Rec.	% R.S.D.
			EPA	Trad	Error Prop.	JackKnife		
$CHCl_3$	0.04	15	0.02	0.02	0.1	0.04	85.0	2.2
$CHBrCl_2$	0.05	19	0.01	0.01	0.2	0.03	80.7	1.6
$CHBr_2Cl$	0.06	23	0.01	0.01	0.3	0.02	77.1	1.2
$CHBr_3$	0.04	14	0.04	0.04	0.1	0.08	86.5	4.6
Total THMs	---	---	0.05	0.05	0.39	0.10	---	---

The MDL was measured using four different methods: the EPA MDL (Federal Register, 1986; Glaser et al., 1981, USEPA 1996a, b), the traditional MDL (Skoog et al., 1998), error propagation MDL (Harris, 1997), and jackknife resampling MDL (Efron, 1982). The EPA MDL (Federal Register, 1986; Glaser et al., 1981) is calculated by multiplying the standard deviation of the experimental concentrations of the check standards by the associated t-value at a 98% confidence level. The EPA MDL values

ranged from 0.01 to 0.04 μg L^{-1} and represent the statistical estimate of the lowest detectable concentration using the THM-RR. The traditional MDL (Skoog et al., 1998) is determined by multiplying the standard deviation of the peak-to-peak noise by a factor of three. The traditional MDL values also ranged from 0.01 to 0.04 μg L^{-1}. Error propagation methods (Harris, 1997) were used to estimate the uncertainty associated with calculated THMs concentrations for the check standard analysis. For the error propagation MDL, this uncertainty represents the smallest concentration that could be confidently measured. The error propagation MDL values ranged from 0.1-0.3 μg L^{-1}.

Quadratic calibration curves require seven mathematical operations to calculate concentration compared to two mathematical operations using a linear model. With linear models, the error propagation MDL agrees with other MDL methods, but when quadratic models are considered, dependent error propagation estimates becomes inflated compared to the linear MDL methods due to the additional mathematical operations used to calculate the concentration. To compensate, a jackknife resampling (Efron, 1982) method was used instead of dependent error propagation. This approach provides a more reliable estimate of the uncertainty with quadratic models. The jackknife approach is favored over more common bootstrapping techniques because the jackknife approach gives superior empirical variance estimation (Shao & Tu, 1995). The jackknife resampling estimates ranged from 0.02 to 0.08 μg L^{-1}, which is in good agreement with the EPA and traditional MDL estimates. As reported earlier (Brown & Emmert, 2006), the error propagation approach exhibits MDL estimates that are an order of magnitude larger than the other methods and is not recommended for estimating MDL values when quadratic calibration curves are used. However, the MDL values reported here are

improved by essentially an order of magnitude lower (better) than those reported earlier (Brown & Emmert, 2006).

The mean % recovery on the check standard was used to estimate the accuracy. These values ranged from 77.1 to 86.5%. Absolute error and relative error ranged from 0.04 to 0.06 µg L^{-1} and 14 to 23%, respectively, operating within a factor of ten of the MDL estimates (check standard 0.1 µg L^{-1}, MDL is 0.01 µg L^{-1}). The percent relative standard deviation (% R.S.D.) of the check standard concentration values ranged from 1.2 to 4.6% and was used as the estimate of precision. The dynamic range for the THM-RR for this study was 0.1 to 50 µg L^{-1} with correlation coefficients of greater than 0.999 for all THMs species.

The THM-RR was designed to observe the changes in THMs concentrations that occur (or do not occur) over time and on-site at a water treatment plant. It is envisioned as a "THMs meter" for water treatment operators to observe on the fly during operation. To borrow a phrase from one operator, it is important to know how sensitive the "needle" (or the number being viewed on the display) on the "meter" is to change. Extending this concept, in order for a change (positive or negative) to be considered detectable, that change must be greater than the MDL of the instrument. Similarly, a quantifiable change is based upon the limit of quantitation (LOQ) and is generally considered to be ten times the standard deviation of the noise (Christian et al., 2014; Harris, 1997), or put another way, 3.182 times the EPA MDL of the instrument. Thus, any change greater than the MDL for Total THMs of 0.05 µg L^{-1} would be a detectable change and any concentration change greater than the LOQ of 0.14 µg L^{-1} would be considered quantifiable change.

Throughout the course of the on-line monitoring program, there were 5239 measurements of individual and Total THMs concentrations and thus 5238 instances of change between a given measurement and the next measurement in sequence. Of these changes, 4975 (or 95.0%), were greater than or equal to 0.05 µg L^{-1} and therefore classified as detectable changes while 4533 (or 86.5%) of the measurements were greater than or equal to 0.14 µg L^{-1}, making them quantifiable changes. Of the 5239 measurements taken, 102 (<2%) resulted in an apparent non-THM measurement (failed analysis). For example, an air bubble caught in the CMS device or condensed water vapor in the gas lines might cause a failed analysis; however, out of the total number of measurements, there were only two instances where more than two consecutive analyses were failures and the majority of instances appeared to correct themselves before the next sample injection.

Using the THM-RR for Process Mapping and Optimization

A THMs monitoring program was started at the Lebanon WTP in April 2013 and continues at the time of submission. The data presented here was collected over the time period April 19, 2013 to January 31, 2014. During this period, the hourly THMs measurements provided practically real-time information about individual and Total THMs concentrations. No other study has demonstrated hourly resolved THMs monitoring for such an extended period of time. Prior to this ten month study, the longest reported hourly monitoring studies were carried out for approximately 10 days (Brown & Emmert, 2006; Emmert et al., 2007).

Over the first week of the study, a procedure called process mapping was employed. During this time, no changes were made to the physical and chemical

treatment processes at the WTP. The goal of process mapping is to establish a baseline for Total THM concentrations and identify any patterns or cycles that may occur during normal treatment operations. Process mapping serves an important role in the THMs control process because it allows operators to distinguish between a change that occurs from a specific alteration in the treatment process and one that might arise due to routine operation. For example, with all treatment operations essentially constant, the on-line individual and Total THMs monitoring data showed daily short-term decreases in THMs concentrations that occurred each weekday and coincided with dredging of settling basin tanks. With a process map in place, such variation can be taken into account. It was possible to evaluate the effects of changes (such a PAC dosage) on THMs production, without confusing normal short-term variability for the results of changing the PAC dose. Knowing how the THM concentrations vary during normal treatment allows for appropriate and reproducible sampling and a better understanding of the true effects of process changes.

The Lebanon WTP uses powdered activated carbon (PAC) for control of TOC, tastes and odor and THMs. During the first week (Days 1 – 7, Figure 6), the PAC dosage was held at 10 mg L^{-1}, TOC concentrations averaged 1.25 mg L^{-1}, and the average Total THMs concentration were 13.2 µg L^{-1}. At the end of the process mapping phase, PAC dose was increased to 15 mg $L^{-1}$and held for the second week (Days 8 – 15, Figure 6). During this time, the TOC concentrations decreased to 1.09 mg L^{-1}, while Total THMs concentrations averaged of 18.7 µg L^{-1}. During the third week (Days 16 − 21, Figure 6), PAC dose was increased to 20 mg L^{-1}, and the average TOC concentration decreased to 0.825 mg L^{-1}, but Total THMs concentrations increased further, averaging 22.1 µg L^{-1}.

These results show that TOC is not always an accurate surrogate for THMs formation and that TOC removal does not necessarily translate to THMs reduction.

From an economic standpoint, a WTP operator may not need to spend money removing TOC that does not become THMs. While increasing PAC certainly removes TOC species, it may not be targeting the specific chemical species that have the greatest potential to form THMs. By optimizing the PAC dose based on the final product, THMs, instead of TOC, WTP operators can significantly reduce the PAC dose and save money. For the Lebanon WTP, a comparison PAC usage for five month periods in 2013 and 2012 indicated that 15,300 lbs. (6954.5 kg) less PAC was consumed in 2013 (after initiation of the on-line THMs monitoring program) relative to the same period in 2012. At a PAC cost of $0.944/lbs., the savings is $14,443 USD.

With PAC dosage satisfactory at 10 mg L^{-1}, the chlorine dose used to minimize bacterial growth on top of filters was decreased resulting in a marked drop in Total THMs from 26.4 µg L^{-1} to 13.9 µg L^{-1}. The concentration of this chlorine dose was chosen as the minimal chlorine dose high enough to prevent observable bacterial growth on the filters. Once this chlorine dose was minimized, Total THM concentrations were maintained well below 20 µg L^{-1} at the point of entry into the distribution system for several weeks.

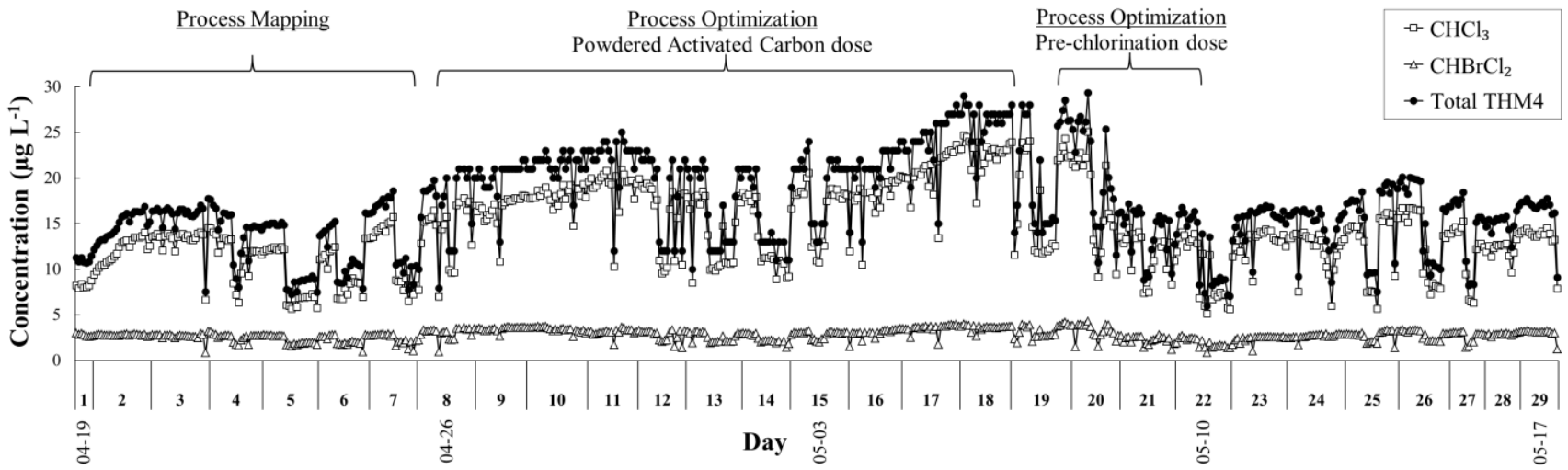


Figure 6. Establishing the Automated On-Line THMs Monitoring Program at the Lebanon, TN WTP. The THM-RR is used for process mapping, followed by process optimization of PAC dose, and process optimization of pre-chlorination dose. Data collected over time period April 19, 2013 through May 17, 2013.

Observations on Long-Term Monitoring of Individual and Total THMs Concentrations

Figure 7 plots the Total THMs concentration data from the beginning (April 19, 2013) until January 31, 2014. The plot has notations indicating rainfall events (RE) as well as other documented events such as operational errors, extreme temperature changes and one seasonal river turnover event.

Rainfall events result in a short term increase in Total THMs concentrations. Runoff from the rainfall washes organic matter into the river and this is typically followed by a peak THMs event. Just as examples, consider that there is a sharp increase in Total THMs on April 29th that was proceeded by 3.96 inches of rainfall on April 27th. A similar situation is observed on May 23rd after 1.22 inches of rain on the 21st. After two days of rain on June 8th and 9th, adding up to 1.71 inches, there was an increase in THMs seen on June 12th.

In addition to rainfall events, temperature changes can potentially affect Total THMs concentrations. Temperature changes that occur seasonally result in water inversion in the Cumberland River. The turnover event occurred this past year during late September through early October and is accompanied by a corresponding increase in organic matter in the source water. During this time, a broad increase in Total THMs occurred. In going forward from September to October, there was a corresponding decrease in the average water temperature of approximately 5.6°C. An abrupt decrease of 17.8 °C occurred on 12/6-12/7 along with four consecutive days of rain totaling 4.3 inches. This was followed by a sharp 10.6°C increase in temperature on 12/16-12/17.

Operator errors are also documented on the plot. A sharp increase just prior to 8/30/2013 labelled OE1 resulted from an error that caused a gas leak. The instrument was

shut down, the leak repaired and the instrument recalibrated and brought back on line. Similarly, event OE2 resulted from an operator error during a carrier gas tank exchange. Cylinder change procedures have been implemented to minimize such issues going forward.

Detailed analysis of how various environmental and water quality parameters affect Total THMs formation is beyond the scope of this research. However, the THM-RR clearly provides unprecedented highly time resolved on-line monitoring data that aids in THMs process control.

Instrument Maintenance, Ruggedness and Robustness

In terms of instrument maintenance, the THM-RR does not pose a large time or capital commitment. The instrument at the Lebanon WTP has been operating for over ten months at the time of submission and with the exception of changing the tank of nitrogen carrier gas approximately every three and a half weeks and one change of desiccant in the moisture trap, there have been no major maintenance tasks needed. In particular, the peristaltic pump tubing typically operates for more than 10 months with satisfactory performance. The CMS device is functioning satisfactorily. The capillary GC column has exhibited good stability. Over the course of the study thus far, the retention factor (k) for $CHCl_3$ averaged 3.39 ± 0.02, ranged from 3.34 to 3.77 with a % R.S.D. of 0.6%. For $CHBrCl_2$, k averaged 5.55 ± 0.04, ranged from 5.47 to 5.90 with a % R.S.D. of 0.7%. The average peak asymmetry at 10% for $CHCl_3$ averaged 0.93 ± 0.03, ranging from 0.85 to 1.0 with a % R.S.D. of 3.1%. The average peak asymmetry at 10% for $CHBrCl_2$ averaged 0.94 ± 0.04, ranging from 0.90 to 1.0 with a % R.S.D. of 3.8%.

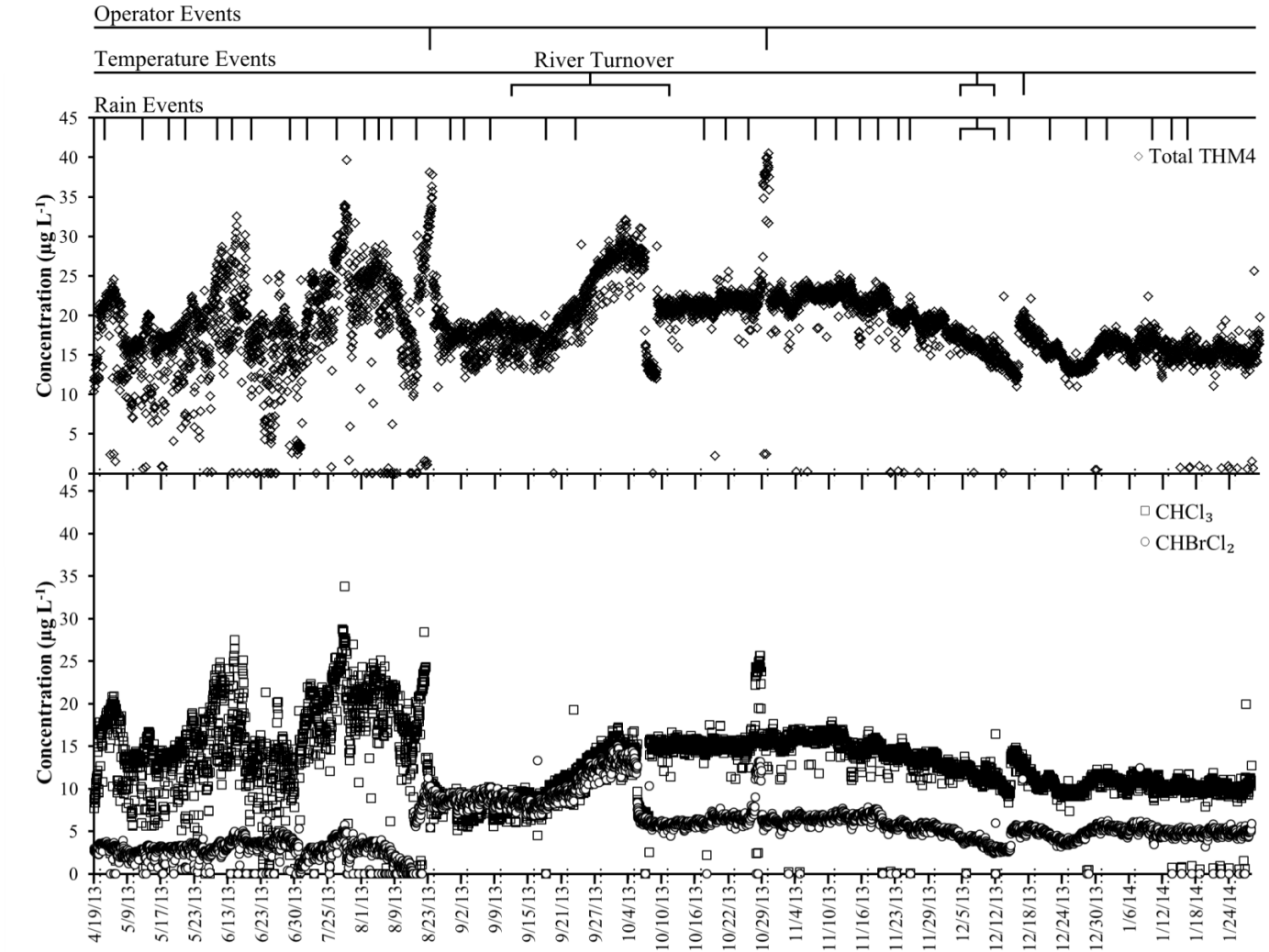


Figure 7. Plot showing Total THM concentration versus Time (Top) and individual THMs species versus Time (Bottom) for the Lebanon WTP study to date. Rainfall events, Temperature events and operator errors are indicated as well.

A controlled study evaluating the performance for a single $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$ and Total THMs calibration set over the period of one month exhibited average differences between the experimental concentration of the standard and the theoretical concentration of the standard of 1.4 ± 4.2 µg L^{-1}, 3.9 ± 5.2 µg L^{-1}, 3.1 ± 5.0 µg L^{-1}, 3.7 ± 5.0 µg L^{-1} and 12.1 ± 19.2 µg L^{-1} respectively. Mean % recoveries averaged 105 ± 17%, 115 ± 21%, 113 ± 20%, 115 ± 20% and 112 ± 19% for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$ and Total THMs, respectively. The % R.S.D. estimates over the same time period for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$ and Total THMs was 16.1%, 17.8%, 17.8%, 17.6% and 17.1%, in the same order. For quantitative results, more frequent calibrations would improve data quality, but for purposes of process control these results are acceptable.

Over the past year, duplicate THM-RR instruments have been used to make measurements at six different water utilities in Arkansas, Texas and Tennessee. Nitrogen from several different vendors and of various grades has been used as the carrier gas. Different sources of deionized and/or distilled water have been employed as reagent water. Two different analysts carried out the studies. The THM-RR response to THM species has not shown significant variability. Three different calibration curves were developed by two different analysts. One was done in the "home" laboratory in Memphis, TN and two others were done at separate water treatment plants in Texas and Tennessee. A single set of check standard data comprised of seven consecutive measurements was used along with the three different calibration curve datasets to evaluate performance across the different calibration curves. The check standard was a 4.0 µg L^{-1} Total THM4. For Total THMs, the Memphis calibration gave 3.3 ± 0.1 µg L^{-1} with a %R. S. D. of

3.4%. The Texas calibration gave 6.3 ± 0.2 µg L^{-1} with a % R.S.D. of 4.0%. The Tennessee site gave 5.6 ± 0.2 µg L^{-1} with a % R.S.D. of 3.4%. To evaluate how the accuracy would vary over the three different curves, the average difference was calculated as the experimentally determined concentration minus the theoretical concentration of total THMs. The same check standard dataset was used for all comparisons. For the Memphis, Texas and Tennessee curves, the difference between the experimental and theoretical measurements was -0.7 µg L^{-1}, 2.3 µg L^{-1}, and 1.6 µg L^{-1}, respectively.

Conclusions

The commercially available THM-RR system is presented that is uses capillary membrane sampling-gas chromatography and demonstrates unprecedented performance for on-site and on-line automated THMs monitoring of drinking water. The rugged and robust THM-RR exhibits superior MDLs for individual and Total THMs values over earlier versions. The THM-RR is designed to be operated and maintained by typical water treatment operators. The THM-RR automates sampling, sample analysis, data treatment and reporting. The THM-RR automatically produces plots of the individual and total concentrations of THMs species with data updated hourly. This greatly simplifies use of the device and making it essentially a sensitive "THMs meter" that operates in essentially real-time at a WTP. The plot of THMs can then be superimposed upon the daily operations of the plant so that reproducible patterns emerge in the baseline behavior of individual and Total THMs at the point of measurement (typically near the point of entry to the distribution system). With such a device, WTP operators can learn

the unique cycles and patterns in their plant (the “process map”) and respond in real time to peak THMs formations events as they arise, if necessary. Ultimately, the THM-RR has provided insight on THMs production for the operator, who has been able to bring the WTP into control with respect to THMs and delivers more consistent water to the customers.

CHAPTER 3
MEASURING THE AGREEMENT BETWEEN TRIHALOMETHANES CONCENTRATIONS IN DRINKING WATER PREDICTED BY EMPIRICAL MODELS AND ON-SITE AUTOMATED MEASUREMENTS

Introduction

With the implementation of Stage 2 of the Disinfectant/Disinfection By-Product Rule in the United States (USEPA, 2006), many water treatment plants (WTPs) are paying closer attention to the concentrations of disinfection by-products (DBPs) in their finished drinking water. The most common class of regulated DBPs is the trihalomethanes (THMs). The four regulated trihalomethanes include chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). The United States Environmental Protection Agency (USEPA) has established a maximum contaminant level (MCL) of 0.080 mg L^{-1} for the total concentration of these four THMs species (Total THMs) (USEPA, 1998).

THMs formation involves the degradation of humic acids through reaction with hypochlorous acid (Rook, 1977). Peters et al (Peters et al., 1980) showed that not only is there the possibility for more than one mechanism of formation, but both the rate and formation pathway are dependent upon several factors. Further research by Boyce and Hornig (Boyce & Hornig, 1983) demonstrated that most dihydroxyaromatic model compounds are efficient THMs precursors; however, certain substrates are less reactive than others. In fact, the size and composition of natural organic matter (NOM) (Chang et al., 2006; Gang et al., 2002; Zhao et al., 2006) affects the concentration and rate of THMs formation. Changes in NOM composition have marked effects on the formation of DBPs

(Nguyen et al., 2013). Large variability in NOM, especially in surface water sources, through the watershed supplying the raw water can occur. Between biological activity, meteorological changes and patterns, and runoff from the surrounding area, the type and quantity of precursors can vary dramatically.

Precursors are not the only factors capable of influencing THMs formation. Other raw water parameters, such as specific ultraviolet absorbance (SUVA), pH, chlorine demand, and ammonia (NH_3) concentration (Abdullah et al., 2009) have been shown to have significant impact on THMs concentrations. Additionally, the presence of bromide ion and its subsequent formation of aqueous bromine species can increase the rate of formation for DBPs (Westerhoff et al., 2004).

Each WTP presents a unique set of conditions, not only because of the differences in source water but also because of the different treatment practices that are adopted. While many WTPs use similar methods, there are many variables that can cause dramatic differences between plants. A lot of effort has been aimed at understanding the variability that arises in DBP formation. Studies have shown seasonal variations (Liu et al., 2011; Toroz & Uyak, 2005), which are perhaps the most easily explained and predicted. Similarly, temperature is a major factor in the rate of any reaction, and differences in temperature between seasons vary greatly between geographical locations. Other meteorological factors such as rainfall may have a significant effect. Many areas experience variability in precipitation throughout a typical year. Along with this, several states in the American Southwest are currently experiencing severe drought. WTPs using surface water sources are particularly susceptible to these changes. Both rivers and lakes may experience turnover events between seasons and such events can affect organic

matter composition in source water. Many of these variations occur not only on a seasonal level but also on much shorter time frames. Variability has been shown on the yearly (Parvez et al., 2011), monthly (Villanueva et al., 2007), daily (Chaib & Moschandreas, 2008), and even hourly (Brown & Emmert, 2006; Brown et al., 2007; Brown et al., 2014; Emmert et al., 2007; Pereira et al., 2004) Not only do these occur in the distribution itself, but also at the point of entry into the distribution system (Pereira et al., 2004)

Due to the number of factors involved in the formation of THMs, it is difficult to isolate one determinant factor. A variety of models have been developed to predict the formation of THMs. Classical chemical kinetics has been explored (Gallard & von Gunten, 2002), while others have used chemometrics to identify which factors have the greatest impact (Platikanov et al., 2007). A common approach is to relate either the chlorine demand (Courtis et al., 2009) or the chlorine decay (Brown et al., 2011) to the formation of THMs. Finally, empirical models (Amy et al., 1998; Rodriguez et al., 2000; Serodes et al., 2003; Uyak et al., 2005) have been developed that use a variety of raw and treated water parameters in order to predict the formation of THMs.

Until recently, it has been difficult and expensive to subject these empirical models to testing and evaluation. A new commercially available instrument (Brown et al., 2014) has been developed that allows for automated hourly monitoring of individual and total THMs in drinking water. This device, called the THM-Rapid Response system (THM-RR) operates on-site for fully automated on-line measurements. These hourly measurements provide unparalleled data showing the behavior of individual and total THMs concentrations over time. Rigorous method detection limit, accuracy and

precision studies were reported for the device. Additionally, the device was used to maintain drinking water quality with respect to THMs concentrations while significantly reducing costs associated with the use of treatment chemicals. Finally, the ruggedness and robustness of the device was considered. The approximately ten month dataset was subjected to very preliminary scrutiny to ascertain potential environmental trends.

In this chapter, four different empirical models were chosen from the literature (Amy et al., 1998; Rodriguez et al., 2000; Serodes et al., 2003; Uyak et al., 2005) to be evaluated with respect to the degree of their agreement with the measured Total THMs concentrations using the THM-RR system. The models were chosen based on their ability to be applied using the normal water quality data collected by each WTP participating in the study. The point of the research effort is not to "test" the empirical models proposed by previous researchers, but to see if it is possible to use the THM-RR system to "fine tune" the empirical models to agree with newly available on-line concentration data in a given system. These models should not be expected to provide acceptable results when taken out of the context of their original development.

Specifically, the focus was to compare the Total THMs concentration data to the Total THMs concentrations predicted by each of the four empirical models in three different water treatment plants, one each in Tennessee (TN), Texas (TX) and Arkansas (AR) in the United States. The degree of agreement between the THM-RR Total THMs results and those from the empirical models is quantified as the bias calculated using Bland-Altman analysis (Bland and Altman, 1983, 1986, 1987). Once the base-line agreement is measured using the original model parameters, the data is subjected to two methods to minimize the bias between the THM-RR Total THM concentration data and

each empirical model. Ultimately, the best potential empirical model for each system is proposed as well as a discussion of the most "generic" empirical model that could be generally applied broadly.

Experimental

Chemicals and Reagents

All water used was deionized by a Barnstead E-pure four cartridge system (Thermo Scientific, Dubuque, IA, USA) to a resistivity of at least 18.2 MΩ cm. The resulting reagent water does not contain any measurable organic or inorganic contaminants. All THMs primary stock standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). Primary dilution standards were made from these stock standards by adding certain aliquots to 25 ml of methanol in a volumetric flask. Working standards were then made by diluting an appropriate volume of the primary dilution standard in 100 mL of reagent water using a gastight syringe and volumetric flask.

Instrumentation

All THM measurements were made using the THM rapid response instrument (THM-RR, Foundation Instruments, Collierville, TN). The THM-RR is described in detail in (Brown et al., 2014) and is capable of measuring both individual and Total THMs every hour. It is fully automated from sampling to data processing. Previous studies have shown that the THM-RR has method detection limits (MDL) of 0.01 to 0.04 µg L^{-1} for individual THMs species and 0.05 µg L^{-1} for Total THMs. The THM-RR is capable of detecting changes in Total THMs concentration of 0.05 µg L^{-1} and quantifying changes equal to or greater than 0.14 µg L^{-1} (Brown et al., 2014). Over the course of a 10

month study, the THM-RR has demonstrated that it is a reliable device that requires minimal maintenance. The percent relative standard deviation for the retention factor over this study was less than 1.0 %, while the average peak asymmetry at 10% was above 0.90. Using data from several calibrations done by different operators at different sites, it was also shown that there was little difference in the calibration data (Brown et al., 2014).

On-line Setup

For on-line sampling, a sample loop is made by attaching a length of Tygon® directly to a water tap. The tubing is arranged into a loop to help prevent siphoning effects. To sample from the loop, a length of 1/16" PEEK tubing is inserted directly through the side of the Tygon®. With the use of a PEEK union, this is connected to a length of 1/16" PTFE tubing which leads directly to the instrument. The THM-RR is setup to automatically sample for 15 minutes every hour. Whenever it is not sampling from the loop, the THM-RR will pull from a reagent water reservoir to rinse the membrane.

Empirical Models for Predicting Total THMs Concentrations

Water quality data was obtained from each sampling site. This data was used to calculate predicted Total THM values using previously published THM formation models. Four separate models were tested (Amy et al., 1998; Rodriguez et al., 2000; Serodes et al., 2003; Uyak et al., 2005). The equations associated with each model are summarized in Table 3.

Table 3. Equations used for Total THMs model predictions: Total Organic Carbon (TOC); chlorine dose (D); bromide ion concentration (Br^-); temperature (T); contact time (t); and pH.

Model	Equation
Amy (Amy et al., 1998)	$THMs = 0.0412(TOC^*)^{1.10}(D)^{0.152}(Br^-)^{0.068}(T)^{0.61}(pH)^{1.60}(t)^{0.260}$
Rodriguez (Rodriguez et al., 2000)	$THMs = 0.044(TOC^*)^{1.030}(t)^{0.262}(pH)^{1.149}(D)^{0.277}(T)^{0.968}$
Serodes (Serodes et al.,2003)	$THMs = 16.9 + 16.0(TOC) + 3.319(D) - 1.135(T) + 1.139(t)$
Uyak (Uyak et al., 2005)	$THMs = 0.0707(TOC + 3.2)^{1.314}(pH - 4.0)^{1.496}(D - 2.5)^{-0.197}(T + 10)^{0.724}$

* TOC was used in place of DOC because of the available water quality data.

The model by Amy et al. (Amy et al., 1998) was developed using a range of natural waters from both surface and ground sources. It was designed to be a predictive model for Total THMs formation from chlorinated non-coagulated water. It uses a combination of raw water parameters, as well as several treatment parameters. As applied here, total organic carbon (TOC) measurements were used instead of dissolved organic carbon (DOC) measurements. In addition, the bromide term was not used either because none of the water treatment plants monitored this parameter.

The model developed by Rodriguez et al. (Rodriguez et al., 2000) combined data from several previous studies into one database. This was used in conjunction with field-scale data from small water utilities in order to validate the model. Like the Amy model, the Rodriguez model uses a combination of raw water parameters and treatment parameters to predict Total THMs concentrations. As with the Amy et al. model, TOC measurements were used instead of DOC measurements.

The model by Serodes et al. (Serodes et al., 2003) was developed using treated water collected before final chlorination from three treatment plants. Bench-scale chlorination experiments were done in order to develop regression models for the prediction of THMs. One of the advantages of this model is that it was developed using water collected over a 6 month period in an attempt to take into account seasonal variations in water quality. The Serodes model does not use pH as a factor in determining THMs formation. An interesting factor in this model is that the water temperature term is negative. This means that increases in water temperature will result in a decrease in predicted Total THMs, which is the opposite of what one would expect to occur. The Serodes model is the only model that is based on a linear fit.

Uyak et al. (Uyak et al., 2005) developed a multiple regression model for predicting THMs using raw water obtained from two sources in Istanbul. Sampling was done over a 12 month period in order to account for changes in water quality and treatment processes. This model was designed to be used with the chlorination of raw water. It does not contain a contact time term. It was originally meant to predict the THMs in finished water at a single treatment plant.

To calculate the predicted Total THMs concentration for each model the water quality data from each plant is inserted directly into the original model. The model was adjusted using a spreadsheet by identifying spots during the study in which the bias between the two methods was the greatest. By looking at changes in the water quality data at these points, it was possible to identify changes in a particular parameter that caused the increase in bias. The exponent for that parameter was then altered and the bias recalculated to see if it was reduced. The TOC and pH terms were found to be the most

effective in reducing the average bias. While altering of other terms may have helped in specific instances within a study, it often caused other portions to become worse. This resulted in either a similar or even greater bias over the entire study.

Multivariate nonlinear regression (MVNL) was done by first creating a user defined function in SigmaPlot 12.5 using the Amy model as a starting point. The function was:

$$f = u(a^v)(b^w)(c^x)(d^y)(e^z) \quad (1)$$

where *a*=TOC, *b*=pH, *c*=chlorine dose, *d*=water temperature and *e*= contact time. The THM-RR values were used as the dependent variable, *f*. A nonlinear dynamic fit was initially used with all of the parameters as unknowns. The range for the parameter "*u*" was modified so that it was greater than 0. Each parameter was individually changed while the others were held constant. The initial parameters used were the numbers from the Amy model. Once a parameter had been optimized, it was held constant with the new calculated value, and optimization of the other variables was performed in the same fashion.

Measuring Agreement between Measurements and Empirical Models

It is common practice to compare two analytical methods by plotting the results of each method against each other to assess correlation between the two methods. However, this practice of using the correlation coefficient (r) to compare two methods has been strongly criticized (Bland & Altman, 1983, 1986, 1987) for multiple reasons. The important question pertains as to whether or not the empirical predictions agree with the THM-RR experimental measurements and if they do not, can they be adjusted to exhibit better agreement.

While there are multiple ways to evaluate agreement, Bland and Altman (1983, 1986, 1987) proposed a straightforward graphical procedure designed for non-statisticians to estimate agreement between two methods. They suggest that to evaluate method agreement, instead of correlation, it is best to consider a plot of the difference between two methods plotted as a function of averaged result of the two methods. Since bias is defined as the experimental result minus the "true value" (Skoog et al., 1998). This difference (the bias) can be further defined by using the convention in this chapter that the Total THMs concentration from the THM-RR system is the "true value" while the Total THMs concentration predicted by each empirical model is considered the experimental value. Thus, Bland-Altman (BA) analysis allows for estimation of the bias between two the THM-RR result and the empirical model and also the error associated with that bias.

The experimental design was as follows: Total THMs measurements were made using the THM-RR for extended times at three different WTPs (one each in TN, TX and AR). The Total THMs concentrations measured using the THM-RR system were compared to the Total THMs concentrations generated using the four aforementioned empirical models. In each case, the bias was measured from BA plots using each model as is with original fitted parameters reported in the literature. This was followed by calculating an adjusted model based upon a spreadsheet that minimized bias as selected parameters in the model were changed. Finally, optimized fits using multivariable non-linear fitting are presented and the differences in the two approaches are compared in practical terms of ease of use and error.

Results and Discussion

For each WTP studied, the THM-RR system was used to monitor individual and total THMs concentrations on-site and on-line over time at the point of entry into the distribution system. The measured Total THMs concentration data (THM-RR data) was then compared to the concentrations predicted by the aforementioned empirical models using water quality data obtained directly from the WTP. The TN WTP study lasted for 10 months and both the AR and TX WTP studies lasted for 1 month. The number of values for each site was dependent upon how often a certain measurement was taken. In most cases this was limited by TOC which is usually only measured once a day.

TN WTP Study

The TN WTP is a 12 million gallon a day (MGD) plant located in Lebanon, TN. It draws its source water from the Cumberland River. Powdered activated carbon (PAC) is used to treat taste and odor problems and to reduce DBP precursors. Polyaluminum chloride is used as a coagulant for flocculation. After settling and passing through tube settlers, the water is filtered using dual media gravity filters. A small pre-chlorination dose is added before the filters to prevent bacteriological growth in the filter media. Primary disinfection is then performed using gaseous chlorine, followed by the addition of blended phosphates to prevent corrosion. After the required contact time, the water enters the distribution system.

Consider the Bland-Altman (BA) plots (Figure 8) comparing the THM-RR and the empirical models (Figure 9) which highlight aspects of agreement. The data for all plots show varying degree of bias that increases with average Total THMs concentration. The Amy model exhibits a bias without adjustment of 0.7 ± 6.1 μg L^{-1} with a 95%

confidence interval (95% CI) of -0.2 to 1.6 µg L^{-1}, while the other three models exhibit large positive bias estimates and over-predict Total THMs concentrations when applied at the TN WTP. A horizontal trendline in the BA plots would indicate a realatively consistent bias that was independent of the concentration. This time of systematic error can be adjusted if it is both identified and accurately quantified.

Table 4 collects the results of BA analysis for the TN WTP. The Amy model exhibited the smallest bias (0.7 ± 6.1 µg L^{-1}), and thus best agreement with the THM-RR measurements using these models with the same numerical parameters as originally published. Figure 9 shows four plots with one plot representing each model. Each compares the Total THMs concentration measured as a function of time by the THM-RR to the Total THMs concentration predicted as a function of time by the original model, the spreadsheet adjusted model, and the multivariable non-linear fitted model.

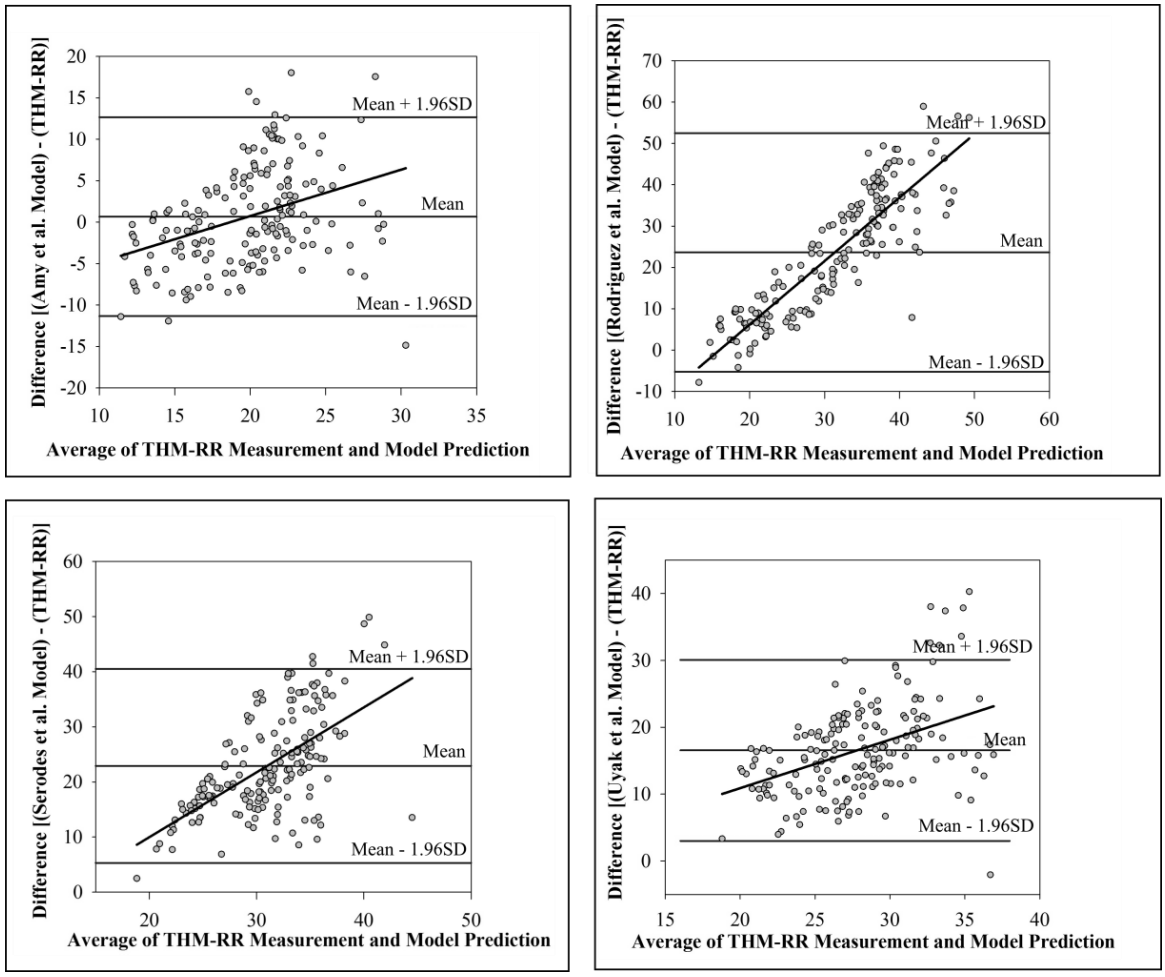


Figure 8. TN WTP Study: Bland-Altman Plots for Measuring the Bias between the Empirical Model Predicted Total THMs Concentration and the THM-RR Measurement of Total THMs Concentration.

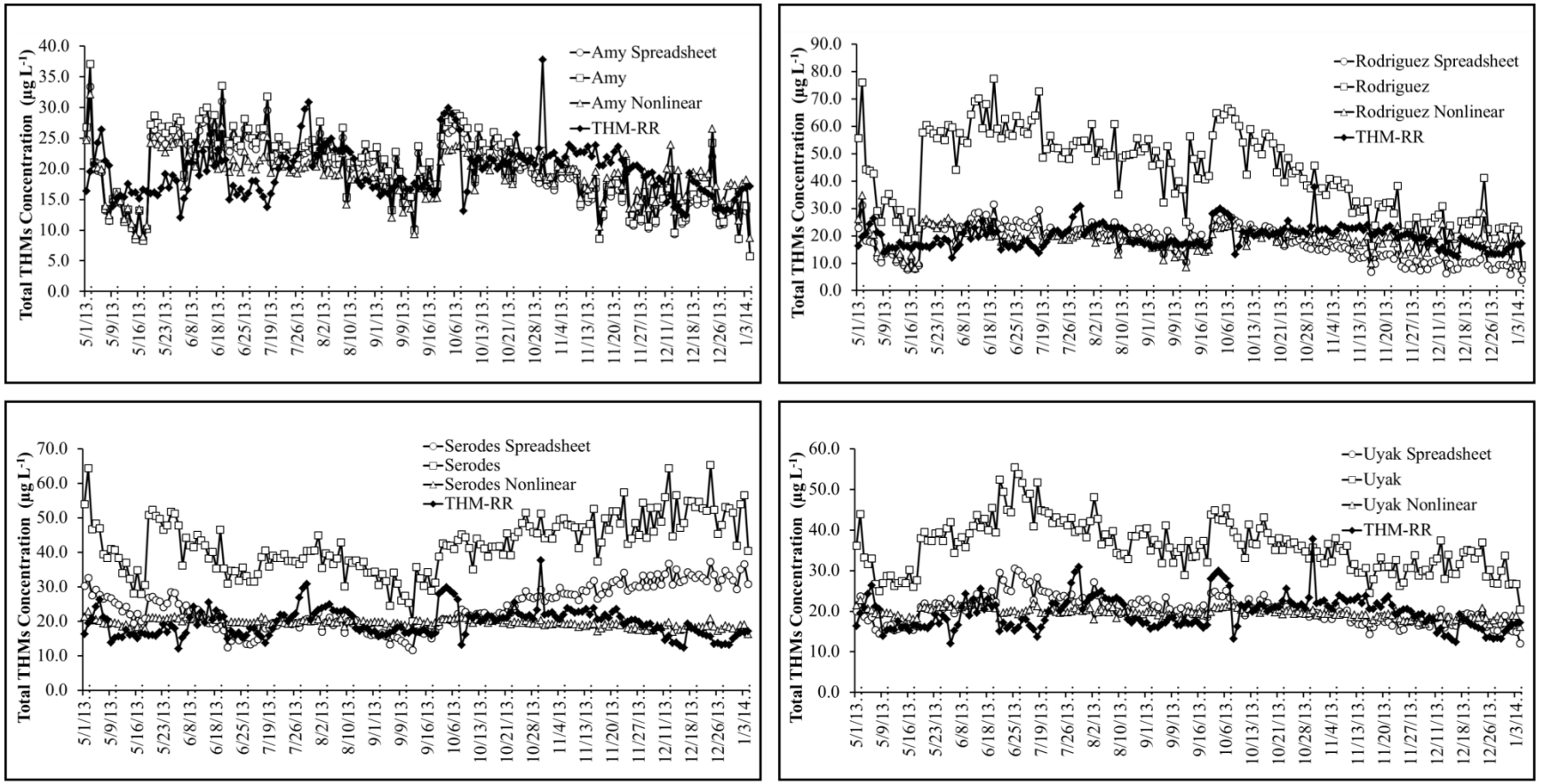


Figure 9. Plot of the Total THMs concentration for the THM-RR and the predicted concentrations for both the original empirical models and the adjusted empirical models for the TN study.

Table 4. Results of the Bland-Altman analysis for all of the sites.

Sampling Site	Unadjusted Bias ($\mu g\ L^{-1}$)	Spreadsheet Adjusted Bias ($\mu g\ L^{-1}$)	Multivariable Non-Linear Fit Bias ($\mu g\ L^{-1}$)
TN-WTP			
Amy Model	0.7 ± 6.1	0.4 ± 5.7	-0.6 ± 4.8
Rodriguez Model	23.6 ± 14.7	-1.9 ± 6.5	-0.7 ± 5.0
Serodes Model	22.9 ± 9.0	4.5 ± 7.7	0.0 ± 3.9
Uyak Model	16.5 ± 6.9	0.8 ± 4.8	0.001 ± 3.9
AR-WTP			
Amy Model	-9.5 ± 7.3	0.3 ± 8.5	-0.1 ± 5.6
Rodriguez Model	11.3± 8.9	1.1 ± 7.7	-0.02 ± 5.6
Serodes Model	11.9 ± 6.6	1.0 ± 6.3	0.0 ± 6.7
Uyak Model	19.8 ± 16.6	-0.03 ± 11.3	-1.6 ± 9.6
TX-WTP			
Amy Model	16.9 ± 7.1	0.6 ± 6.0	0.003 ± 4.2
Rodriguez Model	67.4 ± 12.0	-1.3 ± 5.9.	0.003 ± 4.2
Serodes Model	40.5 ± 5.3	-0.4 ± 5.0	-0.008 ± 4.7
Uyak Model	36.8 ± 10.5	0.7 ± 6.6	0.1 ± 4.0

The spreadsheet adjusted Amy model was generated by reducing the exponent of the TOC term from 1.1 to 1.0 which translated to a reduction of the bias to -0.4 ± 5.7 $\mu g\ L^{-1}$ with a 95% CI of -1.2 to 0.4 $\mu g\ L^{-1}$. For the adjusted Amy model (Figure 9, top left), there are periods where the model does not accurately predict changes in the Total THMs concentration. Consider between 5/18 and 5/19, there is an observed increase in TOC concentration of 1.29 $mg\ L^{-1}$, but even after minimization of the bias, the adjusted Amy model predicts an increase in Total THMs concentration of 14.9 $\mu g\ L^{-1}$ while experimentally there was only a change of -0.3 $\mu g\ L^{-1}$. Additionally, from 6/20 to 6/21 there was an decrease in the THM-RR value 6.4 $\mu g\ L^{-1}$, but the adjusted model only showed a change of -0.4 $\mu g\ L^{-1}$. These instances could possibly indicate times in which

the type or structure of the TOC is changing, which none of the models have terms to account for.

Table 5. Multivariate nonlinear equations used for Total THMs model predictions: Total Organic Carbon (TOC); chlorine dose (D); bromide ion concentration (Br^-); temperature (T); contact time (t); and pH.

Sampling Site	Multivariate Nonlinear Equations
TN-WTP	
Amy Model	$THMs = 0.0394(TOC^*)^{0.925}(D)^{0.152}(T)^{0.17}(pH)^{1.62}(t)^{0.9957}$
Rodriguez Model	$THMs = 0.458(TOC^*)^{1.03}(t)^{-0.2066}(pH)^{1.35}(D)^{0.375}(T)^{0.1251}$
Serodes Model	$THMs = 24.4109 + 2.2058(TOC) + 1.1424(D) - (-0.0947)(T) + (-2.467)(t)$
Uyak Model	$THMs = 3.3405(TOC + 3.2)^{0.5066}(pH - 4.0)^{0.3697}(D - 2.5)^{0.0981}(T + 10)^{0.148}$
AR-WTP	
Amy Model	$THMs = 0.0503(TOC^*)^{-0.6233}(D)^{-0.0195}(T)^{0.618}(pH)^{2.4381}(t)^{0.26}$
Rodriguez Model	$THMs = 0.1798(TOC^*)^{1.3}(t)^{0.262}(pH)^{-0.0872}(D)^{0.277}(T)^{2.0144}$
Serodes Model	$THMs = 0.2619 + 14.8143(TOC) + 10.4874(D) - 1.135(T) + 1.139(t)$
Uyak Model	$THMs = 0.0184(TOC + 3.2)^{1.5698}(pH - 3.0)^{1.413}(D - 0.5126)^{-0.0903}(T + 10)^{0.797}$
TX-WTP	
Amy Model	$THMs = 45.1911(TOC^*)^{0.8026}(D)^{0.0557}(T)^{0.61}(pH)^{-1.7519}(t)^{0.260}$
Rodriguez Model	$THMs = 1.3178(TOC^*)^{0.8026}(t)^{1.6213}(pH)^{-1.7519}(D)^{0.0557}(T)^{0.9891}$
Serodes Model	$THMs = 16.69 + 3.4882(TOC) + 1.89(D) - 0.27(T) + 1.139(t)$
Uyak Model	$THMs = 0.108(TOC + 3.2)^{0.4249}(pH - 4.0)^{-0.9079}(D - 2.5)^{0.2217}(T + 10)^{1.8716}$

The bias from multivariable non-linear fits (Amy et al., 1998; Rodriguez et al., 2000; Systat Software, 2013; Uyak et al., 2005;) were in good agreement with the adjusted models. The bias for the fitted data was -0.6 ± 4.8 µg L^{-1} with a 95% CI of -1.3

to 0.6 µg L^{-1}. Looking at Figure 9, there are spots in which the MVNL fit gives a more accurate prediction, such as around 6/25, but there are still instances in which it does not work. Neither the spreadsheet nor MVNL fits were able to adjust the model to fit the experimental data around 5/18 to 5/19. This spots are likely the result of changes in parameters that the models do not account for or chemical changes that purely empirical models do not consider.

The Rodriguez model, (Figure 9, top right), as directly applied at the TN-WTP, exhibited a bias of 23.6 ± 14.7 µg L^{-1} with a 95% CI of 21.5 to 25.8 µg L^{-1} which is a rather significant over-prediction (~30% of the MCL values for Total THMs with 62% relative error). Such a large bias used for be unacceptable for the purposes of process control and optimization. This behavior suggests that one or more parameters is weighted too heavily as applied in the TN-WTP. The exponent for the pH term was reduced from 1.349 to 0.9 in order to minimize the impact changes in pH would have on the model. Changing this value reduced the bias to -1.9 ± 6.5 µg L^{-1} with a 95% CI of -2.8 to -0.9 µg L^{-1}, essentially reducing the bias by a factor of ten and reducing the error by half. The bias calculated using the multivariable non-linear fitted model was -0.7 ± 5.0 µg L^{-1} with a 95% CI of -1.4 to 0.1 µg L^{-1}.

The Serodes model (Figure 9, bottom left) exhibited bias of 22.9 ± 9.0 µg L^{-1} with a 95% CI of 21.6 to 24.2 µg L^{-1}, similar to those of the Rodriguez model. The bias was minimized by reducing the TOC coefficient 16 to 5, thus reducing the bias to 4.5 ± 7.7 µg L^{-1} with a 95% CI of 3.3 to 5.6 µg L^{-1}. The main disadvantage observed in the Serodes model is the negative water temperature term which causes the model to have a larger bias during the winter months when temperatures are lower. Correction of this term

during winter months leads to increases in errors during the other months of the year. Since this model was originally developed using samples taken during the months between May and November (i.e., warmer months), this increased bias in colder months.

The Uyak model (Figure 9, bottom right) exhibited a bias of 16.5 ± 6.9 μg L^{-1} with a 95% CI of 15.5 to 17.6 μg L^{-1} for the TN-WTP. To compensate for this over prediction, the exponent attached to the TOC term was reduced from 1.314 to 1.1, and the pH exponent was reduced from 1.496 to 1.3. This combination predicted bias estimates of 0.8 ± 4.8 μg L^{-1} with a 95% CI of 0.08 to 1.5 μg L^{-1}, a 20 fold reduction.

Using the MVNL fitting did not work well for both the Serodes and Uyak models. Reducing the bias in a purely mathematical fashion produced a relatively unchanging series of values. The experimental values pass above and below these values which results in an overall low bias. While this may work well for estimating an average Total THMs concentration over time, based on Figure 9 it is clearly not a good predictor of concentration at a specific point in time. On the other hand, the MVNL fitting was able to adjust for the increase in concentration that the Serodes model saw during the summer months.

In addition to BA analysis, another consideration is how two methods "track" one another at any particular point in time. The term *analyte tracking* (Emmert et al., 2009) is used to refer to the instantaneous behavior of two particular methods used simultaneously to predict the same concentration of Total THMs. If there is a change in Total THMs concentration, one would expect THM-RR and the empirical models to respond accordingly. One would expect that both methods (THM-RR and empirical model) should ideally exhibit the same "instantaneous change." Both the THM-RR and the

empirical model should both exhibit concentrations that are either both positive, either both negative, or both unchanged, if they "track" one another.

The plots can be visually inspected for agreement and the human eye will typically note several points of apparent agreement between the THM-RR data and the empirical model that may or may not be real. Analyte tracking was developed to more quantitatively evaluate this behavior by calculating the instantaneous concentration change for two adjacent samples at a particular point in time for each method. At each point in time, the concentration at sampling time T1 and sampling time T2 (where T2 is greater than T1 and the two times are in consecutive order in the study), was calculated by subtracting the concentration of analyte at T1 from the concentration of analyte at T2. The two methods agree if both exhibit positive, negative or no change in concentration. The two methods will agree 33% of the time by random chance.

In terms of tracking of Total THMs concentrations, all four models performed similarly to the values observed in the TN WTP, whether in original form, spreadsheet adjusted or multivariable non-linear fit. The original Amy, Rodriguez, Serodes and Uyak models tracked 48.9%, 48.3%, 45.5% and 42.6%, respectively. The spreadsheet adjusted models tracked 43.2%, 43.3%, 52.3% and 42.6% in the same order. The multivariable non-linear fitted models tracked 51.1%, 46.6%, 51.7% and 52.8% in the same order given earlier. Overall, a significant increase in the tracking was not seen with any of the models.

AR WTP Study

The AR WTP is larger than the TN WTP, producing about 50-60 MGD. The source water comes from man-made reservoirs. Permanganate and lime are added as a pretreatment to the source water, followed by flash mixing with alum and lime. Activated

carbon is added before flocculation, followed by pre-dosing with sodium hypochlorite before filtration. Additional sodium hypochlorite feedstock is added to effect the final chlorine disinfection before introducing the water into the distribution system.

As in the TN-WTP study, the BA plots for the AR-WTP (Figure 10) for the models applied as originally published demonstrate some observable trends for each model. For example, the Amy and Serodes models both exhibit a decrease in the bias as the average Total THMs concentration increases—both skewing negative in the process. In contrast, the Rodriguez and Uyak models exhibit markedly larger bias values that increase as the average Total THMs concentration increases. The Amy and Rodriguez models demonstrate a more random distribution of data points while the Serodes and Uyak models both exhibited clearer trends. The Serodes model exhibits a negative trend in the bias that increases with average concentration of Total THMs. This behavior may result from the failure of the model to account for pH variation that occurred quite frequently in the AR-WTP during the course of the study. The Amy model exhibits a negative bias (meaning it under predicts) with respect to predicting the Total THMs concentration. The remaining three models all exhibit large positive biases and therefore over-predict Total THMs concentrations. The Uyak model exhibits a large positive bias that appears to increase as average concentration of Total THMs increases.

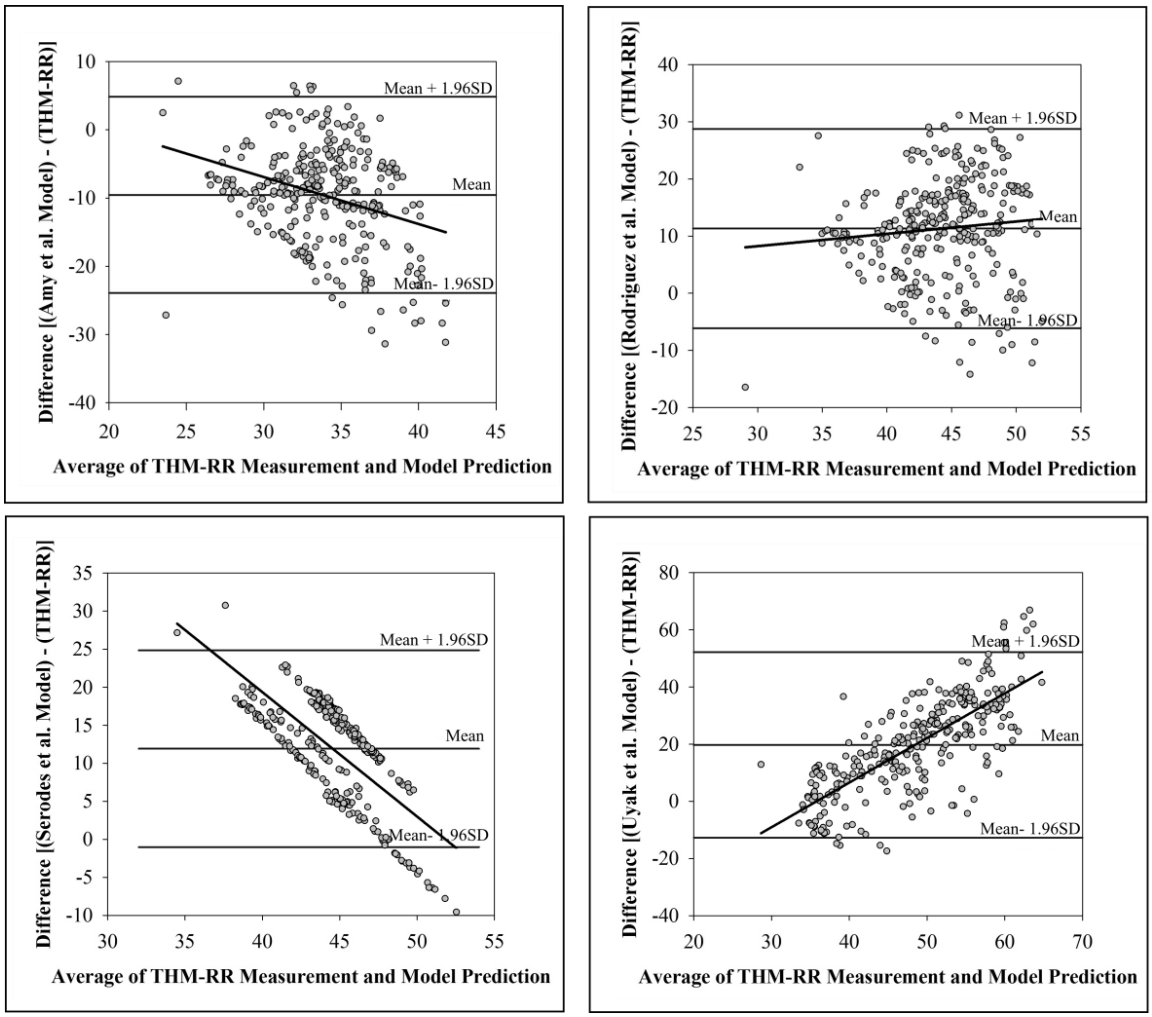


Figure 10. AR WTP Study: Bland-Altman Plots for Measuring the Bias between the Empirical Model Predicted Total THMs Concentration and the THM-RR Measurement of Total THMs Concentration.

Similar to the TN site, the original Amy model (Figure 11, top left) exhibited the lowest bias of the AR sites. However, the bias was larger at -9.5 ± 7.3 µg L^{-1} with a 95% CI of -10.4 to 8.7 µg L^{-1} than with the TN-WTP. At the TN-WTP, it the TOC exponent was reduced to minimize the bias of the model. The negative bias exhibited by the AR-WTP precludes such an approach. Hence, the TOC exponent was increased from 1.1 to 1.4, and the bias was reduced to 0.6 ± 8.5 µg L^{-1}.Similar observations are made with the pH term. Increasing the pH exponent from 1.6 to 1.75, while leaving the TOC exponent

at its original value reduces the bias to 0.7 ± 8.7 µg L^{-1}. By increasing the TOC exponent to 1.25 and the pH exponent to 1.67, the best minimal bias of 0.3 ± 8.5 µg L^{-1} with a 95% CI of -0.7 to 1.2 µg L^{-1} is achieved. It is important to note that while all three of these adjustments are capable of decreasing the bias, they have the side effect of increasing the standard deviation. The bias measured using multivariable non-linear fits (Amy et al., 1998; Rodriguez et al., 2000; Systat Software, 2013; Uyak et al., 2005) was in good agreement with the adjusted model, however there was no significant decrease in the standard deviation of these biases.

The bias for the fitted data was -0.1 ± 5.6 µg L^{-1} with a 95% CI of -0.7 to 0.5 µg L^{-1}, opposite in sign, and marginal improvement in relative error over the adjusted model. Looking at Figure 11, the MVNL model was able to reduce the bias without losing all of the features seen in the experimental values. While there are still spots where all three models do not match the experimental, for example 6/28, the MVNL is able to minimize the difference without resulting in a flat line.

The bias for the original Rodriguez model (Figure 11, top right) was 11.3 ± 8.9 µg L^{-1} with a 95% CI of 10.3 to 12.3 when applied at the AR-WTP. With the TN-WTP, the bias was reduced by reducing the pH exponent. A reduction in the pH exponent from 1.349 to 1.2 reduced the bias to -1.6 ± 7.5 µg L^{-1}. As with the Amy model just discussed, adjusting both the TOC and pH term led to improved bias estimates. By decreasing the pH exponent to 1.25 and the TOC exponent from 1.03 to 1.0 an the bias decreased to 1.1 ± 7.7 µg L^{-1} with a 95% CI of 0.2 to 2.0 µg L^{-1}, which is marginally improved over increasing the pH term alone. In contrast to the observations with the Amy model, the adjustments with the Rodriguez improved both the bias and the standard deviation. The

bias measured using multivariable non-linear fits (references) was -0.02 ± 5.6 µg L^{-1} with a 95% CI of -0.7 to 0.6 µg L^{-1}, opposite in sign to the original and adjusted models, but still within 0.4 µg L^{-1} of the adjusted model.

The original Serodes model (Figure 11, bottom left) exhibits a bias of 11.9 ± 6.6 µg L^{-1} with a 95% CI of 11.2 to 12.7 µg L^{-1} at the AR WTP. The Serodes model is unique among the four models in that it does not have a term to account for changes in pH. The pH at the AR-WTP showed a relatively high degree of variation, and as such the Serodes model was seen to produce very little variation in Total THMs concentration. Since the model had a positive bias, the TOC coefficient was reduced from 16 down to 12 leading to a corresponding reduction in bias to 1.0 ± 6.3 µg L^{-1} with a 95% CI of 0.3 to 1.7 µg L^{-1}. The bias measured using multivariable non-linear fits (references) was 0.0 ± 6.7 µg L^{-1} with a 95% CI of -0.8 to 0.8 µg L^{-1} or within 1.0 µg L^{-1} of the adjusted model. While the magnitude of the bias predicted by the adjusted model seems low, the Serodes model is not a good match for this system as it misses almost all of the variation in THMs concentration that was seen experimentally.

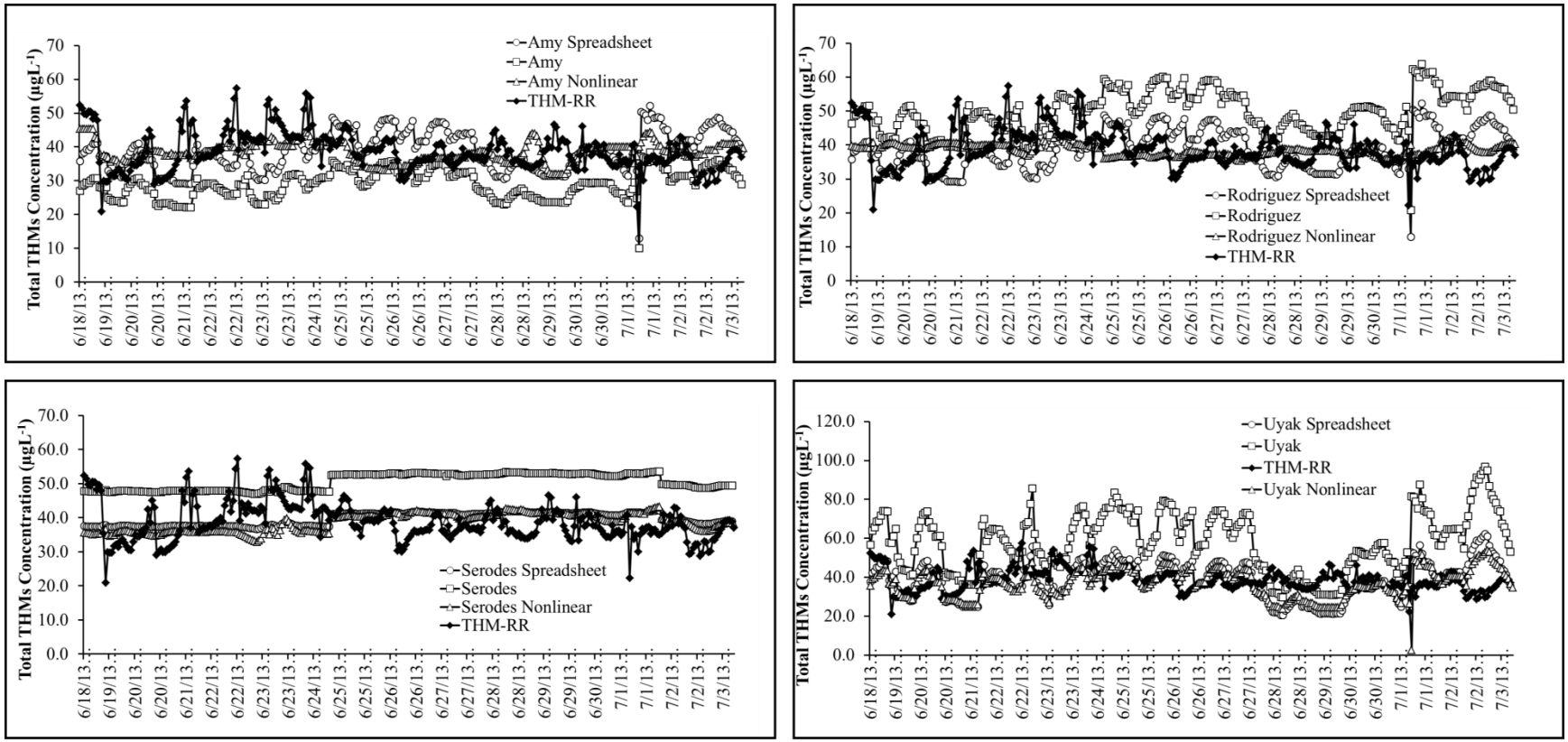


Figure 11. Plot of the Total THMs concentration for the THM-RR and the predicted concentrations for both the original empirical models and the adjusted empirical models for the AR study.

The bias for the original Uyak model (Figure 11, bottom right) was 19.7 ± 16.6 µg L^{-1} with a 95% CI of 17.9 to 21.6 µg L^{-1}. Again this model showed a large positive bias. As with the previous studies, this was first adjusted by reducing the TOC exponent from 1.314 to 1.1. This dramatically reduces the bias to 1.3 ± 12.1 µg L^{-1}. For the other models it was beneficial to reduce both the TOC and pH exponents slightly. If the pH exponent is reduced from 1.496 to 1.4 and the TOC from 1.314 to 1.15, then the bias is reduced to -0.03 ± 11.3 µg L^{-1} with a 95% CI of -1.3 to 1.2 µg L^{-1}. While this is a significant decrease in the magnitude of the bias, the estimate exhibits relatively large error. The bias measured using multivariable non-linear fits was -1.6 ± 9.6 µg L^{-1} with a 95% CI of -2.6 to -0.5 µg L^{-1}, agreeing in sign with the adjusted model, but opposite in sign to the original model. The Uyak MVNL model fitted bias agrees with the adjusted model in terms of bias to about 2 µg L^{-1}. It is likely that this bias results from positive and negative bias values cancelling each other out when averaged.

In terms of tracking of Total THMs concentrations, all four models performed similarly to the values observed in the TN WTP, whether in original form, spreadsheet adjusted or multivariable non-linear fit. The original Amy, Rodriguez, Serodes and Uyak models tracked 47.2%, 55.7%, 50.5% and 49.2%, respectively. The spreadsheet adjusted models tracked 49.2%, 50.8%, 55.7% and 48.2% in the same order. The multivariable non-linear fitted models tracked 46.9%, 56.1%, 55.7% and 47.2% in the same order given earlier. Again there was no significant improvement seen in the percent tracking after either of the adjustments.

TX WTP Study

The TX WTP is a large (over 100 MGD) plant that uses a conventional process facility with a surface water source. Chlorine and ammonia are added at the low lift station (before the treatment for contact time), then ferric sulfate and coagulant aid polymer (cation) are added at the coagulation point. After the flocculation, filter aid polymer (anion) is added to improve filtration, followed by pumping the finished water into storage tanks for delivering to customers. The utility maintains an active laboratory where common drinking water parameters are measured and logged with each shift including: water temperature, residual chlorine, alkalinity, hardness, manganese, iron, phosphate, turbidity, pH, fluoride, coliform, total dissolved solids, and TOC.

The TX site presents an interesting opportunity for comparing the models to experimental data because it uses chloramination (the addition of both free chlorine and ammonia to form chloramines) as the primary disinfection process. All of the models were developed for systems that use chlorination as a primary disinfection method. In general, chloramination results in slowing the formation of DBPs such as THMs. As such, all of the models should exhibit even larger positive bias values than were observed at the chlorination WTPs. This is a result of none of the models having a term that accounts for the chloramination process. The models respond only to dose and since all the models will assume formation will occur at a faster rate, they would be expected to over-predict. Such behavior is observed in Figure 12 as all four models exhibit a large positive bias.

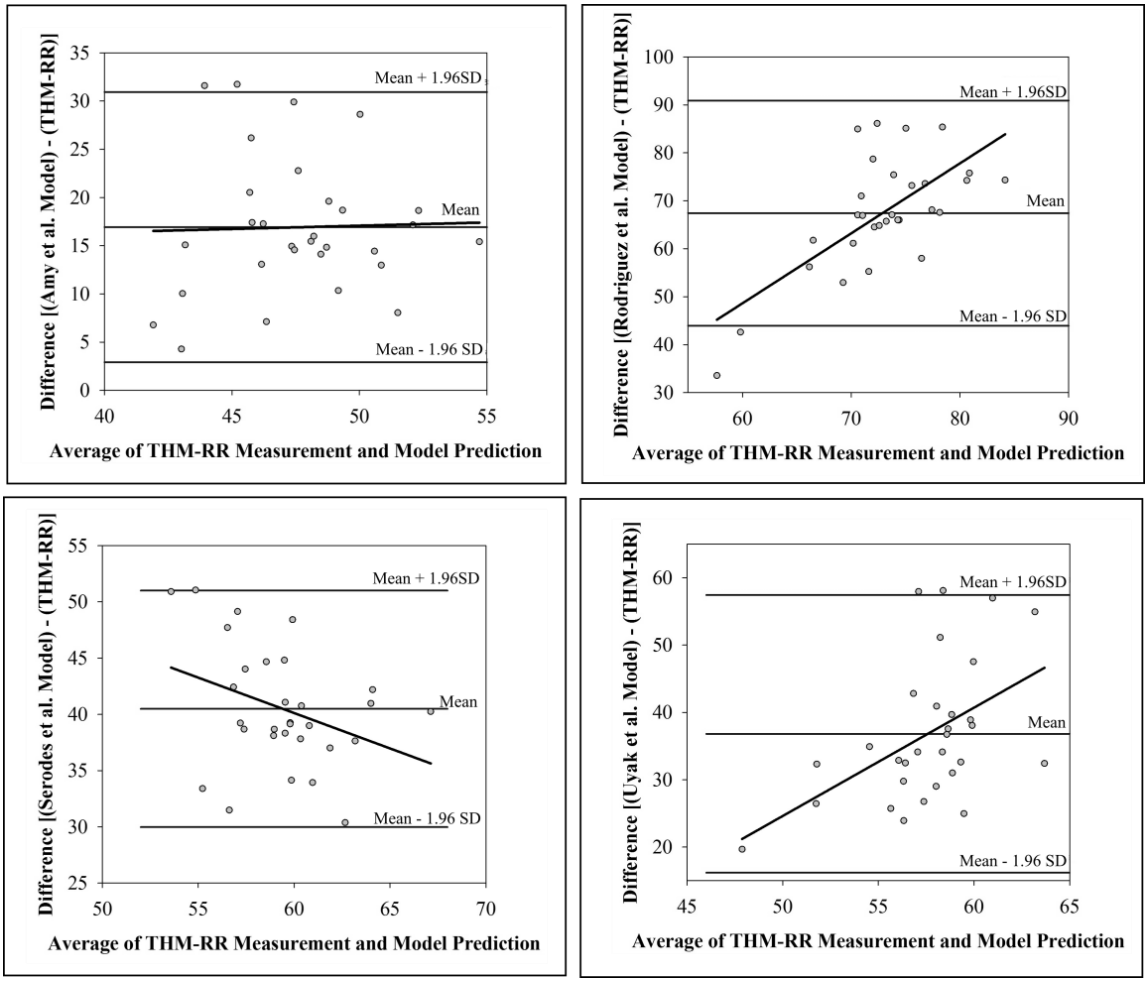


Figure 12: TX WTP Study: Bland-Altman Plots for Measuring the Bias between the Empirical Model Predicted Total THMs Concentration and the THM-RR Measurement of Total THMs Concentration.

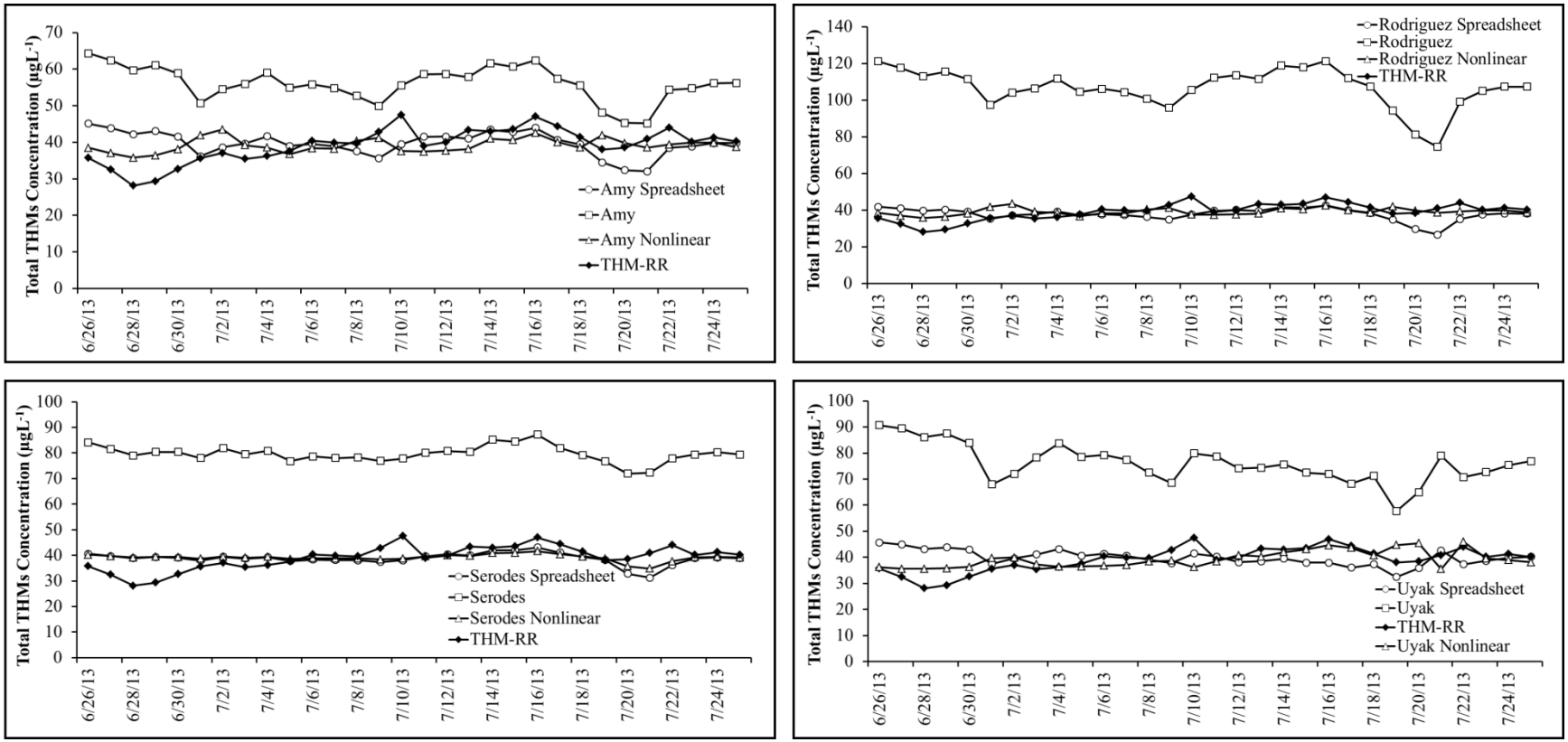


Figure 13. Plot of the Total THMs concentration for the THM-RR and the predicted concentrations for both the original empirical models and the adjusted empirical models for the TX study.

Similar to the previous two sites, the original Amy model (Figure 13, top left) gave the most accurate unadjusted results having a bias of 16.9 ± 7.1 µg L^{-1} with a 95% CI of 14.2 to 19.6 µg L^{-1}. The bias for the original Amy model is nearly independent of average concentration of Total THMs. While this model was the most accurate for this site, the bias is still larger than those seen with the two chlorination WTPs in this study. As before, it was possible to minimize this positive bias by slightly reducing some of the parameters exponents. In this case, because of the large bias both the pH and the TOC exponents were reduced. By lowering the pH exponent from 1.6 to 1.5 and the TOC exponent from 1.1 to 1, the bias was reduced to 0.6 ± 6.0 µg L^{-1} with a 95% CI of -1.7 to 2.8 µg L^{-1} for the adjusted model. This is similar to the biases presented earlier for this model. The bias calculated using the multivariable non-linear fit model was 0.003 ± 4.2 µg L^{-1} with a 95% CI of -1.6 to 1.6 µg L^{-1}, but still within 0.6 µg L^{-1} of the adjusted model.

For the TX site, the original Rodriguez model (Figure 13, top right) showed the largest bias with 67.4 ± 12.0 µg L^{-1} with a 95% CI of 63.0 to 71.9µg L^{-1}. The bias increases positively as the average concentration of Total THM increases. Because of this large bias, both the TOC and pH exponents were altered for this site as well. By reducing the TOC exponent from 1.03 to 0.8 and the pH exponent from 1.349 to 1, the adjusted model bias is -1.3 ± 5.9 µg L^{-1} with a 95% CI of -3.5 to 0.9 µg L^{-1}. Using the multivariable non-linear fit model, the bias was 0.003 ± 4.2 µg L^{-1} with a 95% CI of -1.6 to 1.6 µg L^{-1}, or within -1.3 µg L^{-1} of the adjusted model.

The original Serodes model (Figure 13, bottom left) exhibited bias of 40.5 ± 5.4 µg L^{-1} with a 95% CI of 38.5 to 42.5 µg L^{-1} for the TX site. This bias decreases as the

average concentration of Total THMs increases. As with the two previous models, this bias was larger than observed at the chlorination sites. Since this model has no pH term, only the TOC coefficient was reduced in an effort to minimize the bias. By lowering the TOC coefficient from 16 to 6, the bias was decreased to -0.4 ± 5.0 μg L^{-1} with a 95% CI of -2.2 to 1.5 μg L^{-1}. Unlike the Rodriguez model, there was not a significant decrease seen in the standard deviation. For the TX site, the adjusted Serodes model worked the best with a bias of -0.4 ± 5.0 μg L^{-1}. As with the other two sites, there are instances in which the model fails to track with the experimental values (Figure 13, bottom left). For example, from 6/26 to 6/28 there was a decrease in TOC concentration of 0.33 mg L^{-1}. This resulted in an experimental decrease in Total THMs of 7.6 μg L^{-1} while the model only predicted a decrease of 1.8 μg L^{-1}. In the case of this model, the coefficient for the TOC term was reduced in order to reduce the large positive bias. Unfortunately, it appears that important detail is lost in the process as change from point to point disappears. The MVNL fitted model exhibited a bias of -0.008 ± 4.7 μg L^{-1} with a 95% CI of -1.8 to 1.8 μg L^{-1}, which is within 0.7 μg L^{-1} of the adjusted model.

A bias of 36.8 ± 10.5 with a 95% CI of 32.9 to 40.7 μg $L^{-1}$was measured for the original Uyak model (Figure 13, bottom right). This model, like the Rodriguez model, exhibits an increase in bias as the average concentration of Total THMs increases. Unlike the Rodriguez and Amy models, the minimized bias was achieved by adjusting only the pH exponent. By lowering the pH exponent from 1.496 to 1.0, the adjusted model exhibited a bias of 0.7 ± 6.6 μg L^{-1} with a 95% CI of -1.8 to 3.2 μg L^{-1}. The MVNL fitted model exhibited a bias of 0.1 ± 4.0 μg L^{-1} with a 95% CI of -1.4 to 1.6 μg L^{-1} which is in good agreement with the adjusted model.

The TX sampling site was unique in that it used chloramination as the major disinfection method. None of the models used were specifically designed to account for this. As a result all of the models had larger biases compared to the other studies. However, this did not appear to adversely affect their tracking whether in original form, spreadsheet adjusted or multivariable non-linear fit. The original Amy, Rodriguez, Serodes and Uyak models tracked 55.2%, 65.5%, 55.2% and 55.2%, respectively. The spreadsheet adjusted models tracked 37.9%, 37.9%, 34.5% and 48.4% in the same order. The multivariable non-linear fitted models tracked 55.2%, 37.9%, 31.0% and 31.0% in the same order given earlier.

Conclusions

On-line monitoring studies to measure THMs were performed at three WTPs of varying size and treatment processes. During these studies additional water quality data was obtained from each WTP. This additional data was used in conjunction with four empirical models to calculate predicted Total THMs concentrations. When compared to the experimental values through observation and statistical analysis there are certain instances in which the models begin to break down. This is a result of applying them to systems they were not originally designed for. The models were adjusted for each site using two different approaches. The first method used a simple spreadsheet approach to reduce the bias between the two values. The second more complicated approach used multivariable nonlinear regression to optimize each model based on the experimental values and water quality data. Using these two methods it was possible to reduce the bias for every model to reasonable levels. When comparing each model's performance over

all of the sites, the model developed by Amy et al. (Amy et al., 1998) gave the most consistent results. It had the lowest bias at each site without any adjustment. With minimal changes it was possible to achieve a bias of less than 1.0 µg L^{-1} with error less than 9.0 µg L^{-1} for all three sites using this model.

Chapter 4

APPLICATION OF TRIHALOMETHANE FORMATION KINETICS TO THE CONTRIBUTION OF DISINEFECTION BY-PRODUCTS TO DRINKING WATER BY BULK SODIUM HYPOCHLORITE SOLUTIONS

Introduction

Chlorination is the most widely used water disinfection process in the United States. Chlorine gas has been used as the primary water chlorinating agent for many years, and about two-thirds (63%) of US water utilities use it. Most of the remaining utilities (31%) use bulk hypochlorite solutions for disinfection (Snyder et al., 2009).

It is well known that disinfection by-products (DBPs) (Krasner et al., 2006; Krasner, 2009; Richardson, 2003; Richardson & Ternes, 2011; Richardson & Postigo, 2012; Sadiq & Rodriguez, 2004) are found in drinking water and researchers have studied the formation of DBPs in water distribution systems. The vast majority of these studies have focused on the chemistry that occurs in the distribution system. Some of the compounds originally thought to have formed out in the distribution system have been shown to come largely from bulk hypochlorite solutions. For example, chlorite ion (Asami, 2009; Gordon et al., 1995), chlorate ion (Asami, 2009; Gordon et al., 1993; Gordon et al., 1995; Stanford et al., 2011), bromate ion (Asami, 2009; Garcia-Villanova, 2010; Stanford et al., 2011) and perchlorate ion (Asami, 2009; Synder et al., 2009; Stanford et al., 2011) all may form in bulk hypochlorite solutions.

Recently, it has been shown that there is also the presence of organic DBPs in bulk hypochlorite solutions. Specifically, quantifiable amounts of haloacetic acids

(HAAs) have been identified (Emmert et al., 2012). Through the use of post-column reaction ion chromatography (PCR-IC) it was possible to directly measure the concentration of HAAs in bulk hypochlorite solutions obtained from a variety of utilities.

A total of 30 individual bulk hypochlorite solutions collected from 24 utilities were analyzed for total chlorine, THMs, HAAs and hexavalent chromium. All of the bulk hypochlorite solutions contained concentrations of HAAs that could potentially contribute to the MCL through dilution. Conversely, none of the bulk hypochlorite solutions contained THMs or hexavalent chromium, and thus did not contribute to concentrations of THMs or hexavalent chromium in drinking water or the MCL (Emmert et al., 2012).

While the detection of these compounds in bulk hypochlorite solutions was an important step it does not give a complete picture as to what the final impact is on finished drinking water. During its use in the disinfection process these bulk solutions become diluted. This means whatever concentration of HAAs is present in the bulk solution will be diluted as well. The amount of hypochlorite solution used is unique to each utility. In order to determine the actual contribution the HAAs from the bulk hypochlorite solutions to the amount found in finished drinking water, a dose-dilution model was created.

The concept of the Dose-Dilution Model is relatively simple. The concentration of the FAC and HAAs are measured in the hypochlorite solution and these concentrations are used to predict the concentration of HAAs measured at the “First Tap”. The First Tap is defined as a sampling point close enough to the point of chlorination that one would not expect enough time has passed for HAAs to form through conventional mechanisms.

The HAAs detected at this point would be expected to have arisen from the dilution of the bulk hypochlorite solution and could be predicted based on the FAC dose (Emmert et al., 2012).

At the start of a Dose-Dilution Model, the FAC concentration in the bulk hypochlorite solution is determined using potentiometric iodometry. After FAC analysis, the bulk hypochlorite solution is analyzed by PCR-IC for HAA9 species (Ranaivo et al., 2011; Simone et al., 2006). At the same time, the treated source water is used with the specific utility's hypochlorite solution to construct a FAC demand curve of the utility's treated source water. The HAAs/FAC ratio (units of $\mu g\ L^{-1}$ HAAs/ $mg\ L^{-1}$ FAC) is calculated by dividing the concentration of HAAs in the hypochlorite solution (units of $\mu g\ L^{-1}$) by the concentration of FAC in the hypochlorite solution ($mg\ L^{-1}$). The FAC dose of the utility is calculated by using the FAC residual measured at the First Tap during sample collection and FAC demand curve. Thus, the predicted THAAs at the First Tap are calculated when the THAAs/FAC ratio is multiplied by the determined FAC dose. Once all measurements and calculations have been carried out, the percent contribution of HAAs to the MCL can be determined (Emmert et al., 2012).

On average, when THAA3 is considered, 35 ± 14 % of the HAAs observed could be arising from hypochlorite solution. If THAA9 is included, then this estimate changes to 42 ± 19 %. It is possible slightly more than two fifths of HAAs may be arising from HAAs present in the hypochlorite solution. The percent contribution ranged from 11 to 109 %. So, about a tenth up to more than 100 % of HAAs found in finished drinking water could be contributed by the hypochlorite solution. It was determined that on

average, slightly less than a third of the HAAs in finished drinking water are likely introduced through the use of hypochlorite solutions (Emmert et al., 2012).

The advantages of the Dose-Dilution Model are that it is relatively simple to carry out, based on a relatively small number of analyses, and is specific for a particular utility's treatment practices. Unfortunately, the Dose-Dilution Model has some inherent limitations. For example, there is little control over the experimental measurements. Specifically, temperature, mixing, reaction (contact) time, FAC dosing and sampling from the First Tap are all hard to keep consistent. Thus, the Dose-Dilution Model is difficult to compare across utilities from site to site.

During the course of the original study (Emmert et al., 2012) THMs were detected in all of the finished waters, but were never found in the hypochlorite solutions. This implied that the contact was enough to allow at least some THMs to form. Assuming the THMs and HAAs form on about the same timescale, this would imply that there are at least a portion of the HAAs measured in the finished drinking water that do arise from conventional mechanisms. Thus, perhaps the most important disadvantage of the Dose-Dilution Model is that the implicit assumption of a small contact time does not hold. With this in mind, the kinetic and kinetic-observed models were developed.

The Kinetic Model was developed to account for the presence of THMs (and HAAs) at the First Tap. The results of the Dose-Dilution Model had not taken into account the time required to reach the First Tap and had merely assumed this time was negligible. The presence of THMs at the First Tap indicated that this was likely not a valid assumption. Assuming that the THMs and HAAs form on approximately the same timescale, then the HAAs concentrations measured at the First Tap could be a

combination of HAAs from the hypochlorite solutions and from conventional mechanisms.

Since THMs were not detected in the hypochlorite solutions, the THMs measured at the First Tap must arise through conventional mechanisms. On the other hand, the HAAs measured at the First Tap arise from both the bulk hypochlorite solution and from conventional mechanisms. Treated source samples were dosed with hypochlorite solution from the specific utility and the concentration of THMs and HAAs were monitored as a function of time. The formation of TTHMs and the HAAs were fitted to an apparent first order rate law and the apparent first order rate constant was calculated for TTHMs and for HAAs. The integrated first order rate law for TTHMs was then used to calculate the time required to form the concentrations of TTHMs measured at the First Tap. This time was then used with the integrated first order rate law for HAAs formation to predict the concentration of HAAs that would form in that time. This allowed for an alternate prediction of the concentration of HAAs that would be expected at the First Tap.

A variation of the Kinetic Model, named the Kinetic-Observed Model, was determined using the same data as the Kinetic Model, but with one difference. Instead of using the first order rate law for HAAs concentration prediction, the concentration of HAAs was interpolated from the HAAs concentration over time profiles that were used to generate the Kinetic Model. Since this model is a combination of the THMs *kinetic* model with the *observed* concentration of HAAs in the modeling studies, it is referred to as the Kinetic-Observed Model.

Experimental

Chemicals and Reagents

All reagents and standards were prepared in reagent grade water with a resistivity of at least 18.2 MΩ·cm and total organic carbon (TOC) concentrations of ≤ 10 μg L^{-1}, produced by a Barnstead E-pure four cartridge system, purchased from Thermo Scientific (Waltham, MA). All chemicals used during the study were reagent grade, HPLC grade, ACS Certified grade or better when available. The purities of standards and reagents were 97 % or higher, with the exception of the reagent grade potassium hydroxide (85 %). Sodium thiosulfate ($Na_2S_2O_3$), potassium iodate (KIO_3), concentrated sulfuric acid (H_2SO_4), potassium iodide (KI), potassium hydroxide (KOH), methyl tert-butyl ether (MTBE), sodium sulfate (Na_2SO_4), and methanol were all purchased from Fisher Scientific (Waltham, MA). All HAA9 standards, THM4 standards and nicotinamide were purchased through Sigma Alrich (St. Louis, MO). The DPD (N,N-diethyl-p-phenylenediamine) free chlorine reagent 10 mL pillow packets, and SPEC color standard DPD-Chlorine secondary standards kit for low range calibration were purchased from Hach Company (Loveland, CO).

Analysis of Total Chlorine by Iodometry

The concentration of FAC species in solution is commonly measured using iodometry (Greenberg et al., 1992), and in this work, potentiometric measurement of the titration endpoint is used. For each site, the bulk hypochlorite solution was analyzed. Each hypochlorite solution was titrated 5 times.

The standard method 4500-Cl B (Greenberg et al., 1992) was modified slightly in this project. A Radiometer VIT 90 video titrator (Copenhagen, Denmark) with a M231

Pt-9 Platinum electrode and calomel REF-421 electrode pair (Hach) was employed to carry out the titration. The titration was carried out using a potentiometric determination of the end point where the delivery of the titrant, $Na_2S_2O_3$, stops (titration stops) when the titration curve has reached its inflection point.

$$Cl_2 + 2\,I^- \rightarrow I_2 + 2\,Cl^-$$
$$I_2 + I^- \rightarrow I_3^-$$
$$I_2 + 2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\,I^-$$

Figure 14. Iodometric titration reaction

Analysis of FAC by the DPD colorimetric method

DPD (N,N-diethyl-p-phenylenediamine) is used for colorimetric analysis of FAC residual. FAC reacts with the DPD reagent to form a red color of increasing absorbance with the FAC residual concentration (APHA-AWWA-WEF, 1994). Care must be taken with this measurement, as the colored product is in equilibrium with colorless products of the reaction (Gordon et al., 1992) The absorbance measurement is made by a filter photometer with a light-emitting diode (LED) source, with transmission and absorbance measured from 490 to 530 nm, with a cell with path length of at least 1.0 cm or longer (Hach Company, 2006).

The Hach Pocket Colorimeter II was used to measure all FAC residual in water samples (Hach, 2006). The colorimeter operates at a wavelength of 528 nm and cell path lengths are 1.0 cm for high range measurements (2 to 10 mg L^{-1} FAC) and 2.54 cm for low range measurements (0.02 to 2.1 mg L^{-1} FAC). In this study, the FAC residual was measured in the treated source water, First Tap and Old Tap in the distribution system.

The treated source water was not expected to have a measurable FAC residual; however, in systems that prechlorinated or use chlorine dioxide pretreatment, there was a measurable concentration that alerted the researchers to potential interferences during sample analysis and chemical kinetic modeling. The FAC residual was measured in duplicate at the drinking water treatment plant concurrent with sample collection.

Chlorine Demand Curves

Here a FAC demand plot is constructed to determine the FAC dose of a utility. The FAC demand is the difference between the concentration of FAC dosed into a water sample and the concentration of FAC remaining after a given contact period. Determination of FAC demand is made by dosing the treated source water samples collected from a utility with known but varying concentrations of the utility's specific bulk hypochlorite solution and measuring the FAC after the contact period. A chlorine demand curve is produced by plotting the dose concentration (x-axis) versus the residual concentration (y-axis) and used to determine the breakpoint at which the combined chlorine residuals no longer predominate and free chlorine residual dominates (Sawyer et al., 2003).

A plot of FAC concentration dosed versus the FAC residual measured is fitted with a linear regression trend line (Sawyer et al., 2003). The dose of the utility is calculated by inserting the residual FAC measured at the First Tap into the linear equation for "y" after is has been rearranged to solve for "x".

Analysis of THMs by USEPA Method 524.2

USEPA Method 524.2 (1995) is a method used for the identification and measurement of purgeable volatile organic compounds in water samples and in this work

specifically for the THM4 species. This method uses purge and trap for sample introduction, followed by separation by gas chromatography, and detection and quantification of the analytes by mass spectrometry (MS) (USEPA, 1995). Unlike the DELCD, the MS provides confirmation of chemical identity and the opportunity to identify potential, halogenated interferences that may arise during the kinetic modeling. This method was used to determine the THMs concentration in the water samples that were pulled from each utility.

USEPA 524.2 (1995) uses purge and trap gas chromatography with mass spectrometry (USEPA, 1995). An AQUA Tek 70 liquid autosampler (Teledyne-Tekmar, Mason, OH) was used to introduce the samples to the purge and trap system. The purge and trap was performed by a Tekmar 3100 sample concentrator (Teledyne-Tekmar). The sample was purged with ultra-high purity helium, and the volatile organic compounds were collected on a Supelco VOCARB 3000 trap (Sigma Aldrich). The trap was then. The desorbed compounds were injected onto a Varian CP-3800 gas chromatograph (Agilent, Santa Clara, CA). Detection was performed by a Varian Saturn 2000 mass spectrometer using electron impact ionization and a linear ion trap.

Analysis of THMs by on-line purge and trap gas chromatography

The on-line purge and trap gas chromatograph with a dry electrolytic conductivity detector (OPT-GC) is a method used to detect and quantify individual and Total THM4 species (Brown et al., 2007) in drinking water. This method was used to measure the formation of THMs during the kinetic modeling studies.

The sample is pulled through the gas extraction cell (GEC) by a peristaltic pump. When samples pass through the inside of the membrane in the GEC, the THMs

pervaporate across the membrane. These are then carried by a sparge gas stream of ultra-high purity helium to a heated 10-port injection valve (Valco Instruments). The THMs pass through the valve and onto a Tenax®-GR trap. The traps are then heated to desorb the THMs and the valve is rotated so that GC carrier gas will carry them to be separated and detected by a dry electrolytic conductivity detector (DELCD). Following each injection the GEC is purged with sparge gas and reagent water and the traps are baked out to prevent carryover.

Analysis of HAAs by USEPA Method 552.3

USEPA Method 552.3 (2003) determines HAAs in drinking water by liquid-liquid microextraction, derivatization and gas chromatography with electron capture detection. Each sample is adjusted to a pH at or below 0.5 and extracted MTBE containing an internal standard. The HAAs are then converted to their methyl esters by the addition of acidic methanol followed by heating for 2 hours. Concentrated sodium sulfate solution is added in order to separate the solvent phase containing the methylated HAAs from the acidic methanol. The lower aqueous phase is discarded. The remaining phase is neutralized with a saturated solution of sodium bicarbonate. The upper solvent layer is transferred to a vial for analysis. Gas chromatography using an electron capture detector (GC-ECD) is used to identify and quantify the target analytes. This method was used to determine the HAAs concentration in all of the finished water samples obtained from each utility.

Analysis of HAAs by PCR-IC

PCR-IC is an on-line and near-real time method capable of measuring individual HAA9 and THAA9 concentrations in drinking water, and has been previously reported

(Ranaivo et al., 2011; Simone et al., 2009). The HAA9 species are separated using anion-exchange chromatography followed by post-column reaction with nicotinamide and base to form glutaconaldehyde which fluoresces with an excitation of 365 nm and emission of 455 nm. An update of the PCR-IC has been published using a hydroxide-selective column and internal standardization by Ranaivo et al (2011); however, hypochlorite ion and the internal standard (2-bromobutanoic acid) co-elute, thus this method is used here with external calibration only. For this work, a PCR-IC analyzer was used without modification to analyze the HAA9 species present in hypochlorite solutions.

Kinetic Modeling Studies

A reaction vessel made of PVC pipe materials was constructed to simulate and normalize the dosing and mixing conditions of a utility's bulk hypochlorite solution and water such that a comparison could be made across utilities (Figure 15). The vessel was constructed using a 30.5 cm section of 10.2 cm diameter PVC pipe fitted with a flush cleanout cap to give it a flat bottom surface. A 1.3 cm PVC valve was placed approximately 2.5 cm from the bottom to allow for samples to be pulled from the reaction vessel for analysis by USEPA 552.3 (2003) and 524.2 (1995). The lid to the reaction vessel was a PVC "knock out plug" modified to float in the reaction vessel and allow sample lines for the OPT-GC (Brown et al., 2007) and PCR-IC (Ranaivo et al., 2011; Simone et al., 2009) to draw sample from the vessel but also allow for a near zero headspace condition.

Two liters of the treated source water were poured into the reaction vessel and then dosed with the appropriate amount of hypochlorite solution previously determined by the FAC demand curve. The OPT-GC (Brown et al., 2007) and PCR-IC (Ranaivo et

al., 2011; Simone et al., 2009) are used to simultaneously monitor THMs and HAAs in the reactor vessel in real-time. These values are then used to create first order kinetic models for both species.

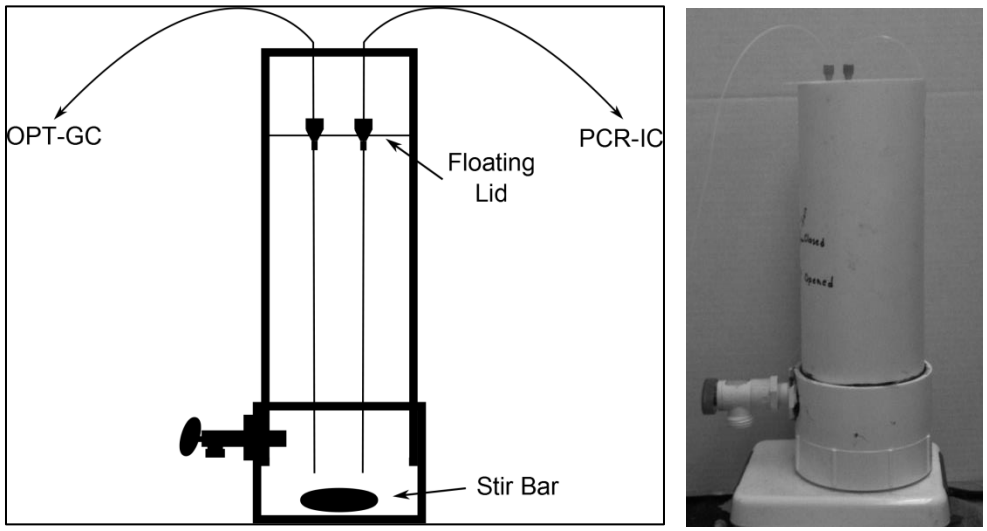


Figure 15. Diagram and photograph of the reaction vessel used for kinetics studies.

Calculations

Using the results from the studies a plot of TTHMs concentration versus time can be created. From this a kinetics model for THMs was created by assuming first order kinetics and creating a plot of ln[THMs] versus time. A linear regression was applied to this plot then the resulting slope of the line represents the rate of THMs formation, "k". Using this THMs kinetics model, the first tap time was calculated using the equation shown below in which "c_i" is the initial concentration of THMs in the chemical kinetic modeling study, "c_f" is the concentration of TTHM4 from the First Tap sample determined by USEPA method 524.2, "k" is the rate constant from the THMs kinetics study and "t" is the predicted first tap time.

$$t = \frac{ln(\frac{c_i}{c_f})}{-k} \quad (2)$$

A plot of HAAs concentrations versus time can be created from the data obtained from the studies. This plot can be transformed into natural log (ln) of the concentrations and plotted against time. This natural log versus time plot can be fit to linear regression and the slope of the line is the first order rate constant "k" (in units of min^{-1}). The integrated first order rate law is used with the calculated First Tap time from the THMs first order integrated rate law to determine the concentrations of the HAAs at the First Tap, previously discussed in the outline of the Kinetic and Kinetic-Observed Models. The equation used for the first order integrated rate law is shown below (Harris, 2006).

$$[A] = [A]_0 e^{-kt} \quad (3)$$

where [A] is the predicted concentration; $[A]_0$ is the initial concentration; k is the rate constant; and t is the time.

The integrated first order rate law for TTHMs was then used to calculate the time required to form the concentrations of TTHMs measured at the First Tap using USEPA 524.2 (1995). This time was then used with the integrated first order rate law for HAAs formation to predict the concentration of HAAs that would form in that time. This allowed for an alternate prediction of the concentration of HAAs that would be expected at the First Tap. In this model, the percent contribution of HAAs from the hypochlorite solution was calculated

$$\%\ Contribution\ of\ HAAs\ from\ NaOCl = \frac{Kinetic\ Predicted\ HAAs\ @\ First\ Tap}{HAAs\ Measured\ @\ First\ Tap} \quad (4)$$

In the Kinetic Model, the denominator is calculated in the same way as the Dose-Dilution Model, with USEPA Method 552.3. While the numerator is now derived as stated above,

predicted from the THMs and HAAs kinetic models that come from the dosing of the treated source water samples with appropriate hypochlorite solution.

A variation of the Kinetic Model, named the Kinetic-Observed Model, was determined using the same data as the Kinetic Model, but with one difference. Instead of using the first order rate law for HAAs concentration prediction, the concentration of HAAs was interpolated from the HAAs concentration over time profiles that were used to generate the Kinetic Model.

Results and Discussion

Samples were collected from 8 different utilities and analyzed as described earlier so that the Kinetic Model and the Kinetic-Observed Model could be applied to estimate the percent contribution of HAAs from hypochlorite solution to those measured at the First Tap. These utilities included 8 utilities were designated: AR-3, IL-2, OK-3, NJ-1, NY-1', TN-12, TN-14 and TN-15.

AR-3 Site

The AR-3 site is a surface water site that prechlorinates at the water source. The bulk hypochlorite solution is purchased from a regional vendor and stored in a climate controlled facility. Their rate of use of the bulk hypochlorite solution varies with water production, but in general they consume their supply of bulk hypochlorite solution about every two weeks. Even though the samples were collected one week apart, the two models presented are derived from two different bulk hypochlorite solution deliveries. Historically, this site has struggled with THMs, but has not had significant issues with HAAs concentrations near the MCL.

The Kinetic Model was developed to provide an independent and reproducible estimate of the HAAs measured at the First Tap. In a carefully controlled laboratory environment, an aliquot of the hypochlorite solution collected from the utility is dosed into an aliquot of the treated source water sample in a way to simulate the chlorination process. The formation of HAAs and THMs concentrations are monitored as a function of time using real-time, automated methods following the dosing. The concentration versus time data for HAAs and THMs is fitted to separate, first order kinetic models. Since THMs are not present in the hypochlorite solution, they come only from conventional formation mechanisms. The first order rate constant for TTHM4 formation is used in conjunction with the integrated first order rate to determine the amount of time it takes to form the concentration of TTHM4 species observed at the First Tap. This provides a measure of the time it takes to reach the First Tap (First Tap time). The measured First Tap time from THMs formation and measurement was 171 ± 26 minutes.

The First Tap time is used with the first order rate constant and the integrated first order rate law for the HAAs formation to calculate the concentrations of HAAs that form in the time required to reach the First Tap. Thus the Kinetic Model provides an independent way to measure the concentrations of HAAs that would be observed at the First Tap (the denominator of the percent contribution formula). The Kinetic Model predicts that 38 ± 13 % of the THAA3 observed at the First Tap would be expected to arise from the hypochlorite solution. When THAA9 is considered, the estimate of the percent contribution is also 38 ± 13 %.

A slight variation of the Kinetic Model, called the Kinetic-Observed Model, uses the same approach as the Kinetic Model. The apparent first order rate law for TTHM4

formation is used to determine the First Tap time as in the Kinetic Model. Then at this First Tap time, the concentration of HAAs is interpolated from the HAAs concentration over time profile rather than predicting this concentration using the first order fit. With the Kinetic-Observed Model, the percent contribution of HAAs to the First Tap is predicted to be 47 ± 25 % for both THAA3 and THAA9.

With AR-3, there are significant concentrations of THM4 species detected indicating that the time required to reach the First Tap is long enough for conventional formation mechanisms (assuming THMs and HAAs form on the same timescale). Thus the Dose-Dilution Model assumption, that the First Tap time is small enough that minimal HAAs formation occurs, no longer holds in this case.

For many utilities, the maximum residence time (Old Tap) is one of the sites used for Stage 2 DBP rule compliance monitoring (USEPA 2006). The percent contribution of HAAs from the hypochlorite solution to concentration of HAAs at the Old Tap can be calculated. The percent contribution of HAAs observed at the Old Tap was 20 ± 3 % for THAA3 and 18 ± 4 % for THAA9. The percent contribution of the hypochlorite solution HAAs to the HAAs MCL (0.060 mg L^{-1} HAA5) (USEPA, 2006) is estimated to be 6 ± 1 % for the AR-3 site. The relationship between the HAAs in the hypochlorite solution at the time of collection and the Old Tap HAAs concentration is not as straightforward. The amount of time required to reach the Old Tap is estimated by the utility to be approximately 2-3 days.

One week later, the AR-3 site was sampled again. As before, there were substantial concentrations of THMs measured at the First Tap indicating the time to reach to reach the First Tap was large enough that a portion of the HAAs at the First Tap are likely contributed by conventional formation mechanisms. $CHCl_3$ and $CHBrCl_2$ concentrations at the First Tap were 5.8 ± 0.4 and 1.3 ± 0.1 μg L^{-1}, respectively. The TTHM4 concentration was 7.2 ± 0.4 μg L^{-1}. Using the Kinetic Model and THMs concentrations, the time required to reach the First Tap was 121.6 ± 26.3 minutes leading to an estimate that 59 ± 15 % of the THAA3 observed at the First Tap was from hypochlorite solution contribution. For THAA9, the estimate of the percent contribution is 17 ± 4 %. When the Kinetic-Observed Model is considered, the estimates for THAA3 and THAA9 are both 34 ± 13 %.

What does this all mean? Are the HAAs a problem for AR-3? Probably not, the utility does not have a history of HAAs violations or HAAs concentrations near the MCL. But more to the point, are the HAAs in the bulk hypochlorite solution a substantial contributor to the concentration of HAAs typically observed in the system? Here the answer seems to be yes. The Kinetic Model predicts the range for THAA3 is 38 to 59 %. For the Kinetic-Observed Model, the range is 34 to 47 %. For reasons which will be discussed in more detail, the Kinetic-Observed Model appears to provide the more conservative estimate and likely the most robust model when all things are considered.

The IL-2 Site

The IL-2 treatment plant uses surface water as its source and uses delivered bulk hypochlorite solution rather than on-site generation. The utility purchases bulk hypochlorite solution from a regional vendor uses climate control for the bulk

hypochlorite solution and does not combine new with old bulk hypochlorite solution. During the treatment process, the source water is both prechlorinated and preoxidized using permanganate ion. The survey reported contact time and First Tap time are both 24 hours, in this case indicating the First Tap and contact time are taken at the same point. The utility uses chloramination and historically reports both THMs and HAAs concentrations in the range of 10 – 20 μg L^{-1}.

The $CHCl_3$ concentration at the First Tap was 10.0 ± 2.0 μg L^{-1} and was the only THM4 species detected and as such the TTHM4 concentration was 10.0 ± 2.0 μg L^{-1}. Using the Kinetic Model, the time required to reach the First Tap (contact time) was assumed to be 15 ± 5 min leading to an estimate that 33 ± 8 % of the THAA3 observed at the First Tap arises from the hypochlorite solution. For THAA9, the estimate of the percent contribution is 32 ± 7 %. These results agree well with the estimates form the Kinetic-Observed Model which is 32 ± 7 % for both THAA3 and THAA9.

The measured First Tap time and the reported time from the survey do not agree. However, the measured First Tap is a snapshot of the utility's treatment process and matrix during the sample collection visit and the kinetic model represents an attempt to model the processes in the utility. In many cases, the exact treatment process is difficult to replicate – thus all utilities were treated the same during kinetic modeling process. The matrix in IL-2 reacts quickly with FAC and IL-2 uses chloramination for disinfection to slow THMs formation. The Kinetic Modeling did not use chloramination, thus contributing to the differences in First Tap time. The model First Tap time is calculated by using the measured THMs at the First Tap in the first order kinetic rate law. In the case of IL-2, the concentration of THM4 measured at the First Tap is less than

concentration at 15 min in the THMs concentration versus time profile developed. Thus leading to a case where the First Tap time could not be measured. In this case, a 15 minute first tap time was used for the remaining kinetic modeling of HAAs.

The NJ-1 Site

The NJ-1 utility is a surface water treatment plant that uses permanganate ion as a preoxidizer. The bulk hypochlorite solution is delivered from a regional vendor and the utility combines the newly delivered bulk hypochlorite solution with the old bulk hypochlorite solution already present in the storage tanks. The bulk hypochlorite solution is used in about seven days from the time of delivery. The survey reported contact time is four hours with a six hour first tap time. Historically, the average concentrations of THMs range from 25 to 45 μg L^{-1}, with average HAAs less than 20 μg L^{-1}.

Significant concentrations of $CHCl_3$ and $CHBrCl_2$ were measured at the First Tap. These results indicated that the time required to reach the First Tap (244.3 ± 55.9 minutes) is long enough such that formation of THMs and HAAs through conventional mechanisms is possible. The Kinetic Model predicts that 14 ± 11 % of the THAA3 as well as THAA9 observed at the First Tap is contributed by the hypochlorite solution. The Kinetic-Observed Model predicts approximately the same contribution as the Kinetic Model at 15 ± 6 % for both THAA3 and THAA9 species.

The reported First Tap time by the utility and the measured First Tap time by Kinetic Modeling agree quite well in this utility. Both IL-2 and NJ-1 use chloramination; however, the modeled NJ-1 matrix in this case forms a factor of 8 less HAAs than the IL-2 matrix. Indicating the matrix collected and modeled plays a significant role in the ability of the Kinetic Model to provide an accurate First Tap time.

The NY -1' site

The NY-1' utility is a surface water treatment plant that uses prechlorination with chlorine gas. The bulk hypochlorite solution is delivered by a regional vendor, and the utility combines new bulk hypochlorite solution with old bulk hypochlorite solution. The self-reported contact time is 3.5 hours,the first tap time is 2 to 5 hours depending on demand and the target chlorine residual is 0.6 mg L^{-1}. Historically, the THMs and HAAs concentrations average between 35 and 55 µg L^{-1}.

There were significant concentrations of $CHCl_3$ measured at the First Tap, 16.8 ± 0.7 µg L^{-1}, but no other species. These results indicated that the time required to reach the First Tap (60 ± 17.1 minutes) is long enough that a portion of the THMs and HAAs formation may be from conventional mechanisms. The Kinetic Model predicts that 8 ± 6 % of the THAA3 as well as THAA9 observed at the First Tap is contributed by the hypochlorite solution. The Kinetic-Observed Model predicts approximately the same contribution as the Kinetic Model at 7 ± 3 % for both THAA3 and THAA9 species. The measured First Tap time is on par with the time reported by the utility, indicating a relatively simple matrix for modeling THMs and HAAs formation.

The OK-3 site

The OK-3 utility uses a mix of purchased and surface water in the treatment plant. They also use permanganate preoxidation on source water. The utility is small with typically high levels of THMs and low levels of HAAs present in their finished water. The bulk hypochlorite solution is delivered to the treatment plant and the utility does not combine new bulk hypochlorite solution with old bulk hypochlorite solution. The survey

reported contact time is 24 hours and the First Tap time as reported by the utility is 9 minutes (0.15 hours) with a target chlorine residual of 2.5 mg L^{-1}.

High concentrations of THM4 species were measured at the First Tap. The TTHM4 concentration at the First Tap was 248.7 ± 2.5 µg L^{-1}. The Kinetic Model predicts a time to the First Tap of 285.4 minutes (~5 hours) with a corresponding estimate that 37 ± 9 % of the THAA3 observed at the First Tap arise from hypochlorite solution contribution. With THAA9, the percent contribution of the hypochlorite solution is 31 ± 7 %. The results of the Kinetic-Observed Model are in good agreement at 40 ± 16 % and 23 ± 6 % for THAA3 and THAA9, respectively.

The measured First Tap time is ~5 hours, and while this does not agree with the First Tap time reported by the utility, it does seem to be a reasonable estimate and in line with other measured First Tap times. The percent contributions across all empirical models agree within the error for THAA3, indicating the chlorine demand curves and formation of THMs and HAAs concentrations are well modeled by the analyses. For THAA9, all empirical models are less than the equivalent THAA3 models showing that the Kinetic and Kinetic-Observed Models at least partially account for the THAA9 that have formed at the First Tap.

The TN-12 site

The TN-12 utility uses surface water and recently converted from chlorine gas to delivered bulk hypochlorite solution. The bulk hypochlorite solution storage building and tanks are small, thus the utility receives deliveries from a regional vendor every 3-7 days, depending on the season, and did not report on combination of new and old bulk hypochlorite solution. The utility did not report using prechlorination or permanganate

preoxidation. The utility's target FAC concentration is 2.9 mg L^{-1}, with historical THMs and HAAs concentrations are near the MCLs for both classes of DBPs.

Significant concentrations of TTHM4 consisting of $CHCl_3$ and $CHBrCl_2$ were measured at the First Tap indicating that the time required to reach the First Tap (120.0 ± 23.3 minutes) is long enough for some THMs (and likely, HAAs) to form through conventional mechanisms. The Kinetic Model predicts that 31 ± 8 % of the THAA3 observed at the First Tap is contributed by the hypochlorite solution. For THAA9, 31 ± 8 % of the HAA3 species arise from the hypochlorite solution. Similar results were observed from the Kinetic-Observed Model which are 23 ± 6 % for both THAA3 and THAA9 species. As in the case of NJ-1, NY-1' and OK-3, the three empirical models agree indicating that the matrix is well modeled by the treatment simulation process.

The TN-14 site

The TN-14 utility is a surface water site that prechlorinates the source water using delivered bulk hypochlorite solution from a regional vendor. The new bulk hypochlorite solution is combined with the old bulk hypochlorite solution upon delivery. The survey reported contact and First Tap times are 9 hours, with a target FAC residual of 2.5 mg L^{-1}. The dose from the measured demand curve is 3.7 ± 0.3 mg L^{-1} and the measured First Tap time is 134 ± 34 minutes. Again, the First Tap time does not agree with the utility's reported time; however, the measurement is more representative as a snapshot of the utility's treatment conditions for modeling the THMs and HAAs formation.

There were significant concentrations of three of the four TTHM4 species ($CHCl_3$, $CHBrCl_2$, and $CHBr_2Cl$) detected at the First Tap. The concentration of $CHBr_3$ was less than the MDL. These results indicated that conventional THMs and HAAs

formation mechanisms were in operation over the time required to reach the First Tap (133.6 ± 23 minutes). The Kinetic Model predicts that 72 ± 43 % of the THAA3 and 84 ± 50 % of the THAA9 observed at the First Tap is contributed by the hypochlorite solution. The Kinetic-Observed Model predicts a lower contribution more in agreement with the Dose-Dilution Model in this case, 39 ± 12 % for THAA3 and 46 ± 14 % for THAA9. The Kinetic Models are fit to a linear regression line on a first order fit, whereas the Kinetic Observed interpolates between points and does not require a regression line which can over- or under-estimate concentrations directly measured at particular points in time. In this case, the first order kinetic plot of the HAAs underestimates the concentrations produced and measured in the Kinetic Observed concentration versus time profiles.

The TN-15 site

TN-15 treatment plant uses surface water that is prechlorinated prior to the treatment process. The utility did not self-report any other additional information about the delivery of the bulk hypochlorite solution, whether it is combined, the contact time or the First Tap time. Table 6 presents the results from the TN-15 site. The FAC concentration for the bulk hypochlorite solution was 117,739 ± 348 mg L^{-1}. The FAC residual measured at the First Tap was 2.6 ± 0.1 mg L^{-1} with a measured FAC dose of 2.6 ± 0.3 mg L^{-1}.

There were significant concentrations of three of the four TTHM4 species ($CHCl_3$, $CHBrCl_2$ and $CHBr_2Cl$) detected at the First Tap, but $CHBr_3$ was less than the MDL. These results indicated that the time required to reach the First Tap (assumed to be ~15 minutes) is long enough for THMs and HAAs formation to occur through conventional mechanisms. TN-15 was heavily prechlorinating their source water at the

time of sample collection. The THMs concentration profile was relatively flat and THMs concentrations were near those measured at the First Tap. Thus, when the First Tap THMs concentrations are used as a parameter for predicting the First Tap time, the model shows its limitations. The Kinetic Model predicts that 41 ± 19 % of the THAA3 and THAA9 observed at the First Tap is contributed by the hypochlorite solution. The Kinetic-Observed Model predicts a lower contribution more in line with the Dose-Dilution Model in this case, 13 ± 5 % for both THAA3 and THAA9 species.

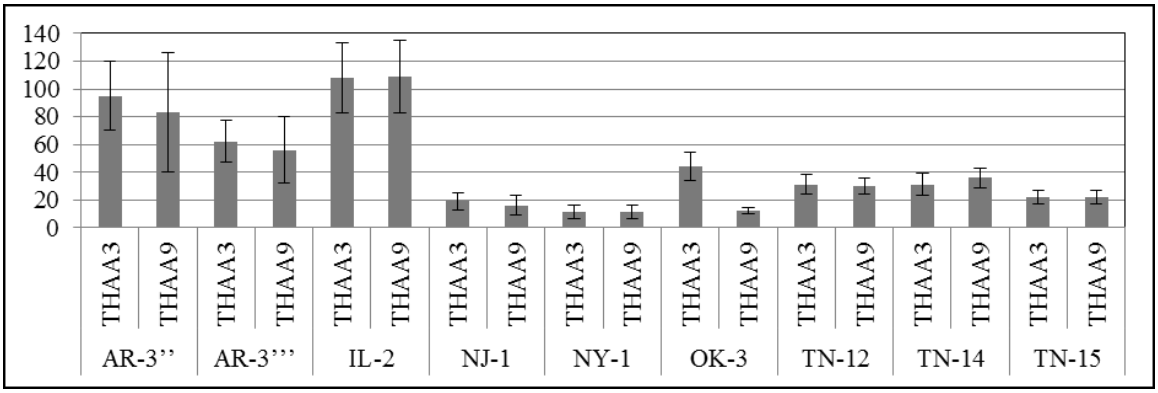
The results of both empirical models as well as the results from the Dose-Dilution model that was used in previous research are summarized in Table 6 and Figure 16. The best overall estimate is given by the Kinetic-Observed Model, discussed below. On average, when THAA3 is considered, 29 ± 15 % of the HAAs observed at the First Tap could be arising from hypochlorite solution. If we broaden the study to include THAA9, then this estimate changes to 28 ± 16 %, thus slightly less than one third of HAAs may be arising from HAAs present in the hypochlorite solution. In both cases, the percent contribution ranges from 7 to 46 %, meaning that anywhere from less than a tenth to almost one half of HAAs found at the First Tap could be contributed by the hypochlorite solution. Overall, the Kinetic Observed Model seems to provide the most consistent and conservative estimates of the percent contribution.

Conclusions

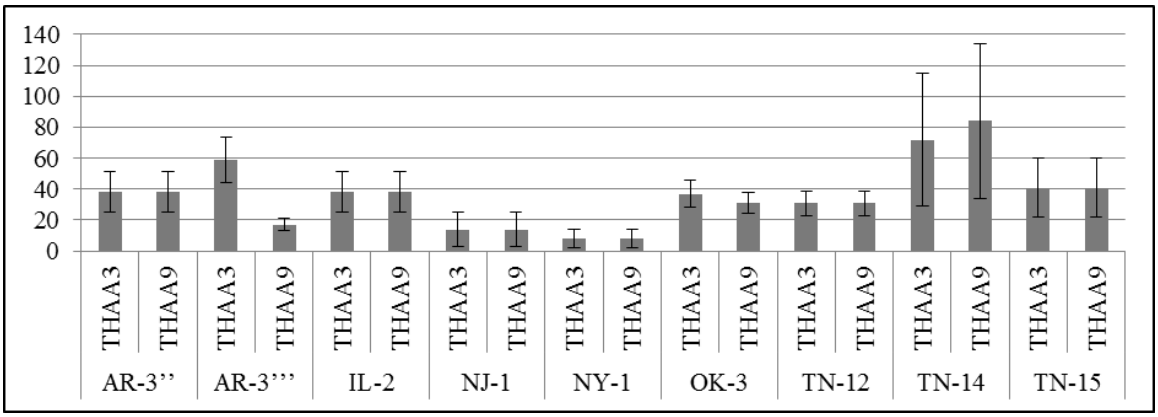
The Kinetic Model of the First Tap is more difficult to execute than the Dose-Dilution Model, but does not rely on USEPA 552.3 (2003). The individual measurements of each parameter are simpler to carry out, but there are more of them and can lead to

more errors propagated. Even with more measurement errors propagated, the Kinetic Model has propagated errors on par with those seen in Dose-Dilution Model. The Kinetic Model inherently provides more control than the Dose-Dilution Model because the measurement is carried out in the laboratory, thus the FAC dosing, mixing and sampling are all carried out identically, resulting in better comparisons across utilities.

Dose Dilution Model



Kinetic Model



Kinetic-Observed Model

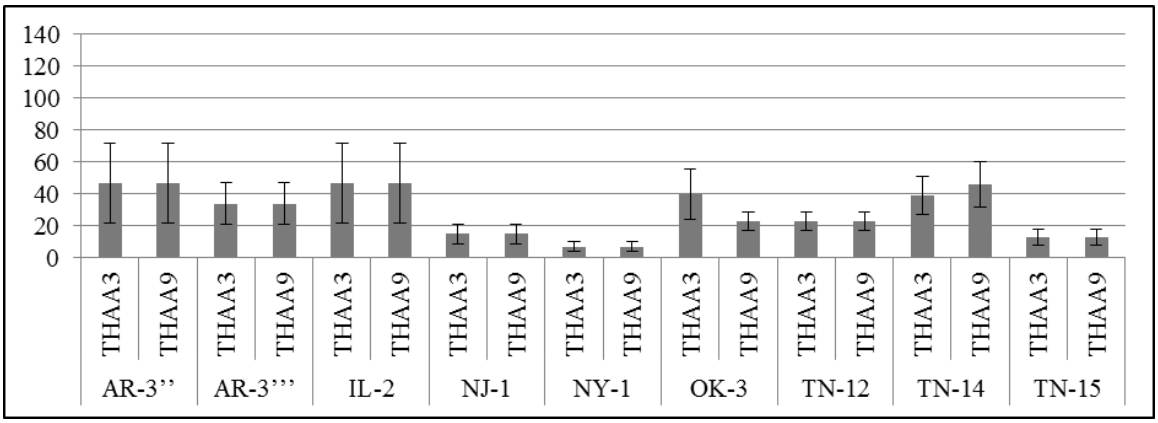


Figure 16 Graphical presentation summarizing the Percent Contribution of HAAs in hypochlorite solution to HAAs measured at the First Tap using the Dose-Dilution Model, the Kinetic Model, and the Kinetic-Observed Model.

The weakness of the Kinetic Model stems from fitting the formation of THMs and HAAs to first order kinetics. Previous studies that fit THMs and HAAs formation to kinetic rate laws focused on various timescales. Gallard and von Gunten (2002) focused on reaction times up to 500 hours (8 days) for DBPs formation using second order kinetics; Rossman et al. (2001) studied formation in a simulated distribution system on the time scale of 24 hours with second order fits; and Westerhoff et al. (2004) looked at formation on the 1 to 2 hours timescale using pseudo-first order and second order fits. The studies presented here were on the timescale of 1 – 4 hours and Westerhoff's timescales best match those presented here; however, Westerhoff controlled the types of TOC reacted (2004). Using the matrix as collected resulted in THMs and HAAs kinetic rate law fits, which included TOC that reacted at differing rates and resulted in weaker kinetic rate law fits.

The Kinetic-Observed Model alleviates the weakness of the Kinetic Model by limiting the need to use kinetic fits and instead interpolating the concentration versus time profile. The interpolation of concentration versus time profiles removes the differing rates of reaction noted by Gallard and von Gunten (2002), Rossman et al. (2001) and Westerhoff et al. (2004). This provides a more conservative modeling (fewer assumptions about the chemistry) of the HAAs formation and thus a more conservative estimate of the contribution of concentrations of HAAs present in hypochlorite solution to the concentrations of HAAs present at the First Tap.

In the end, the Kinetic Model is capable of distinguishing between HAAs from the bulk hypochlorite solution and those formed through conventional mechanisms, but it is more complex to carry out the measurements needed to make appropriate estimates.

The Kinetic-Observed Model is similar to the Kinetic Model, but provides estimates based upon observed HAAs rather than a kinetic model. Both the Kinetic and Kinetic-Observed Models tend to make more conservative (and perhaps realistic) estimates of the contribution of bulk hypochlorite solution HAAs to HAAs detected in the finished water.

Even with these conservative estimates, it is clear that the HAAs present in bulk hypochlorite solutions can be a significant contributor to the concentrations detected in finished water. On average, approximately 30% of the HAAs being detected in finished water could be a result of the dilution of bulk hypochlorite solutions. This has several implications for both water treatment plants as well as hypochlorite manufacturers.

From the standpoint of a water utility this could be seen as either an opportunity or an obligation. For a utility on the edge of being in compliance, it offers the chance to possibly reduce the HAAs found in their finished drinking water by taking steps to either limit the formation of or remove the HAAs found in their bulk hypochlorite solutions. However, depending on the changes to procedures or treatment processes this could also be a costly undertaking for a treatment plant. This could include temperature controlled storage, dilution of bulk solutions upon delivery, or additional filtering steps. The water treatment plants themselves are not responsible for what happens to the bulk hypochlorite solutions before they are delivered to the plant, this lies with the manufacturer.

In order for the formation of HAAs to occur in hypochlorite solutions, there needs to be the presence of organic precursors. There are several possible ways in which these could be introduced during the manufacturing or delivery process. In order to reduce the chance of this occurring, certain steps would need to be taken by manufactures. In the actual manufacturing process, quality control would need to be increased to ensure that

all of the raw materials being used were free of contamination. On the delivery side minimizing the amount of time that the solution spent in a non-climate controlled environment, such as a delivery truck, would be a practical solution. Whether it falls on the treatment plants or the manufacturers to take action, it is clear that the HAAs shown to be present in bulk hypochlorite solutions can have a significant contribution to the concentrations detected in finished drinking water.

Table 6. Summary of the results estimating the contribution of HAAs in hypochlorite solutions to the concentrations of HAAs found at the First Tap.

Site, Old Tap Time, (FAC Conc)	HAA Species	Meas. Conc. (μg L^{-1})	Dose-Dil. (μg L^{-1}) / (%)	Kinetic (μg L^{-1}) / (%)	Kinetic Obs. (μg L^{-1}) / (%)	MCL (%)
AR-3''						
t=2.8 hr	THAA3	3.5 ± 0.8	3.3 ± 0.5 / *(95 ± 25)*	8.8 ± 1.8 / *(38 ± 13)*	7.1 ± 3.6 / *(47 ± 25)*	*(6 ± 1)*
FAC=1.2 mg L^{-1}	THAA9	4.0 ± 2.0	3.3 ± 0.5 / *(83 ± 43)*	8.8 ± 1.8 / *(38 ± 13)*	7.1 ± 3.6 / *(47 ± 25)*	*(6 ± 1)*
AR-3'''						
T=2.0 hr	THAA3	4.6 ± 0.8	2.8 ± 0.5 / *(62 ± 15)*	4.8 ± 0.9 / (59 ± *15)*	5.2 ± 1.8 / (34 ± *13)*	*(5 ± 1)*
	THAA9	5.1 ± 2.0	2.8 ± 0.5 *(56 ± 24)*	16.4 ± 2.1 / (17 ± *4)*	5.2 ± 1.8 / (34 ± *13)*	*(5 ± 1)*
IL-2						
t=0.25 hr	THAA3	19.5 ± 1.5	21.2 ± 4.5 / (108 ± *25)*	64.8 ± 6.7 / (33 ± *8)*	67.4 ± 3.4 / (32 ± *7)*	*(35 ± 5)*
FAC=3.0 mg L^{-1}	THAA9	19.5 ± 1.5	21.2 ± 4.5 /(109 ± *26)*	64.8 ± 6.7 / (32 ± *7)*	67.4 ± 3.4 / (32 ± *7)*	*(35 ± 5)*
NJ-1						
t=4 hr	THAA3	5.4 ± 1.9	1.0 ± 0.2 / *(19 ± 6)*	7.6 ± 5.7 / *(14 ± 11)*	6.6 ± 5.7 / *(15 ± 6)*	*(2 ± 0)*
FAC=0.7 mg L^{-1}	THAA9	6.7 ± 2.1	1.0 ± 0.2 / *(16 ± 7)*	7.6 ± 5.7 / *(14 ± 11)*	6.6 ± 5.7 / *(15 ± 6)*	*(2 ± 0)*
Site, Old Tap Time, (FAC Conc)	HAA Species	Meas. Conc. (μg L^{-1})	Dose-Dil. (μg L^{-1}) / (%)	Kinetic (μg L^{-1}) / (%)	Kinetic Obs. (μg L^{-1}) / (%)	MCL (%)
NY-1						
t=1 hr	THAA3	11.5 ± 1.1	1.3 ± 0.6 / *(11 ± 5)*	16.1 ± 10.5 / *(8 ± 6)*	21.9 ± 1.5 / *(7 ± 3)*	*(2 ± 1)*
FAC=0.6 mg L^{-1}	THAA9	12.1 ± 2.1	1.3 ± 0.6 / *(11 ± 5)*	16.1 ± 10.5 /*(8 ± 6)*	21.9 ± 1.5 / *(7 ± 3)*	*(2 ± 1)*

Table 6 Continued						
OK-3						
t=5 hr	THAA3	*33.1 ± 1.2*	14.6 ± 3.0 / *(44 ± 10)*	39.3 ± 5.1 / *(37 ± 9)*	40.6 ± 7.4 / *(40 ± 16)*	*(24 ± 3)*
FAC=0.6 mg L^{-1}	THAA9	137.8 ± *2.9*	16.3 ± 3.1 / *(12 ± 2)*	52.3 ± 5.6 / *(31 ± 7)*	70.8 ± 6.9 / *(23 ± 6)*	*(27 ± 3)*
TN-12						
t=2 hr	THAA3	*26.3 ± 1.8*	8.2 ± 1.6 / *(31 ± 7)*	26.6 ± 4.1 / *(31 ± 8)*	34.3 ± 5.4 / *(23 ± 6)*	*(14 ± 2)*
FAC=2.0 mg L^{-1}	THAA9	27.0 ± *2.1*	8.2 ± 1.6 / *(30 ± 6)*	26.6 ± 4.1 / *(31 ± 8)*	34.3 ± 5.4 / *(23 ± 6)*	*(14 ± 2)*
TN-14						
t=2.2 hr	THAA3	*26.8 ± 1.8*	8.4 ± 1.7 / *(31 ± 8)*	11.6 ± 6.5 / *(72 ± 43)*	21.3 ± 4.9 / *(39 ± 12)*	*(14 ± 2)*
FAC=2.0 mg L^{-1}	THAA9	27.2 ± *2.0*	9.8 ± 1.8 / *(36 ± 7)*	11.6 ± 6.5 / *(84 ± 50)*	21.3 ± 4.9 / *(46 ± 14)*	*(16 ± 2)*
TN-15						
t=0.25 hr	THAA3	*22.3 ± 2.0*	4.9 ± 0.9 / *(22 ± 5)*	11.9 ± 5.1 / *(41 ± 19)*	37.9 ± 13.5 / *(13 ± 5)*	*(8 ± 1)*
FAC=2.6 mg L^{-1}	THAA9	22.3 ± *2.0*	4.9 ± 0.9 / *(22 ± 5)*	11.9 ± 5.1 / *(41 ± 19)*	37.9 ± 13.5 / *(13 ± 5)*	*(8 ± 1)*

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The main goal of this research was to develop a method that would allow for on-line near real time collection of trihalomethanes (THMs) concentrations over extended periods of time. Previous research (Brown et al., 2007; Brown & Emmert, 2006; Cao, 2004; Duty, 2000; Emmert et al., 2004a, 2004b,2006, 2007; Liao, 2001) has shown the viability of membrane based sampling methods coupled with gas chromatography for this type of analysis. Through this research it was possible to refine the capillary membrane sampling gas chromatography (CMS-GC) method to achieve new levels of on-line THMs monitoring and find new applications for the resulting data.

Conclusions for the THM-RR

Improvements upon the CMS-GC method led to the development of the commercially available THM Rapid Response system (THM-RR). The THM-RR has been used to collect unprecedented on-line near real-time THMs data. The THM-RR has demonstrated superior MDLs for both individual and Total THMs compared to earlier versions. The ruggedness and robustness of this new system has been shown through the longest on-line monitoring studies to date. The THM-RR system has been designed so that it can be operated and maintained by a typical water treatment operator. The entire process has been automated from sampling and sample analysis to data treatment and reporting. The result is plots of both individual and Total THMs concentrations that are automatically updated hourly. This simplification allows the instrument to be used as a type of "THMs meter" operating in near real-time. These plots can be superimposed over

the daily operations of the plant in order to determine reproducible patterns in the concentration of individual and Total THMs. This allows operators to identify cycles or patterns in their plant ("process map"). It also gives them the ability to respond in real time to changes that may occur in the system. The THM-RR has been use to provide insight on THMs production for a water treatment facility, which has been able to bring the WTP into control with respect to THMs, going from approximately a 15-20 μg L^{-1} range of concentrations to a consistent 20 ± 5 μg L^{-1}. This allows the utility to deliver more consistent water to their customers.

Future Work for the THM-RR

The ten month on-line study conducted at the Lebanon water treatment plant was the longest to date. It allowed for an unprecedented look into how THMs behave on time frames from hours to months. As the instrument continues to collect data, it will be important to determine patterns and trends on an even longer time frame. Looking at how THMs behave year to year could possibly provide new insights. Changes in the water treatment process, whether through experimentation or plant restructuring, will give valuable information on how different process affect THMs formation.

As more THM-RR instruments are introduced into additional water treatment facilities, it will be necessary to perform studies of similar length and detail as the one performed in Lebanon. By replicating this study at a various plants, additional information can be gathered that is not possible at a single plant. The large amount of variation that exists between treatment plants, source waters, and treatment processes and the effects this has on THMs formation needs to be investigated.

Studies into additional volatile organic compounds (VOCs) need to be performed. There are other halogenated VOCs that are regulated by the USEPA. It should be possible to use the current method, or easily adapt it to measure these compounds as well. While these other compounds are rarely found in drinking water, having the ability to measure these other compounds could open up other markets for the THM-RR such as wastewater treatment, industrial water treatment, and environmental sampling.

Conclusions for Empirical Model Comparisons

On-line monitoring studies were performed at three water treatment plants that varied in both size and treatment process. In addition to THMs data collected using the THM-RR system, other water quality data was obtained directly from the plant. Using four empirical models it was possible to calculate predicted Total THMs concentrations based on this water quality data. Using Bland-Altman analysis it was determined that there was a significant bias between the predicted values and the experimental values. Two different approaches were taken in order to fit the models to the experimental data. The first approach used a simple spreadsheet method to adjust individual parameters in order to observe the effects on the bias. This method was able to reduce the bias by altering one or two of the parameters of each model. The second approach used multivariate nonlinear regression to optimize each model based on the experimental values and water quality data. Using this second method it was possible to achieve the lowest bias calculated using Bland-Altman analysis. Comparing all of the models throughout all of the studies, it was determined that the model developed by Amy et al. (Amy et al., 1998) was the most robust. This model gave the lowest unadjusted bias at each site. All of the models were applied to systems that they were not originally

designed for and in some cases with slightly different parameters, such as TOC instead of DOC. Even so, it was possible, with adjustment, to achieve biases of less than 1.0 μg L^{-1} for all three sites with each model.

Future Work for Empirical Model Comparisons

Now that it has been established that it is possible to adjust an empirical model based on experimentally obtained THMs data, the next step would be to use this adjusted model to predict future THMs concentrations. With THM-RR instruments already in place at both the TN and AR sites it is possible to collect water quality data and attempt to predict the results of the THM-RR. Based on the results of this comparison, it can be determined if the adjusted empirical models are capable of accurate prediction or if further calibration is needed. Studies should be performed in additional water treatment systems.

Conclusions for THMs Formation Kinetics

While the Kinetic Model is a more difficult approach than the Dose-Dilution Model, it does not rely on the use of USEPA 552.3. While the individual measurements themselves are easier to obtain, the increased number of them can lead to an increased error when propagated. Even with the increased number of propagations, the Kinetic Model has errors similar to those seen with the Dose-Dilution Model. The Kinetic Model also allows for an increased level of control, since the experiment is carried out in the laboratory, which allows for increase reproducibility and consistency between utilities.

The weakness of the Kinetic Model comes from the use of first order kinetics. Studies from the literature attempting to fit THMs and HAAs formation to kinetic rate laws have used differing timescales. Gallard and von Gunten (2002) focused on reaction

times up to 500 hours (8 days) for DBPs formation using second order kinetics; Rossman et al. (2001) studied formation in a simulated distribution system on the time scale of 24 hours with second order fits; and Westerhoff et al. (2004) looked at formation on the 1 to 2 hours timescale using pseudo-first order and second order fits. The studies presented here were on the timescale of a few hours which match best with the studies done by Westerhoff et al. (2004); however, Westerhoff controlled the types of TOC reacted. By performing the studies in an unaltered matrix, TOC reacting at differing rates was present. This resulted in weaker kinetic rate law fits.

The Kinetic-Observed Model is able to avoid some of the weakness of the Kinetic Model by relying more on the interpolation of the concentration versus time instead of kinetic fits. By using this interpolation the effects of differing reaction rates are removed. Of all the models developed the Kinetic-Observed Model provided the most conservative estimate of HAAs concentration in hypochlorite solutions.

Future Work for THMs Formation Kinetics

This work was the first attempt at using membrane based gas chromatography methods to develop kinetic models for the formation of THMs. Improvements in instrumentation since the original project, the THM-RR system, could allow for more accurate fits. With increased sensitivity and full automation the THM-RR presents the opportunity to setup formation experiments that can be allowed to run for extended periods. If multiple THM-RR systems can be utilized to take alternating measurements then it would be possible to look at shorter time frames. Since the THM-RR is fully automated, these experiments could be allowed to run for extended periods of time

without requiring much attention. This would allow for both short term and long term formation to be observed from each experiment.

Controlled kinetics experiments within the laboratory would allow for the investigation into how specific parameters affect THMs formation. By systematically varying things such as TOC, chlorine dose, and pH the effects each has on the formation of THMs could be determined. This would lead to a better understanding of ways to reduce formation in treatment plants. New experiments need to be designed to account for alternative treatment processes such as chloramination.

References

Abdullah, M.P., Yee, L.F., Ata, S., Abdullah, A., Ishak, B., Abidin, K.N.Z. (2009). The study of interrelationship between raw water quality parameters, chlorine demand and the formation of disinfection by-products. Physics and Chemistry of the Earth, 34, 806-811.

Aeppli, C., Berg, M., Hofstetter, T.B., Kipfer, R., Schwarzenbach, R.P. (2008). Simultaneous quantification of polar and non-polar volatile organic compounds in water samples by direct aqueous injection-gas chromatography/mass spectrometry. Journal of Chromatography A, 1181 (1-2), 116-124.

Amy, G.L., Siddique, M., Ozekin, K., Zhu H.W., Wang, C. (1998). Empirical based models for predicting chlorination and ozonation byproducts: haloacetic acids, chloral hydrate, and bromate. USEPA 1998 EPA report CX 819579.

APHA-AWWA-WEF. (1994). *Standard methods for the examination of water and wastewater: 18th edition supplement*. American Public Health Association., American Water Works Association., Water Environment Federation (U.S.), & American Public Health Association. Washington, D.C.

Asami, M., Kosaka, K., Kunikane, S. (2009). Bromate, chlorate, chlorite and perchlorate in sodium hypochlorite solution used in water supply. Journal of Water Supply: Research and Technology.—*AQUA* 58(2), 107–115.

Bellar, T.A., Lichtenberg J.J., & Kroner, R.C. (1974, December). The occurrence of organohalides in chlorinated drinking waters. Journal of American Water Works Association.

Biziuk, M., Namiesnik, J., Czerwinski J., Gorlo, D., Makuch, B., Janicki, W., Polkowska Z., Wolska L. (1996). Occurrence and determination of organic pollutants in tap and surface waters of the Gdansk district. Journal of Chromatography A, 733 (1-2), 171-183.

Bland, J.M., Altman, D.G. (1986). Statistical methods for assessing agreement between two methods of clinical measurement. Lancet, i, 307-310.

Bland, J.M., Altman, D.G. (1987). Statistical methods for assessing agreement between measurement. Biochimica Clinica, 11, 399-404.

Bond, T., Goslan, E.H., Parsons, S.A., Jefferson, B. (2012). A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. Environmental Technology Reviews, 1, 93-113.

Boyce, S.D., Hornig, J.F. (1983). Reaction pathways of trihalomethanes formation from the halogenation of dihydroxyaromatic model compounds for humic acid. Environmental Science & Technology, 17(4), 202-211.

Brown, A.W., Simone, P.S., Jr., York, J.C., Emmert, G.L. (2014). A device for fully automated on-site process monitoring and control of trihalomethane concentrations in drinking water. Analytica Chimica Acta. Ms. No. ACA-14-1023.

Brown, D., Bridgeman, J., West, J.R. (2011a). Predicting chlorine decay and THM formation in water supply systems. Reviews in Environmental Science and Bio/Technology, 10, 79-99.

Brown, D., Bridgeman, J., West, J.R. (2011b). Understanding data requirements for trihalomethane formation modelling in water supply systems. Urban Water Journal, 8, 41-56.

Brown, M.A., Emmert, G.L. (2006). On-line monitoring of trihalomethanes concentrations in drinking water distribution systems using capillary membrane sampling-gas chromatography. Analytica Chimica Acta, 555, 75-83.

Brown, M.A., Miller, S., Emmert, G.L. (2007). On-line purge and trap gas chromatography for monitoring of trihalomethanes in drinking water distribution systems. Analytica Chimca Acta, 592, 154-161.

Brush, R.C., & Rice, G.W. (1994). Trihalomethanes produced in humic acid reactions- a GC-MS experiment for instrumental analysis. Journal of Chemical Education, 71(12), A293-296.

Bunce, N. (1994). Environmental Chemistry (2^{nd} ed.). Wuertz Publishing Ltd., Winnipeg, Canada.

Buszewski, B., Ligor, T. (2001). Application of different extraction methods for the quality control of water. Water, Air, & Soil Pollution. 129 (1-4), 155-165.

Cao, G. (2004). Further explorations of supported capillary membrane-gas chromatography. Unpublished master's thesis, University of Memphis, Memphis, TN.

Chaib, E., Moschandreas, D. (2008). Modeling daily variation of trihalomethane compounds in drinking water system, Houston, Texas. Journal of Hazardous Materials, 151, 662-668.

Chowdhury, S., Champagne, P., McLellan, P.J. (2009). Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review. Science of the Total Environment, 407, 4189-4026.

Courtis, B.J., West, J.R., Bridgeman, J. (2009). Chlorine demand-based predictive modeling of THM formation in water distribution networks. Urban Water Journal, 6, 407-415.

Chang, EE., Chiang, P.C., Chao, S.H., Lin, Y.L. (2006). Relationship between chlorine consumption and chlorination by-products formation for model compounds. Chemosphere, 64, 1196-1203.

Christian, G.D., Dasgupta, P.K., Shug, K.A. (2014). Analytical Chemistry, 7th ed., John Wiley and Sons, Inc., Hoboken, NJ.

Culea, M., Cozar, O., Ristoui, D. (2006) Methods validation for the determination of trihalomethanes in drinking water. Journal of Mass Spectrometry. 41 (12), 1594-1597.

Di Christo, C., Esposito, G., Leopardi, A. Modelling trihalomethanes formation in water supply systems. Environmental Technology, 34, 61-70.

Duty, C.N. (2000). Application of a supported capillary membrane sampler for the analysis of organic compounds in water. Unpublished master's thesis, Arkansas State University, Jonesboro, Arkasas.

Efron, B. (1982). The jackknife, the bootstrap, and other resampling plans. Capital City Press, Monpelier, VT, USA.

Emmert, G.L., Cao, G., Geme, G., Joshi, N., Rahman, M. (2004a). Methods for real-time measurements of THMs and HAAs in distribution systems. Denver, CO: AwwaRF-AWWA.

Emmert, G.L., Cao, G., Duty, C., & Wolcott, W. (2004b). Measuring trihalomethanes concentrations in water using supported capillary membrane sampling-gas chromatography. Talanta, 63 (3), 675-682.

Emmert, G.L., Brown, M.A., Liao, Z., Cao, G., Duty, C. (2006). Supported capillary membrane sampling-gas chromatography on a valve with a pulsed discharge photoionization detector. Analytica Chimica Acta, 560(1-2), 197-206.

Emmert, G.L., Brown, M.A., Simone, P.S., & Geme, G. (2007). Methods for real-time measurement of THMs and HAAs in distribution systems part 2. Denver, CO: AwwaRF-AWWA.

Emmert, G.L., Geme, G., Brown, M.A., Simone, P.S. (2009) A single automated instrument for monitoring total trihalomethane and total haloacetic acid concentrations in near real-time. Analytica Chimica Acta, 656, 1-7.

Emmert, G.L., Brown, M.A. (2012). On-line analysis for the quantification of trihalomethanes species within drinking water supplies, US Patent 8,336,371, Patent awarded December 25, 2012.

Emmert, G.L., Simone Jr., P.S., Choo, Y.Y., Henson, C.M., Brown, A.W., Watts III, T.E., Stephens III, W.E., Williamson, J.P., Ranaivo, P.L. (2012) Investigating the presence of HAAs and THMs in sodium hypochlorite feedstocks used for drinking water disinfection. Final Report. Water Research Foundation Press. Denver, CO.

Environmental Working Group, National Drinking Water Database (2014), http://www.ewg.org/tap-water/ , April 5, 2014.

Federal Register (1986), Appendix B, Part B, Part 136-Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11.

Gallard H., von Gunten U. (2002). Chlorination of natural organic matter: kinetics of chlorination and of THM formation. Water Research. 36(1), 65-74.

Gang, D., Clevenger, T., Banerji, S.K. (2003). Relationship of chlorine decay and THMs formation to NOM size. Journal of Hazardous Material, A96, 1-12.

Garcia-Villanova, R.J., Leite, M.V.O.D., Hierro, J.M.H., de Castro Alfageme, S., Hernandez, C.G. (2010). Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins. *Sci. Total Environ.* 408, 2616-2620.

Glaser, J.A., Forest, D.L., Mckee, G.D., Quave, S.A., Budde, W.L. (1981). Trace analysis of wastewaters. Environmental Science and Technology, 15, 1426-1435.

Golfinopoulos, S.K., Lekkas, T.D., Nikolaou A.D. (2001). Comparison of methods for determination of volatile organic compounds in drinking water. Chemosphere, 45 (3), 275-284.

Gonzalez-Gago, A., Marchante-Gayon, J.M., Alonso, J.I.G. (2007). Determination of trihalomethanes in drinking water by GC-ICP-MS using compound independent calibration with internal standard. Journal of Analytical Atomic Spectrometry. 22, 1138-1144.

Gordon, G. L.C. Adam, B.P. Bubnis, B. Hoyt, S.J. Gillette, A. Wilczak. (1993). Controlling the formation of chlorate ion in liquid hypochlorite feedstocks. *J. AWWA* 85(9), 89-97.

Gordon, G. L. Adam, B. Bubnis. (1995). Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion is the Chlorinating Agent. Awwa-RF, Denver, CO.

Greenberg, A.E., Clesceri, L.S., Eaton, A.D. (1992). Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, Washington, DC.

Hach. (2006). Pocket Colorimeter II Analysis Systems. (2006-2009) Hach Company, USA.

Harris, D.C. (1997). Quantitative Chemical Analysis. 4th ed., W.H. Freeman and Company, New York, NY, 48-52.

Krasner, S.W., H.W. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Sclimenti, G.D. Onstad, A.D. Thruston, Jr. (2006). Occurrence of a New Generation of Disinfection Byproducts. *Environ. Sci. Technol.* 40, 7175-7185.

Krasner, S.W. (2009). The formation and control of emerging disinfection by-products of health concern. *Phil. Trans. R. Soc. A* 367, 4077-4095.

Kolb, B., Ettre, L.S. (2006). Static headspace-gas chromatography: theory and practice, 2nd ed., John Wiley & Sons, New Jersey, United States.

Kuivinen, J., Johnsson, H. (1999). Determination of trihalomethanes and some chlorinated solvents in drinking water by headspace technique with capillary column gas-chromatography. Water Research. 33 (5), 1201-1208.

Leivadara, S.V., Nikolaou, A.D., Lekkas, T.D (2008). Determination of organic compounds in bottled waters. Food Chemistry, 108 (1), 277-286.

Liao, Z. (2001). Development of a supported capillary membrane sampler-gas chromatograph for the analysis of volatile organic compounds in water. Unpublished master's thesis. Arkasas State University, Jonesboro, Arkasas.

Liu, S., Zhu, Z., Fan, C., Qiu, Y., Zhao, J. (2011). Seasonal variation effects on the formation of trihalomethane during chlorination of water from Yangtze River and associated cancer risk assessment. Journal of Environmental Sciences, 23, 1503-1511.

Nguyen, H.V., Lee, M., Hur, J., Schlautman, M.A. (2013). Variations in spectroscopic characteristics and disinfection byproduct formation potentials of dissolved organic matter for two contrasting storm events. Journal of Hydrology, 481, 132-142.

Nikolaou, A.D., Lekkas, T.D., Golfinopoulus, S.K. (2002). Application of different analytical methods for determination of volatile chlorination by-products in drinking water. Talanta, 56 (4), 717-726.

Nikolaou, A.D., Golfinopoulus, S.K., Rizzo, L., Lofrano, G., Lekkas, T.D., Belgiorno, V. (2005). Optimization of analytical methods for the determination of DBPs: Application to drinking waters from Greece and Italy. Desalination, 176 (1-3), 25-36.

Oliver, B.G., Lawrence, J. (1979, March). Haloforms in drinking water: A study of precursors and precursor removal. Journal of the American Water Works Association.

Parvez, S., Rivera-Núñez, Z., Meyer, A., Wright, J.M. (2011). Temporal variability in trihalomethane and haloacetic acid concentrations in Massachusetts public drinking water systems. Environmental Research, 111, 499-509.

Pavon, J.L.P., Martin, S.H., Pinto, C.G., Cordero, B.M. (2008). Determination of trihalomethanes in water samples: A review. Analytica Chimica Acta 629, 6-23.

Pereira, V.J., Weinberg, H.S., Singer, P.C. (2004). Temporal and spatial variability of DBPs in a chloraminated distribution system. Journal of the American Water Works Association, 96, 91-102.

Peters, C.J., Young, R.J., Perry, R. (1980). Factors influencing the formation of haloforms in chlorination of humic materials. Environmental Science & Technology, 14(11), 1391-1395.

Platikanov, S., Puig, X., Martin, J., Tauler, R. (2007). Chemometric modeling and prediction of trihalomethane formation in Barcelona's water works plant. Water Research, 41, 3394-3406.

Polkowska, Z. (2004). Determination of volatile organohalogen compounds in urban precipitation in Tricity area (Gdansk, Gydnia, Sopot). Chemosphere, 57 (10), 1265-1274.

Pyle, S.M., Gurka, D.F. (1994). Volatile organic analysis by direct aqueous injection. Talanta, 41 (11), 1845-1852.

Ranaivo, P.L., Henson, C.M., Simone Jr., P.S., Emmert, G.L. (2011). Analysis of haloacetic acids in drinking water using post-column reaction-ion chromatography with on-line internal standardization. Analytical Methods, 3, 2873-2880.

Richardson, S.D. (2003). Disinfection by-products and other emerging contaminants in drinking water. Trends in Analytical Chemistry, 22(10), 666-684.

Richardson, S.D., Ternes, T.A. (2011). Water Analysis: Emerging Contaminants and Current Issues. Analytical Chemistry, 83, 4614-4648.

Richardson, S. D., Postigo C. (2012). Drinking Water Disinfection By-Products. Chapter 4, The Handbook of Environmental Chemistry: Emerging Organic Contaminants and Human Health. Springer, New York, NY, 20:93 - 137.

Rodriguez, M.J., Serodes, J., Morin, M., (2000). Estimation of water utility compliance with trihalomethanes regulations using modelling approach. Journal of Water Supply: Research and Technology, 49(2), 57-73.

Rook, J.J. (1974). Formation of haloforms during chlorination of natural waters, Water Treatment and Examination, 23, 234-243.

Rook, J.J. (1977). Chlorination reactions of fulvic acids in natural waters. Environmental Science & Technology, 11(5), 478-482.

Rossman, L.A., Brown, R.A., Singer, P.C., Nuckols, J.R.(2001). DBP Formation Kinetics in a Simulated Distribution System. Water Research, 35(14), 3483-3489.

Sadiq, R., Rodriguez, M.J. (2004). Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. Science of the Total Environment, 321, 21-46.

Sawyer, C. N., McCarty, P. L., Parkin, G. F. (2003). Chemistry for environmental engineering and science. 5th ed. Boston: McGraw-Hill.

Serodes, J.B., Rodriguez, M.J., Li, H., Bouchard, C. (2003). Occurrence of THMs and HAAs in experimental chlorinated waters of the Quebec City area. Chemosphere, 51, 253-263.

Shao, J., Tu, D. (1995). The Jackknife and Bootstrap. Springer-Verlag, New York, NY, pp. 281.

Simone, P.S., Anderson, G. T., Emmert, G. L. (2006). On-line monitoring of µg/L levels of haloacetic acids using ion chromatography with post-column nicotinamide reaction and fluorescence detection. Analytica Chimica Acta, 570(2), 259-266.

Simone, Jr., P.S., Ranaivo, P.L., Geme, G., Brown, M.A., Emmert, G.L. (2009). On-line Monitoring of Nine Haloacetic Acid Species at the µg L^{-1} Level Using Post-Column Reaction-Ion Chromatography with Nicotinamide Fluorescence. Analytica Chimica Acta, 654, 133-140.

Skoog, D.A., Holler, F.H., Nieman, T.A., in: Sherman, M., Bortel, J. (Eds.) (1998). Principles of instrumental analysis, 5th ed., Saunders College Publishing, USA, 11-17.

Snyder, S.A., Stanford, B.D., Pisarenko, A.N., Gordon, G., Asami, M. (2009). *Hypochlorite – An Assessment of Factors that Influence the Formation of Perchlorate and Other Contaminants.* American Water Works Association and Water Research Foundation.

Stanford, B.D., Pisarenko, A.N., Snyder, S.A., Gordon, G. (2011). Perchlorate, bromate, and chlorate in hypochlorite solutions: Guidelines for utiltites. Journal of the American Water Works Association, 103(6), 1 – 13.

Toroz, I., Uyak, V. (2005). Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City. Desalination, 176, 127-141.

USEPA (1995a). Method 502.2: *volatile organic compounds in water by purge and trap capillary gas chromatography with a photoionization and electrolytic conductivity detector in series*. Cincinnati, OH: USEPA, Environmental Monitoring and System Laboratory.

USEPA (1995b). Method 524.2: *Measurement of purgeable organic compounds in waterby capillary gas chromatography/mass spectrometry*. Cincinnati, OH: USEPA, Environmental Monitoring and System Laboratory.

USEPA (1995c). Method 551: *Determination of chlorination disinfection by-products and chlorinated solvents in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection*. Cincinnati, OH: USEPA, Environmental Monitoring and System Laboratory.

USEPA. (1996a). Appendix B, Part 136-Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11. *Fed. Reg*. 40 CFR 136,303-306.

USEPA. (1996b). *DBP/ICR Analytical Methods Manual*, USEPA, Office of Water. USEPA 814-B-96-002, Cincinnati, OH.

USEPA (1998), National primary drinking water regulations: disinfectants and disinfection by-products rule: final rule. *Federal Register*, 63, 241, 68390, December 16, 1998.

USEPA (2003). Method 552.3: *Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection*, Environmental Monitoring and System Laboratory, Cincinnati, OH.

USEPA (2006), National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection By-products Rule: Final Rule. Fed. Reg. 40 CFR Parts 9, 141, and 142, 71, 387–493, January 4, 2006.

USEPA (2013), National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection By-products Rule: Final Rule. Fed. Reg. 40 CFR Parts 9, 141, and 142, 71, 387–493, http://www.epa.gov/ogwdw/disinfection/stage2/.

Uyak, V., Toroz, I., Meric, S. (2005). Monitoring and modeling of trihalomethanes (THMs) for a water treatment plant in Istanbul. Desalination, 176, 91-101.

Villanueva, C.M., Gagniere, B., Montfort, C., Nieuwenhuijsen, M.J., Cordier, S. (2007). Sources of variability in levels and exposure of trihalomethanes. Environmental Research, 103, 211-220.

Westerhoff, P., Chao, P., Mash, H. (2004). Reactivity of natural organic matter with aqueous chlorine and bromine. Water Research, 38, 1502-1513.

Zhao, Z., Gu, J., Fan, X., Li, H. (2006). Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethanes formation characteristics with chlorine and chlorine dioxide treatments. Journal of Hazardous Materials, B134, 60-66.