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I, Bryant E McDonnell, hereby submit this original work as part of the requirements for the degree of Master of Science in Environmental Engineering.

It is entitled:

Controlling disinfection by-products within a distribution system by implementing bubble aeration within storage tanks

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CONTROLLING DISINFECTION BY-PRODUCTS WITHIN A DISTRIBUTION SYSTEM BY IMPLEMENTING BUBBLE AERATION WITHIN STORAGE TANKS

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Abstract

Disinfection by-product formation within drinking water distribution systems is an inevitable circumstance due to reactions between residual chlorine and organic matter. While regulated compounds must be below the maximum contaminant levels, utilities face many challenges such as more stringent regulations, excess capacity within distribution systems, and changes in consumer demands (e.g., conservation efforts) that can compromise a utility’s ability to meet water quality regulations. One technology that can be an effective part of a THM management strategy is aeration. Thus, the overall objective of the research was to evaluate fine bubble aeration as an in-system THM mitigation strategy to satisfy distribution system regulatory concentrations.

The first part of the study performed controlled experiments using a laboratory-scale reactor to estimate the parameters of an aeration model that accounts for both bubble and surface aeration contributions. The resulting model adequately represented THM removal over a range of experimental conditions, and included surface mass transfer coefficients as a function of airflow rate that accounted for changes in tank surface area and volume. The second part of the study developed a complete model of a real-world tank, which included chlorine decay and THM formation, and demonstrated that the model (developed in the laboratory) performed very well when applied to a real-world tank system. The last step of the research incorporated the aeration model into a distribution system hydraulic and water quality solver and demonstrated that aeration could have a significant impact on distribution system THM concentrations.

The development and evaluation of the aeration model provide a modeling framework that can be used as part of a design and operational decision making framework associated with fine bubble aeration as part of a comprehensive THM mitigation strategy.
Acknowledgements

My great experiences and time at the University of Cincinnati during my Master’s will remain unforgettable in my mind. Many of these experiences include wonderful friendships, valuable research experiences, practical jokes on colleagues and professors, tantalizing late-night laboratory work, and etc. All of which played a significant role in the success of my research, work, and interests.

“If you cannot approach your hardships in life with a smile you will be defeated.” - the wise African

Peers and professors at UC have helped me meet my goals of taking further involvement in humanitarian work in the developing world by introducing me to the Village Life Outreach Project. Among the many enriching experiences I have had within my timespan at UC, perhaps the most exhilarating was traveling solo through four countries in East Africa by bus, battling the convolution of transportation logistics and language barriers as I made my way to and through rural Tanzania. Before one of my many 14 hours bus rides began during the long journey from Rwanda to Tanzania via Uganda, a life lesson came to me while watching an old African man doing back-breaking work, loading heavy cylindrical bags, perhaps weighing 150 pounds each. As he passed by, straining and sweating, he said to me with a smile on his face, “if you cannot approach your hardships in life with a smile you will be defeated.”

I would like to thank U.S. Environmental Protection Agency for its financial contributions, enabling this research opportunity in the first place and partnering utility, The Las Vegas Valley Water District. I appreciate Mao Fang and Laura Jacobsen for their rapid responses to our questions and data needs enabling us to forward with this study. Next, I would like to extend my gratitude to my advisor Dr. Dominic Boccelli. Your patience and guidance has been crucial during our progress as we
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Lastly, and most importantly, I would like to thank my mother, Lisa, my father Tim, my sister Tara, and my inamorata, Brittany for all of the needed encouragement and support. There were many instances where your excitement for me being on my path gave me the motivation I needed to keep pushing through.
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Chapter 1

Introduction and Background

The final stages of drinking water treatment processes include a form of primary disinfection, commonly by means of free chlorine or chloramines, as a step to ensure microbial safe effluent water quality. Whether or not a public water utility (PWU) uses a form of chlorination as a primary disinfectant, finished waters leaving a drinking water treatment plant are dosed with a secondary disinfectant of, most commonly, residual chlorine, to provide continued protection against biological contaminants during the hydraulic travel time to the consumers. While residual chlorine serves as a barrier to protect public health from pathogens, the presence of chlorine in treated water produces the formation of disinfection by-products (DBPs) through side reactions with natural organic matter (NOM) that is generally comprised of humic and fulvic acids such as decaying leaf matter (Xie, 2004). These DBPs, some of which are suspected carcinogens, are regulated under the Safe Drinking Water Act of 1974, and, specific to water supply and distribution, the Disinfectants and Disinfection By-Product Rules (DBPRs). The latest DBPR Stage II, effective 2012, provides constraints on how DBPs should be monitored throughout a distribution system as well as MCLs for select DBP groups that include total trihalomethanes
(THMs; 80 \mu g/L) and haloacetic acids (HAAs; 60 \mu g/L) (USEPA, 2006).

The ability of PWUs to maintain disinfectant residuals for microbial protection while satisfying DBP MCLs is a challenging trade-off due to tighter legislation, excess capacity within the distribution system, and changes in water usage such as through conservation efforts. With respect to regulatory changes, the original Stage 1 DBPR was passed in December 1998 that set the MCLs on various DPS and provided monitoring practices that required samples to be collected from areas with the highest water age over the course of one year (USEPA, 1998). These resulting system sample concentrations were to be averaged together and the running annual average of the water concentrations were required to be at or below the MCL. More recently, the Stage 2 DBPR has introduced more stringent monitoring and reporting requirements. Under this new DBPR, utilizes will, dependent upon classification, be required to perform an initial distribution system evaluation to identify locations with high DBP concentrations, which account for both residence time and water quality conditions, and sample more frequently. Additionally, reporting must now be performed as a locational running annual average (LRAA), rather than a “system-wide” average, with each LRAA maintained at or below the MCL (USEPA, 2006). In addition to regulatory changes, the characteristics of the water distribution infrastructure can also contribute to DBP formation. From a water quality perspective, distribution systems are already oversized, to maintain firefighting capacity, resulting in hydraulic residence times that promote the formation of DBPs. More recently, the recent “boom-bust” cycle of the housing market has, at least temporarily, resulted in even greater excess capacity in some markets that will further exacerbate the hydraulic residence times. Ironically, water conservation efforts may have similar impacts on water quality issues by reducing system demand and increasing the hydraulic residence times allowing the reactions that form DBPs to go further to completion. Further influences that may impact water quality through increasing THM formation potential or rates are in-
creased water temperatures (Garcia-Villanova et al., 1997), pipe wall accumulation of organic matter (Rossman et al., 2001), and changes in source water quality.

Strategies for controlling THM formation rates and formation potential to satisfy regulations can be applied to the operation of a current water utility either at the treatment plant or within the distribution system. As the precursor to THM formation is post-treatment carry-over of NOM in the effluent water, improving NOM removal can be one of the most effective approaches to combat DBP formation. One common approach for NOM removal is the optimization of coagulant dose to increase NOM removal. However, there are other mechanistic processes that have demonstrated high NOM removal, including adsorption through granular activated carbon (GAC) (Banks and Wilson, 2002, Kim and Kang, 2008, Potwora, 2006), ultra and nano membrane filtration (Costa and de Pinho, 2006), and slow sand filtration (Logsdon et al., 2002). Further viable options at the treatment plant include changes in chlorination strategy, such as switching disinfectants from chlorine to chloramine, or prechlorinating at the front of the treatment plant and employing a technology such as GAC or air-stripping to remove existing THMs before the water enters the distribution system.

Within the distribution system, the THM formation rate and potential may be reduced by utilizing re-chlorination at distributed locations throughout the distribution system (e.g., Boccelli et al. (1998)). Re-chlorination strategies are intended to reduce the “high” residual doses at the treatment plant and supplement with disinfectant addition throughout the system to ensure adequate residuals are maintained with the intent of reducing the THM formation rate (due to lower chlorine concentrations) and potential (by applying an overall smaller mass of chlorine). In addition to altering disinfectant strategies to impact DBP formation rate and potential, removal strategies may also play a role in DBP mitigation. On a small-scale, there are sev-
eral available point-of-use (POU) commercial applications capable of removing THMs such as: GAC, reverse osmosis membrane filtration, and aeration systems (Harrison, 1999). Generally, POU technologies are engineered to perform best at the household or building level, but ensuring adequate operation to satisfy regulatory compliance becomes a challenging issue. Large-scale, post-treatment DBP removal strategies within a distribution system have generally been focused on aeration technologies (Brooke and Collins, 2011, Sherant, 2008), and is the primary focus of the current study.

Effective aeration strategies to decrease THM concentrations include, spray aeration (Brooke and Collins, 2011), surface mixing mechanical aeration (Hsueh et al., 1991, Munz and Roberts, 1989, Peng et al., 1995, Roberts and Dändliker, 1983), air-stripping towers (Harrison et al., 1993) and bubble aeration (Albin and Holdren, 1985, Matter-Müller et al., 1981, Monteith et al., 2005, Roberts et al., 1984, Sherant, 2008). The common objective associated with the mass transport mechanism for the above THM removal strategies is primarily to increase the water-to-air interfacial area that improves the volatilization rates. However, for surface mixing and bubble aeration technologies, mass may leave the system by either entering into a bubble with subsequent removal or across top liquid surface of the reactor that can be enhanced by mixing intensity. The mixing intensity (whether that be mechanical or from the bubble action) can be equated to the amount of “power” introduced into the system with increasing power per volume shown to have an impact on surface transport rates (Hsueh et al., 1991, Roberts and Dändliker, 1983).

The overall objective of this study was to assess the capability of fine bubble aeration to be part of an adaptation strategy to maintain satisfactory THM levels within a distribution system. The individual objectives of the study were to:

1. perform controlled laboratory-scale experiments to develop and estimate the
mass transport parameters of a fine bubble aeration model for estimating THM removal;

2. develop a model of an actual distribution system storage tank outfitted with a fine bubble aeration system, and evaluate the capability of the aeration model to represent dynamic condition; and

3. assess the potential impact that aeration has on THM reduction within a distribution system through large-scale modeling.
Chapter 2

Materials and Methods

The following chapter presents the materials and methods of the study in three sections. The first part describes the controlled laboratory experimentation and associated modeling, the second discusses the experimental design and modeling associated with our partner utilities’ aeration basin, and the final part presents the methods and modeling to assess the impacts of a DBP control mechanism on a system-wide scale.

2.1 Reactor Experimentation and Modeling

The following sections present the reactor design, experimental details, and modeling approach associated with evaluating THM removal via air stripping in a batch system.

2.1.1 Reactor Design

The reactor design was intended to replicate the aeration system in operation within a storage basin of our partner utility – Las Vegas Valley Water District (LVVWD) – to assess THM removal via fine bubble aeration. Figure 2.1 shows the column reactor
that was operated as a batch reactor to assess the removal potential of fine bubble aer-
ation with respect to the four individual THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform). The reactor was constructed out of sched-
ule 80 polyvinylchloride (PVC) circular pipe 15 feet tall with an inside diameter of 1 foot. A circular FlexAir aeration membrane disk made of ethylene propylene diene monomer (M-class) (EPDM) rubber with an effective diameter of 7 inches served as the fine bubble aerator and was similar to the type of aeration plates installed by LVVWD. The membrane was estimated to supply bubbles with an average diam-
eter of 2-mm and range of 0.5-mm to 4-mm, according to the membrane technical specifications from Environmental Dynamics International (2010a,b).

Figure 2.2 shows a schematic of the airflow and water feed system of the column reactor. Compressed air (provided by the central supply at the University of Cincin-
nati) was passed through a filter / regulator unit to remove aerosolized particulate matter. An airflow meter, following the filter, provided a graduated operating range between zero-detection flow and 6 standard cubic feet per minute (SCFM). Water was pumped into the column from underneath the membrane plate though the liquid flow tube (Figure 2.2), which was intended to limit the volatilization of spiked THMs by decreasing turbulence between the gas and liquid phases. As the column filled, the water level was observed through a piezometer spanning the height of the reactor.

Figure 2.3 illustrates the location of the aeration membrane as well as the seventeen sampling ports. The sampling ports each extended into the column 1.5 inches normal to the column wall to avoid any potential wall dynamic effects. The sample ports were spatially positioned, in feet, more densely over the lower portion of the column and less dense toward the top and located at 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 11 and 11.5 ft above the membrane. One sampling port was located underneath aeration membrane plate, which was labeled 00.
Figure 2.1: Photograph of aeration column located in Rhodes Hall High Bay.
Figure 2.2: Column reactor airflow control and monitoring schematic.

Figure 2.3: Schematic representation of the fine bubble membrane column reactor.
2.1.1.1 Reactor Assumption: Mixing

Using the bubble diameter estimations provided by Environmental Dynamics International (2010a,b), the bubble rise velocity within the column reactor was estimated to be $\sim 22 \text{ cm/sec}$ for a 2-mm diameter bubble according to Stoke’s Law for transitional flow (further details can be found in Appendix A). Given the 1-ft column diameter, an estimated rise velocity greater than $\sim 8 \text{ cm/sec}$, and a bubble diameter greater than or equal to 2-mm, the reactor was assumed to operate in a turbulent mixing regime (Shah et al., 1982). To verify the completely mixed assumption, experiments were performed with a water column height of 11 ft and an air flow rate of 2 SCFM. Nine samples were taken along the height of the column at four time intervals (15, 30, 60, and 120 minutes) with the results evaluated to determine if a spatial concentration gradient existed along the column height. The results did not demonstrate any significant spatial correlation (i.e., concentration gradient) along the column height, suggesting that the completely mixed assumption was satisfactory. The experimental details and supporting results assessing the mixing conditions can be found in Appendix A.

2.1.2 Experimental Design

The following sections present the details associated with performing controlled aeration experiments for evaluating THM removal using air stripping.

2.1.2.1 General Procedures

All experiments were performed with Cincinnati tap water and, in most cases, the batch of water used in an experiment was allowed to reach room temperature over night prior to running an experiment. All glassware was cleaned according to the “uni-
form formation condition” procedure in Summers et al. (1996). Prior to performing any experiment, the water was dosed with sodium thiosulfate to remove all residual chlorine to stop any additional THM formation. Chlorine concentrations were measured using the DPD colorimetric method (Hach Method 8021). Water samples were collected from the column at the initial time step, $t_0$, from predefined sampling ports (dependent on the particular experiment; discussed in the following sections) to determine the initial THM concentrations. After the initial samples were taken, the air supply was operated to achieve the desired air flow rate for the specific experimental run. At predefined sampling times, the aeration was stopped and samples were taken in accordance to the procedures of Summers et al. (1996): rinse the vials twice, fill, and cap with zero headspace. These experimental sampling steps were repeated at subsequent sampling times until the final sampling step was reached.

2.1.2.2 Mass Transport Rate Experiments

The experimental design consisted of a full factorial experimental design including three air flow rates (1, 2, and 4 SCFM), two water depths (6 and 11 ft), and two initial THM concentrations (approximately 50 and 150 µg/L). The range of these experimental variables was intended to represent the anticipated operating conditions and THM concentrations associated with our partner utility. Table 2.1 presents the experimental design matrix including air flow rate, water depth, initial THM concentration, water temperature, and pH.

At $t_0$, initial water samples were collected from three different depths to determine the initial THM concentrations. At all other time steps, samples were collected from five different depths. Tables 2.2 and 2.3 provide the sampling depths for experiments performed at water levels of 11 ft and 6 ft, respectively. The sampling time steps were 15, 30, 60, 120, and 240 minutes after $t_0$ with the exception of Run 10 (Table 2.1) in
Table 2.1: Experimental conditions evaluated to assess aeration as a mitigation strategy and support parameter estimation efforts.

<table>
<thead>
<tr>
<th>Run</th>
<th>Airflow (SCFM)</th>
<th>Height (ft)</th>
<th>Initial Conc. (µg/L)</th>
<th>Temp (°C)</th>
<th>pH¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5</td>
<td>50</td>
<td>23</td>
<td>7.39</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>11</td>
<td>50</td>
<td>25.5</td>
<td>7.97</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>6</td>
<td>150</td>
<td>26</td>
<td>7.93</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>11</td>
<td>150</td>
<td>21.5</td>
<td>7.52</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>6</td>
<td>50</td>
<td>17</td>
<td>7.90</td>
</tr>
<tr>
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<td>2</td>
<td>11</td>
<td>50</td>
<td>23</td>
<td>7.69</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>6</td>
<td>150</td>
<td>23</td>
<td>8.17</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>11</td>
<td>150</td>
<td>19</td>
<td>7.92</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>6</td>
<td>50</td>
<td>22.3</td>
<td>8.13</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>11</td>
<td>50</td>
<td>23</td>
<td>7.56</td>
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<td>8.23</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
<td>11</td>
<td>150</td>
<td>23</td>
<td>7.56</td>
</tr>
</tbody>
</table>

¹Measured initially during respective experimental run.

which the 240 minute samples were replaced with a sample taken after 180 minutes.

Table 2.2: Sampling locations and times for the experiments performed at a water depth of 11 ft; each sampling position is denoted by ‘X’.

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>Height (ft)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>240¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11</td>
<td>H</td>
<td>E</td>
<td>I</td>
<td>G</td>
<td>H</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>3</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>0</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

¹Time step 5 of experimental run 10 was taken at 180 minutes

2.1.2.3 Trihalomethane Analysis

Samples were analyzed for individual trihalomethane concentrations using EPA Method 524.3: *Measurement of Purgable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*. Liquid samples were loaded into a 5-mL
Table 2.3: Sampling locations and times for the experiments performed at a water depth of 6 ft; each sampling position is denoted by ‘X’.

<table>
<thead>
<tr>
<th>Height (ft)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>H</td>
<td>E</td>
<td>I</td>
<td>G</td>
<td>H</td>
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<tr>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
</tr>
<tr>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>2</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

gas-tight injection syringe with an internal standard of fluorobenzene and surrogate of 1,2-dichlorobenzene-d₄ injected into the syringe to concentrations of 5 µg/L. Samples were injected into a Tekmar purge and trap, and purged with ultra high purity helium for 11 minutes. The purged sample was then desorbed from the trap for analysis and quantified using an Agilent 7890A gas chromatograph (GC) in conjunction with an Agilent 5975C mass spectrometer detector (MSD). The GC was outfitted with a Restek RTX-VRX capillary column (30 m, 0.25 mm I.D., 1.4 µm) and the MSD operated in scan mode. Two primary dilution standards (PDSs) at concentrations of 10 µg/mL and 100 µg/mL were produced from 2000 µg/mL stock standards, which came in certified 1 mL sealed ampules. Each calibration standard was prepared in a 100 mL volumetric flask, and was used to rinse the 5 mL injection syringe three times before use. Table 2.4 provides the standard concentrations utilized to calibrate the GC-MS.

2.1.3 Mass Transport Modeling

To represent mass transport kinetics by means of fine bubble aeration the first order model from Monteith et al. (2005) was utilized, which included two mechanisms for the removal of volatile compounds: surface and bubble mass transport. The overall
Table 2.4: Standards for Calibrating the GC-MS

<table>
<thead>
<tr>
<th>Calibration Level</th>
<th>Analyte PDS Concentration (µg/mL)</th>
<th>Analyte PDS Volume (µL)</th>
<th>Final CAL Standard Vol (L)</th>
<th>Final Target (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
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<tr>
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<tr>
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<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
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<tr>
<td>8</td>
<td>100</td>
<td>200</td>
<td>0.1</td>
<td>200</td>
</tr>
</tbody>
</table>

mass removal rate \( \frac{dM_y}{dt} \) of a compound from the system includes removal across the surface air-water boundary (provided by Monteith et al. (2005)) and accumulation within and subsequent removal via fine bubbles (provided originally by Matter-Müller et al. (1981)). The resulting overall rate equation for compound

\[
\frac{dM_y}{dt} = -(V_L K_{Ls,y} a C_{L,y} + Q_g f_y H_y C_{L,y}) \tag{2.1}
\]

where the first term on the right hand side represents removal across the air-water interface at the water surface while the second term represents removal from bubble transport/removal as a function of \( C_{L,y} \). The proposed model includes the variables necessary to account for operational changes and environmental conditions to represent a range of conditions including the gas flow rate \( Q_g \), liquid phase volume \( V_L \) and Henry’s constant \( H_y \) (dimensionless), the latter of which is a function of temperature (specific details on the temperature dependence on Henry’s constants for the compounds of interest in this study are included in Appendix B). The \( f_y \) term (dimensionless) represents the percent saturation, or “bubble efficiency,” of an individual THM species in one rising bubble given by the following equation (Matter-Müller et al., 1981, Monteith et al., 2005, Roberts et al., 1984),

\[
f_y = 1 - e^{\frac{-K_{Lb,y} a V_L}{Q_g H_y}} \tag{2.2}
\]

where \( y \) represents one of the four THM species. The magnitude of \( f_y \) primarily
depends on the contact time between the bubble and the liquid, as well as the mass transport rates of compound \( y \) entering the bubble. The two parameters \( K_{Ls,y}a \) and \( K_{Lb,y}a \) are the surface and bubble transport coefficients, respectively, and were experimentally estimated. The interfacial area between the gas phase (atmosphere or bubble) per liquid volume \( a \) is equal to \( A/V_L \), where \( A \) is the liquid-gas interfacial area at the water surface, which is typically estimated as part of the lumped parameter \( K_{Ls,y}a \) and \( K_{Lb,y}a \).

Equation 2.1 can be written with respect to concentration by dividing through the \( V_L \) term (which is constant for the batch experiments) to give the following:

\[
\frac{dC_{L,y}}{dt} = -(K_{Ls,y}aC_{L,y} + \frac{Q_yf_yH_yC_{L,y}}{V_L})
\]

where \( dC_y/dt \) is the change in concentration of \( y \) over the change in time.

### 2.1.4 Parameter Estimation

The parameter \( K_{Lb,y}a \) for each THM was estimated based on the assumption that \( a \) was constant and did not change with column depth. On the other hand, \( K_{Ls,y}a \) may be affected by the mixing intensity resulting from the “power” produced by the bubbles rising through the column at the different experimental air flow rates. Therefore, three separate estimation approaches were performed for surface transport modeling: 1) estimating a single value of \( K_{Ls,y}a \) using all 12 individual experimental data sets; 2) estimating three individual \( K_{Ls,y}a \) values for each of the individual air flow rates; and 3) estimating three individual \( K_{Ls,y} \) (ft/min) values for each of the individual air flow rates and allowing \( a \) to be represented by \( A/V \), where \( A \) and \( V \) represent the surface area and liquid volume associated with the reactor, respectively.

The parameter estimation associated with bubble and surface mass transport was performed by minimizing the root mean squared error (RMSE) between the observed
and model predicted data using normalized concentration data. The minimization of RMSE was conducted using a 2-dimensional search where a matrix of RMSE values associated with $K_{Ls,y}a$ (or $K_{Ls,y}$ for case 3) and $K_{Lb,y}a$ values ranging from 0 to 0.4. The grid spacing was reduced from $1e^{-1}$ to $1e^{-4}$ to identify the parameters associated with the minimum RMSE values that represent the best estimates of the mass transfer coefficients. This process was conducted in MATLAB and the accompanying scripts can be found in Appendix C.

2.2 Storage Tank Evaluation

The following sections present the LVVWD storage tank specifications, experimental design, and modeling approach associated with evaluating THM removal by air stripping in a continuous flow system using actual LVVWD operational and water quality data.

2.2.1 LVVWD Tank Specifications

Testing was conducted by LVVWD in an effort to study tank aeration performance in the Alpha storage tank. The Alpha tanks operate as three physically separated, but hydraulically connected tanks; two with a 10 MG capacity and one with a 20 MG capacity. During the study, the single 20 MG tank of the Alpha tank system was off-line leaving the two 10 MG tanks active. Both tanks contain large submersible mixers in the non-aerated zones where complete mixing was assumed. Figure 2.4 is a schematic of the Alpha tank with the separation of the tank into North and Middle sections. The Alpha tank system is positioned in the distribution system to maintain the pressure head in a lower pressure zone. The Alpha tank system operates in two general manners: 1) if the pumps that provide water into the distribution system are
on, then the Alpha tank system generally has flow into the tank \( (Q_{in} \text{ on Figure 2.4}) \) and some of the Alpha pumps are operational \( (Q_{pump} > 0) \); or 2) the pumps that provide water into the distribution system are off, then water flows out of the Alpha tank system back into pressure zone 1 \( (Q_{gravity} \text{ on Figure 2.4}) \) and the Alpha pumps are off.

Each tank was outfitted with 1512 aeration diffusors with the airflow supplied by 300 horsepower blowers that can provide air flow rates up to 6,000 SCFM. Both tanks have six sampling locations, two within the aerated zones and four within the non-aerated zones. Sampling positions are labeled as N1 – N6 and M1 – M6 for the North and Middle tanks, respectively, where locations with numbers “1” and “2” represent the aerated zones in each tank (Figure 2.4).

### 2.2.2 Experimental Design

The objective of the experimental field study for the storage tank evaluation was to compare THM dynamics between an aerated and non-aerated tank. Thus, LVVWD only supplied continuous air flow to the Middle tank, discontinuing the aeration to the North tank. Water quality samples were collected at predefined locations over the duration of the study from April 12th, 2010 to May 6th, 2010, described in the following sections.

#### 2.2.2.1 Tank Preparation: Pre-Study

Before the study began, both tanks were aerated for many days under normal operating conditions to achieve similar water quality characteristics with respect to chlorine and THM concentration. Initial base-line water quality samples for chlorine and THMs were collected from both tanks via sampling positions 1, 2, 3, 5, and 6 on
Figure 2.4: Las Vegas Valley Water District Alpha twin tank aeration basin schematic. Both tanks contain large submersible mixers in the non-aerated zones where complete mixing was assumed. The profile view illustrates the influent and effluent flow paths associated with the tank operation.
April 12th, 2010. After completing the pre-study aeration, aeration was continued in the Middle tank with the system otherwise operating under routine conditions.

2.2.2.2 Data Collection

LVVWD provided the necessary data to model the dynamic performance of the Alpha tank. Operational data included hourly tank depths and hourly effluent tank flow rates provided from the supervisory control and data acquisition (SCADA) system, and airflow rates measured by LVVWD personnel typically seven times per week over the length of the study. A total of 22 water quality samples were collected once per day every Monday through Thursday at positions 2 and 5 throughout from both tanks for the duration of the study (April 12th, 2010 to May 6th, 2010) and analyzed for free chlorine and THM concentrations.

2.2.3 Alpha Tank Model

The dynamical tank model with respect to THM concentrations follows the conservation of mass by incorporating the mass in and out of the system through fluid flow in and out of the tank, as well as formation via chlorine decay and removal via aeration. The overall tank mass rate model is as follows:

\[ V_L \frac{dC_{L,y}}{dt} = Q_{in}C_{in,y} - Q_{out}C_{L,y} + \frac{dM_{aeration,y}}{dt} + \frac{dM_{formation,y}}{dt} \]  

(2.4)

where \( C_{L,y} \) is the concentration within the tank, \( C_{in,y} \) is the influent concentration, \( Q_{in} \) and \( Q_{out} \) are influent and effluent flow rates, respectively, and \( V_L \) is the total Alpha tank liquid volume. The \( dM_{aeration,y}/dt \) term represents the mass leaving the system due to aeration and the \( dM_{formation,y}/dt \) term represents the formation rate of THM \( y \) due to the decay of free chlorine in water. The Alpha tank model is presented
in three sections starting with the hydraulic modeling, mass removal due to aeration, and THM formation due to chlorine decay.

2.2.3.1 Hydraulic Model

Tank volumetric flows were simulated by conservation of mass with respect to liquid volume in the tank as shown in Equation 2.5.

\[
\frac{dV}{dt} = Q_{in} - Q_{out}
\]  

(2.5)

where \( Q_{out} \) represents the flow out of the tank through the sum of two pathways: 1) the under drain back to pressure zone 1, \( Q_{gravity} \), and 2) the Alpha pumps, \( Q_{pump} \). LVVWD provided hourly data for the Alpha tank depths as well as the effluent pump flow rates to pressure zone 2 (\( Q_{pump} \)) from the SCADA system. LVVWD also provided a relationship between water depth and tank volume for the Alpha tank to estimate the actual storage volume at every hour. The change in tank volume over each hour, \( \Delta V \), and the averaged \( Q_{pump} \) were used to estimate the value of \( Q_{in} \) if \( \Delta V > 0 \) or \( Q_{gravity} \) if \( \Delta V < 0 \). The supporting information for the relationship between tank volume and depth, tank operating flow rates, and operating depths from the basin study can be found in Appendix D.1.

2.2.3.2 Mass Transport Modeling Through Aeration

The reduction of THMs within the storage tank via fine bubble aeration will be simulated using the estimated mass transfer coefficients and Equation 2.3. To represent mass transport kinetics due to aeration within the Alpha basin, an simple assumption was made to consider the effective liquid tank volume aerated resulting in:

\[
\frac{dM_{aeration}}{dt} = (1 - \psi) \frac{dM_{p,aer}}{dt} + \psi \frac{dM_{aer}}{dt}
\]  

(2.6)
where $dM_{\text{aeration}}/dt$ is the overall mass removal rate of the tank, $dM_{n,aer}/dt$ is the mass removal rate due to the non-aerated zone of the tank, $dM_{\text{aer}}/dt$ is the mass removal rate due to the aerated section of the tank, and $\psi$ is the fraction of the tank area to be aerated and is assumed to be:

$$\psi = \frac{A_{L,aer}}{A_{TOT}} \tag{2.7}$$

where $A_{L,aer}$ is the surface area subject to aeration and $A_{TOT}$ is the total surface area of each tank. The resulting value of $\psi$ for the Middle tank was calculated by assuming each of the 1512 diffusers aerated a theoretical 1-ft diameter reactor column, which was divided by the total surface area of the tank ($A_{TOT} = 210 \times 320 \text{ ft} = 67200 \text{ ft}^2$). Thus, $\psi$ for the Middle (aerated) tank was assumed constant at $1.77e-2$ and $\psi = 0$ for the North tank since there was no aeration.

Assuming that mass transport removal was restricted to the aerated portion of the basin,

$$\frac{dM_{n,aer}}{dt} = 0 \tag{2.8}$$

leaving mass transport by the aerated portion based on equation 2.1,

$$\frac{dM_{\text{aer}}}{dt} = -(V_L K_{Ls} a C_{L,y} + Q_g f_y H_y C_{L,y}) \tag{2.9}$$

where $f$ represents the removal efficiency for one diffuser,

$$f = 1 - \exp \left( -\frac{K_{Ls} a V_L^*}{Q_g^* H} \right) \tag{2.10}$$

where, $V_L^*$ represents the equivalent volume of a 1-ft diameter column, and $Q_g^*$ represents the gas flow rate for one diffuser, which estimates the efficiency of an individual diffuser.

As a result, the total system mass removal rate due to bubble aeration reduces to:

$$\frac{dM_{\text{aeration}}}{dt} = -\psi(V_L K_{Ls} a C_{L,y} + Q_g f_y H_y C_{L,y}) \tag{2.11}$$
2.2.3.3 THM Formation Modeling

In addition to aeration, THM dynamics need to consider THM formation resulting from the reactions of chlorine with the dissolved organic material. Previous research has shown that THM formation is linearly related to chlorine decay independent of the reaction order of chlorine decay (Boccelli et al., 2003, Clark, 1998). Thus, the resulting model associated with THM formation can be presented as:

\[ \frac{dM_{\text{formation},y}}{dt} = T_y \frac{dM_{Cl}}{dt} \quad (2.12) \]

where \( \frac{dM_{\text{formation},y}}{dt} \) is the formation rate of THM \( y \), \( T_y \) is the respective THM formation constant based on chlorine decay (\( \mu g/mg \)), and \( \frac{dM_{Cl}}{dt} \) is the chlorine decay rate.

To complete the THM formation model, the appropriate chlorine decay model needs to be estimated. Using chlorine decay data from a simulated distribution system (SDS) test performed by LVVWD, both first and second order models were evaluated and found to behave similarly, which is consistent for waters that have exceeded the “rapid” decay phase (Boccelli et al., 2003). Thus, the first order model was selected to represent the chlorine decay:

\[ \frac{dM_{Cl}}{dt} = -k_{Cl}M_{Cl} \quad (2.13) \]

where \( M_{Cl} \) is the mass of chlorine in the liquid phase (mg) and \( k_{Cl} \) is the first-order decay constant, which was estimated to be 3.07e-3 hr\(^{-1}\).

Using the data from the SDS bottle test, a regression of THM formation against chlorine decay provided for the estimation for \( T_y \). The resulting formation parameter estimates used to model the individual THM formation species of chloroform, bromodichloromethane, dibromochloromethane, and bromoform were 57.87, 14.28, 4.67, and 1.51 (\( \mu g/L \))/(mg/L), respectively. Complete details for the THM formation parameter estimations can be found in Appendix D.2.
2.2.4 Alpha Tank Simulation Methodology

The Middle and North tanks were modeled separately using a similar numerical method to simulate the performance of the aeration model described in Equations 2.5, 2.11, 2.12, and 2.13. For all simulations, the influent and effluent flows were based upon the estimated values from Section 2.2.3.1. Also, given the limited amount of air flow rate data, simulations were performed assuming $Q_g$ remain constant throughout any one simulation. MATLAB scripts were written to evaluate the model by using the Runge-Kutta (4,5) method (ODE45) ordinary differential equation solver with absolute and relative tolerances of 1e-5 (Matlab scripts are provided in Appendix D.3).

2.2.4.1 Initial Conditions

The average tank temperature was 15°C based upon LVVWD data and was used to estimate the Henry’s constant for each THM. As for the initial tank water quality, the averaged initial THM concentrations measured from the Middle tank were 21.2, 17, 14, and 2 $\mu$g/L for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively, and 19.4, 16, 13, and 1.94 $\mu$g/L for the North tank. The initial chlorine concentrations within the Middle and North tanks were 0.83 and 0.82 mg/L, respectively. The initial tank depths for both the North and Middle tanks were 20.79 ft, taken from the LVVWD SCADA data at the start of the basin study.

2.2.4.2 Boundary Conditions

The boundary conditions for the various simulations include the hourly time series of influent and effluent volumetric flow rates entering a leaving the Alpha tanks, and the air flow rate (which was assumed constant), as well as the influent concentrations of
chlorine and THM species. The system was simulated using 1) average initial conditions for airflow rate, and influent THM and chlorine concentrations, 2) combinations of characteristically low/high airflow rate with high/low influent compound concentrations to “bracket” the limited observed data. For the latter simulations, there was not enough temporal data to adequately represent a time series of conditions, thus values that bracket the observed data were select to assess the impact of boundary condition variability.

2.2.4.3 Boundary Conditions: Average

For the “average” simulation study, the influent THM concentrations entering into the Alpha tank were estimated based on the model predicted residence time from the source to the tank and the THM formation model presented in Section 2.2.3.3. Based on the LVVWD data, the average free chlorine concentration at the source that fed the Alpha tank was 0.71 mg/L. The hydraulic residence time from the source to the Alpha tank was estimated to be approximately 3.3 hours, which, using the first-order chlorine decay model, resulted in an average simulated chlorine concentration entering the Alpha tank of 0.703 mg/L. The difference in chlorine concentrations was used to estimate the influent THM concentrations to the Alpha tank resulting in influent THM concentrations of 29.5, 22.3, 15.8, and 2.1 for µg/L for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively. For the Middle tank, the air flow rate, $Q_g$, was assumed constant an the averaged air flow of 5268.4 SCFM used in the simulation. Supporting information regarding the air flow rate values can be found in Appendix D.1.
2.2.4.4 Boundary Conditions: Variability

Based on the observed data, the air flow rate measurements appeared to be “bi-modal” over the duration of the study suggesting two typical, yet different, operating ranges – low and high (see Appendix D.1 for additional information). The two different air flow rates considered were the 25<sup>th</sup> and 75<sup>th</sup> quantile values of 4621.5 and 5792.0 SCFM from the LVVWD data. For modeling the influent water quality, in an effort to retain consistency with the air flow rate, the 25<sup>th</sup> and 75<sup>th</sup> percentile values of influent THM concentrations and free chlorine (taking into account for the 3.3 hours of chlorine decay en route to the tank) were also used as appropriate variable boundary conditions to bracket LVVWD data. Table 2.5 presents the simulated initial airflow and influent concentrations for the boundary conditions for each of the three simulations. The “lower” bound was aimed to simulate the greatest THM removal from the tanks and vice-versa for the “upper” bound.

Table 2.5: Simulation boundary conditions to simulate the variability of the assumptions associated with the air flow rate, influent THM concentrations (µg/L) and influent chlorine concentrations (mg/L) for the Alpha tank simulations.

<table>
<thead>
<tr>
<th>Part</th>
<th>Airflow (SCFM)</th>
<th>CHCl&lt;sub&gt;3&lt;/sub&gt;</th>
<th>CHBrCl&lt;sub&gt;2&lt;/sub&gt;</th>
<th>CHBr&lt;sub&gt;2&lt;/sub&gt;Cl</th>
<th>CHBr&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – Mean</td>
<td>5268.4</td>
<td>29.5</td>
<td>22.3</td>
<td>15.8</td>
<td>2.1</td>
<td>0.703</td>
</tr>
<tr>
<td>2 – Lower</td>
<td>5792.0</td>
<td>28.3</td>
<td>21.1</td>
<td>15.0</td>
<td>2.0</td>
<td>0.604</td>
</tr>
<tr>
<td>3 – Upper</td>
<td>4621.5</td>
<td>31.5</td>
<td>23.1</td>
<td>16.0</td>
<td>2.2</td>
<td>0.792</td>
</tr>
</tbody>
</table>

2.3 System Wide Impacts

The following sections present the methods for applying the THM aeration model to a section of the LVVWD distribution system model to simulate the potential impacts of the associated removal strategy.
2.3.1 Analysis Tools

EPANET 2.0 (Rossman, 2000) was used to conduct basic analyses with respect to system hydraulics, and the EPANET Multi Species eXtention (MSX) v1.2.0 (Shang et al., 2011) was used to simulate the water quality dynamics associated with free chlorine, chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Specific for this application, EPANET MSX was updated (courtesy of L. Rossman) to enable access to the tank volume and depth data structures necessary to simulate the aeration model, which was important because the aeration model utilizes the tank volume and depth of the Alpha tank as dependent variables.

2.3.2 LVVWD Model Description

Figure 2.5 illustrates one section of the Las Vegas water system wide model (SWM). This SWM section is comprised of approximately 6200 nodes, 6500 pipes, 2 tanks, and 2 supply reservoirs to supply an estimated typical demand of 10.8 MGD. The SWM section encompasses around 144 miles of conduit where the typical mean hydraulic residence time based on the system average over the final 24 hour period of a lengthy simulation was estimated to be \( \sim 120 \) hours. The Bravo reservoir (BR) serves as the base supply node pressure zone one while the Alpha tank system supplies the nodes in pressure zone two. The Alpha tank was modeled assuming that all three tanks were operational (maximum total capacity of 40 MG) and aerated. Two separate blowers were used in the Alpha tank system – one supplying the South basin alone and one supplying both the Middle and North tanks.

The Bravo location was modeled as a constant head reservoir that is connected to six pumps that can provide flow into the system using controls specified by the utility. When the BR pumps were “on,” the increased head in pressure zone one causes the
Figure 2.5: LVVWD system wide model section. Pressure zone 2 is the ‘more Westerly’ region while pressure zone 1 is, for the most part, everything to the east (right) of the Alpha tank.
Alpha tank system to fill. Alternately, if the pumps at BR were turned “off,” water generally flowed back out of the Alpha tank system back towards pressure zone one. Similar to the BR pressure zone, the pumps on the effluent side of the Alpha tank system were also simulated using controls provided by the utility. When the Alpha pumps were turned “on,” the increased head in the system would fill a tank known as Delta, which maintained the head within pressure zone two.

2.3.3 Simulations and Data Analysis

To perform an adequate water quality simulation, the simulation duration must be long enough to overcome the initial conditions of the model and behave as a “stationary” system. EPANET was used to simulate hydraulic water age and tracer analyses using BR as the source node. Based on results from several points within the network, including the Alpha and Delta tanks, and the nodes with the greatest water age from the BR supply reservoir, the system appears stationary after about 400 hours. Each simulation duration was then extended by another 100 hours to reach a total simulation length of 500 hours with results from the last 24 hours used in the analysis. Supporting information for the stationary point can be found in Appendix E.1.

For all simulations, the initial global water quality conditions were selected based on typical concentrations measured from the system, which included concentrations of 0.71 mg/L for free chlorine and 29, 22, 16, and 2 µg/L for chloroform, bromodichloromethane, dibromochloromethane, and bromoform concentrations, respectively. These same chlorine and THM concentrations were used as constant BR source concentrations over the simulation duration. All simulations were conducted with a constant temperature of 15.14°C based on the LVVWD data. The 5th order Runge-Kutta (RK5) solver was selected from the EPANET MSX options using a water quality time step of 60 seconds, and absolute and relative tolerances of 1e-4. The
representative MSX input file can be found in Appendix E.2.

To evaluate the potential system-wide impacts of aeration, four water quality simulations were conducted assuming all three of the Alpha tanks were aerated. Aeration was simulated using 6064 aeration diffusers; 1512 in both the North and Middle tanks and 3040 in the South. Simulation 1 was aerated at a combined airflow rate of 11639.5 SCFM from blowers 1 and 2, based on the average Alpha operating airflow rate from August to November. Simulation 2 was performed with double the average airflow rate, and simulation 3 was performed with half of the average airflow rate. A fourth simulation, serving as the control, was conducting using no aeration in the Alpha tank system.
Chapter 3

Results and Discussion

The following chapter will present the results associated with the bench-scale experiments, application of bench-scale model to actual tank data, and exploration of network wide impacts utilizing the model.

3.1 Reactor Experiments and Parameter Estimation

The following section will present the results associated with three separate parameter estimation approaches. The first method was to estimate model mass transport parameters $K_{La}$ and $K_{Lsa}$ using experimental data from all 12 experiments. Next, individual $K_{Lsa}$ values were estimated for each airflow rate to study the impacts of airflow rate (power mixing) on THM removal rate. Finally, individual $K_{Ls}$ values were estimated for each airflow rate while accounting for observed changes in $a$ by utilizing the $A/V$ term.
3.1.1 Estimation of $K_{Lb}a$ and $K_{Ls}a$

Table 3.1 presents the estimated values for the parameters $K_{Ls,y}a$ and $K_{Lb,y}a$ as well as the RMSE from all of the experimental data for each THM. Overall, the parameter estimates of the model represented the data reasonably well with overall RMSE values ranging from 2.74% to 7.57% for chloroform to bromoform. The performance of the model decreased from lightest to heaviest THM (Table 3.1) with the RMSE from the individual experiments ranging from 1.04% to 4.18% for chloroform and 3.12% to 10.6% for bromoform. The experimental data indicated that chloroform had the highest removal rate and bromoform the lowest removal rate likely due to the difference in volatility, which is consistent with the larger Henry’s constant for chloroform relative to the other individual THM species.

Table 3.1: Parameter estimates of the surface ($K_{Ls,y}a$) and bubble ($K_{Lb,y}a$) mass transfer coefficients and goodness-of-fit metric (RMSE) for the four individual THM species utilizing all of the observed experimental data.

<table>
<thead>
<tr>
<th></th>
<th>CHCl3</th>
<th>CHBrCl2</th>
<th>CHBr2Cl</th>
<th>CHBr3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{Ls,y}a$ (min$^{-1}$)</td>
<td>1.76e-2</td>
<td>1.02e-2</td>
<td>5.8e-3</td>
<td>4.1e-3</td>
</tr>
<tr>
<td>RMSE (%)</td>
<td>2.74</td>
<td>3.80</td>
<td>5.05</td>
<td>7.57</td>
</tr>
</tbody>
</table>

Figures 3.1 and 3.2 present illustrative model performance for the experimental data associated with chloroform and bromoform, the lightest and heaviest of the individual THMs that bound the performance of the four individual THMs. These two specific figures depict results from four experimental runs (5 - 8 from Table 2.1; complete experimental results for all of the individual THMs are included in Appendix G). Both figures (3.1 and 3.2) present data from the 2 SCFM experiments where the top row represents the experiments performed with a liquid depth of 11 ft, and the bottom row with a liquid depth of 6 ft; the left column represents an initial THM spike of 150 µg/L, and the right column represents an initial THM spike of 50 µg/L. The
experimental THM concentrations are presented as normalized concentrations with symbols representing the mean of the normalized concentrations, and the 25th and 75th percentiles represented by the lower and upper bars, respectively. Additionally, each experimental plot includes the RMSE for that specific run using the parameters of Table 2.1 as well as the initial water characteristics such as temperature, pH, and Henry’s constant.

![Graphs showing concentration over time for chloroform experiments at 2 SCFM.](image)

Figure 3.1: Results for chloroform experiments at 2 SCFM. The model is shown as a line and is estimated using Equation 2.3 using 1.76e-2 min$^{-1}$ and 3.99 min$^{-1}$ for $K_{Ls,CHCl_3,a}$ and $K_{Lb,CHCl_3,a}$, respectively.

The model represented the shape of the observed data best for the lighter THMs with some observed deviations for the heavier THMs. The results illustrated in Figures 3.1 and 3.2 with an air flow rate of 2 SCFM are generally the “best” case results. In
Figure 3.2: Results for bromoform experiments at 2 SCFM. The model is shown as a line and is estimated using Equation 2.3 using 4.1e-3 min\(^{-1}\) and 5.99e-1 min\(^{-1}\) for \(K_{Ls,CHBr_3} a\) and \(K_{Lb,CHBr_3} a\), respectively.
general, the model slightly under-predicts removal for the 1 SCFM air flow rate, and slightly over-predicts removal for the 4 SCFM air flow rate. The maximum RMSE value associated with individual experiments for chloroform was 4.2% (1 SCFM; \( C_o = 50 \mu g/L; \) Height = 11 ft; shown in Figure G.1 in Appendix G) and for bromoform was 10.6% (2 SCFM; \( C_o = 150 \mu g/L; \) Height = 11 ft; shown in Figure 3.2).

With respect to bubble mass transfer, parameter estimates from Monteith et al. (2005) for \( K_{Lb,y}a \) were \( 2.47e-2 \) and \( 4.37e-3 \text{ min}^{-1} \) for chloroform and bromoform, respectively, and are several orders of magnitude smaller than our estimates. While the study of Monteith et al. (2005) sought to explicitly estimate the values of \( K_{bs,y}a \) through the use of oxygen-transfer tests, the current research numerically estimated the value of \( K_{Lb,y}a \) that best represented the observed data from the column reactor studies.

Further exploration of the “bubble efficiency” term \( f_y \) (Equation 2.2) shows that as the \( K_{Lb,y}a \) term increases the numerator within the exponential term \( \to \infty \), thus \( f_y \to 1 \). For the \( K_{Lb,y}a \) values reported in Table 3.1 and the self-reported values of \( f_y \) by Monteith et al. (2005), the resulting \( f_y \) terms are very close to “1” indicating the mass transfer efficiency for the volatile THMs are very high. While \( f_y \) is dependent on other experimental variables, such as \( Q_g \) and \( V_L \), \( K_{Lb,y}a \) values of 1.55 and 2.32e-1 for chloroform and bromoform resulted in values of \( f_y \) within six decimal places of 1. From a numerical standpoint, there is a large range of \( K_{Lb,y}a \) estimates that will result in \( f_y \simeq 1 \) with indiscernible changes in model predicted performance. Thus, accurately estimating \( K_{Lb,y}a \) using numerical methods when \( f_y \simeq 1 \) is difficult. However, for the objectives of this study, the knowledge that \( f_y \simeq 1 \) is more important than accurate estimates of the individual \( K_{bs,y}a \) values.

With respect to the surface mass transport coefficient \( (K_{Ls,y}a) \) estimates, results from the literature were similar in magnitude to the parameters estimated in the current study. Kyosai and Rittmann (1991) estimated a \( K_{Ls,y}a \) parameter for chloroform
of 1.29e-2 min\(^{-1}\) using a similar reactor diameter with experimental air flow rates ranging from 2.0e-3 to 8.8e-3 SCFM, several orders of magnitude smaller than the current study. \(K_{Ls,y,a}\) rates from Monteith et al. (2005) for chloroform and bromoform were 2.94e-2 min\(^{-1}\) and 1.99e-2 min\(^{-1}\) using a volume of 5 m\(^3\) with a 3 m tank depth and aerating with multiple diffusers at higher air flow rates relative to the current research. Differences between the current parameter estimates and those found in the literature can likely be attributed to differences in experimental designs, such as diffuser type, reactor size, and water depth, but the similarities in values provide confidence in the current estimates of \(K_{Ls,y,a}\).

To further study the impacts of \(K_{Ls,y,a}\), parameter estimates were performed simultaneously using all 12 experiments with \(K_{Ls,y,a}\) set to zero (no surface mass transfer). Figures 3.3 and 3.4 illustrate representative model performance with estimated \(K_{Lb,y,a}\) for chloroform and bromoform of 3.79 min\(^{-1}\) and 6.15e-1 min\(^{-1}\), respectively, and \(K_{Ls,y,a} = 0\). In general, the resulting aeration model tended to over-predict experimental concentrations relative to the results in Figures 3.1 and 3.2. Table 3.2 shows the RMSE values with and without the surface mass transport included in the model. Removing the surface mass transfer term resulted in percent increases of RMSE from 452% to 298% for chloroform and bromoform, respectively. These estimation results indicate that the bubble mass transport mechanism with complete efficiency \((f_y = 1)\) cannot adequately describe the overall mass removal process; further supporting the need for a surface mass transfer component within the model. Supplemental data for all THM figures for \(K_{Ls,y,a} = 0\) are presented in Appendix I.

### 3.1.2 Estimation of \(K_{L,s,a}\): Impact of Power

The use of aeration effectively increases mixing in the system, which impacts surface mass transport rates. Such mixing can be equated to an amount of “power” intro-
Figure 3.3: Results for chloroform experiments at 2 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 0 min\(^{-1}\) and 3.791 min\(^{-1}\) for \(K_{Ls,CHCl_3}a\) and \(K_{Lb,CHCl_3}a\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.

Table 3.2: RMSE percent difference between model results using \(K_{Ls,y}a \neq 0\) vs. \(K_{Ls,y}a = 0\)

<table>
<thead>
<tr>
<th></th>
<th>CHCl(_3)</th>
<th>CHBrCl(_2)</th>
<th>CHBr(_2)Cl</th>
<th>CHBr(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMSE for (K_{Ls,y}a \neq 0) (%)</td>
<td>2.74</td>
<td>3.80</td>
<td>5.05</td>
<td>7.57</td>
</tr>
<tr>
<td>RMSE for (K_{Ls,y}a = 0) (%)</td>
<td>9.64</td>
<td>11.10</td>
<td>11.98</td>
<td>14.96</td>
</tr>
<tr>
<td>Percent Difference (%)</td>
<td>111</td>
<td>98.0</td>
<td>81.5</td>
<td>65.8</td>
</tr>
</tbody>
</table>
Figure 3.4: Results for bromoform experiments at 2 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 0 min⁻¹ and 6.15e-1 min⁻¹ for $K_{L_s, CHBr_3} a$ and $K_{L_b, CHBr_3} a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
duced into the system. Research by Hsueh et al. (1991) and Roberts and Dändlikier (1983) suggested that increasing power per volume has an impact on $K_{L_s,y}a$ rates. These studies were conducted using surface or submersed mechanical mixers to study removal rates of several organic compounds, including chloroform, through surface transport in response to mixing intensity. Since bubble aeration also improves mixing, the power of bubble plumes rising in water can be estimated by the following equation (Sincero and Sincero, 2003):

$$\text{Power} = P_i Q_g \ln\left(\frac{P_a + H \gamma_w}{P_a}\right)$$  \hspace{1cm} (3.1)

where $\gamma_w$ is the specific weight of water (F/L$^3$), $H$ is the water depth (L), $P_a$ is atmospheric pressure (F/L$^2$) and, specific to an aeration membrane plate, $P_i$ is the absolute pressure within an aeration membrane (F/L$^2$), specified as

$$P_i = P_f(Q_g) + P_a + H \gamma_w$$  \hspace{1cm} (3.2)

where $P_f$ is the minimum gauge pressure (F/L$^2$) needed to produce airflow $Q_g$ with no external pressure effects, which is provided by technical specifications for a membrane aeration plate.

While the model employed in our study did not explicitly include the effects of power, parameter estimates associated with $K_{L_s,a}$ were performed separately for each individual air flow rate (1, 2 and, 4 SCFM) to evaluate the impact that different air flow rates had on surface transport rates, which implicitly represents increased amounts of power in the system. The parameter estimation approach followed the same methodology as described in Section 2.1.4 for each set of experiments with a specified air flow rate. Since previous parameter estimates of $K_{L_b,y}a$ were large enough to suggest $f_y = 1$, only $K_{L_s,y}a$ was estimated assuming that $f_y = 1$, which resulted in three $K_{L_s,y}a$ (one for each air flow rate) per individual THM species. Power values were estimated for each air flow rate (Equation 3.1) using an average water height of 8.5 ft.
to approximate the changes in energy due to increased air flow rate (the power values did not impact model performance).

Figure 3.5 illustrates the impact of air flow rate on the $K_{L,s,y} a$ estimates and RMSE for the individual THM species (the complete set of experimental plots can be found in Appendix J). Figure 3.5.a features $K_{L,s,y} a$ vs. air flow rate while Figure 3.5.b provides the total RMSE values for each THM vs. air flow rate. In both plots, the bottom axis represents air flow rate in SCFM while the top axis provides the equivalent power in Watts per ft$^3$ liquid volume.

Figure 3.5: (a) Impact of air flow rate power on $K_{L,s,y} a$ values for each THM using air flow rates of 1, 2 and 4 SCFM and (b) associated RMSE values for estimated $K_{L,s,y} a$ parameters. Power values were calculated using the mean liquid experimental depth 8.5 ft (6.7 ft$^3$) are included on the upper x-axis.
Consistent with the theory that increasing power (i.e., air flow rate) increases the surface mass transfer rate, the parameter estimation results show that as the air flow rate increased the value of $K_{Ls,y}a$ also increased. The increase in $K_{Ls,y}a$ was more rapid for the lighter, more volatile THMs such as chloroform. Research by Roberts and Dändliker (1983) and Peng et al. (1995) suggested that as power within the liquid phase increased, the liquid phase transport resistances decreased, leading to an increased $K_{Ls,y}a$. The results by Roberts and Dändliker (1983) found that power rates above 10 W/m$^3$ (2.8e-1W/ft$^3$) resulted in an increased $K_{Ls,y}a$ for chloroform, which is consistent with estimates from the current research and suggests a correlation between power and the $K_{Ls,y}a$ mass transport rate. With respect to the RMSE based on individual air flow rates, the goodness-of-fit improved with higher air flow rates. When the air flow rates increased, the percent contribution of the surface mass transfer to the overall removal process also increased, which suggests that the first-order assumption with respect to surface mass transfer may be more appropriate than that of the bubble mass transfer. Overall, these results suggest that the amount of power introduced into the liquid phase had an impact on THM removal.

### 3.1.3 Estimation of $K_{Ls,a}$: Incorporating Surface Area and Volume

For the final parameter estimation, $K_{Ls,a}$ term was estimated by assuming that $a$ could be represented by the ratio of reactor surface area to reactor volume, and the value of $K_{L,s}$ estimated for each flow rate using the method outlined in Section 2.1.4. Figures 3.6 and 3.7 illustrate representative model performance with estimated $K_{Ls,y}$ for chloroform and bromoform. As with the previous parameterization approaches, the model predictions represented the chloroform data very well with some observed deviations from the experimental results for bromoform.
Figure 3.6: Chloroform experiments at 2 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $1.63 \times 10^{-1}$ ft/min and 3.99 min$^{-1}$ for $K_{Ls,CHCl_3}$ and $K_{Lb,CHCl_3} a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th quantiles, respectively.
Figure 3.7: Bromoform experiments at 2 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $3.83\times10^{-2}$ ft/min and $5.99\times10^{-1}$ min$^{-1}$ for $K_{Ls,CHBr_3}$ and $K_{Lb,CHBr_3} a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th quantiles, respectively.
Figure 3.8 illustrates $K_{ls,y}$ rate values plotted against the airflow rate on the left hand plot and the right hand plot presents the respective model RMSE values. The resulting $K_{ls,y}$ estimates exhibited a strong linear relationship with respect to airflow rate, similar to the results from estimation case "2". With respect to RMSE values, and unlike the case "2" estimates, the RMSE values exhibit a moderate increase when moving from the 1 SCFM to the 2 SCFM airflow rates. Furthermore, a large RMSE decrease is illustrated when moving from 2 SCFM to 4 SCFM. Table 3.3 presents the slope and intercept values from linear regressions performed on the $K_{ls,y}$ estimates for each THM shown in Figure 3.8.a. These linear relationships were used to support the estimation of the surface mass transport conditions in the tank and network-scale simulations.

Table 3.3: Results for $K_{ls,y}$ (ft/min) parameters estimated by individual airflow rate. Tabulated below is the slope (ft/min-SCFM) and intercepts (ft/min) for a linear regression model for each THM using all airflow rates.

<table>
<thead>
<tr>
<th>SCFM</th>
<th>CHCl$_3$</th>
<th>CHBrCl$_2$</th>
<th>CHBr$_2$Cl</th>
<th>CHBr$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.39e-1</td>
<td>7.40e-2</td>
<td>4.00e-2</td>
<td>2.71e-2</td>
</tr>
<tr>
<td>2</td>
<td>1.63e-1</td>
<td>9.18e-2</td>
<td>5.37e-2</td>
<td>3.83e-2</td>
</tr>
<tr>
<td>4</td>
<td>3.42e-1</td>
<td>1.79e-1</td>
<td>9.48e-2</td>
<td>5.95e-2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.08e-2</td>
<td>4.94e-2</td>
</tr>
<tr>
<td></td>
<td>3.63e-2</td>
<td>3.02e-2</td>
</tr>
<tr>
<td></td>
<td>1.86e-2</td>
<td>1.94e-2</td>
</tr>
<tr>
<td></td>
<td>1.08e-2</td>
<td>1.65e-2</td>
</tr>
</tbody>
</table>

### 3.1.4 Comparison of the Estimation Approaches

Overall, each parameter estimation approach that included the surface mass transport provided reasonable model predicted concentrations to the experimental concentrations. Figure 3.9 provides a comparison of the overall RMSE values for all of the three parameter estimation methods considered. Between cases "1" and "2" for each THM, the RMSE values decreased as much as 22% for chloroform and 10% for bro-
Figure 3.8: (a) Impact of air flow rate power on $K_{Ls,y}$ values for each THM using air flow rates of 1, 2 and 4 SCFM and (b) associated RMSE values for estimated $K_{Ls,y}$ parameters. Power values were calculated using the mean liquid experimental depth 8.5 ft (6.7 ft$^3$) are included on the upper x-axis.
moform. The decrease in RMSE values suggest that the model performs better when the surface transport term is a function of air flow rate. However, the RMSE values going from estimation case “2” to estimation case “3” tended to increase slightly. For chloroform the RMSE value increased roughly 8% with only a 2% increase for bromoform. Ultimately, the proposed model performed well and incorporating the additional parameter flexibility improved model performance.

Figure 3.9: A comparison for the overall RMSE normalized values for all of the three parameter estimations method considered. Cases “2” and “3” the $K_{L,s}a$ terms are a function of air flow rate.

Finally, while the primary removal pathway might be assumed to result from bubble mass transfer, the percent contributions of the two THM removal routes can vary significantly among the four THMs. Monteith et al. (2005) evaluated the relative contribution of surface aeration by estimating the percent contribution relative to the
surface and bubble aeration removal rates given by

\[ \text{Contribution}_{s,y} = \frac{V_L K_{Ls,y} a}{V_L K_{Ls,y} a + Q_g f_y H_y} \]  \tag{3.3} 

which estimates the fraction removal due to surface aeration relative to the combined removal rates. Using Equation 3.3, the impact of surface aeration from the twelve experimental studies ranged, on average, from approximately 35% removal for chloroform to approximately 50% for bromoform while Monteith et al. (2005) estimated percent contributions to be \( \sim 28\% \) and \( \sim 65\% \), respectively. These data suggest that surface mass transport, not just bubble mass transport, can play a significant role in predicting the fate of THMs.

### 3.2 Storage Tank Simulations

The following section presents the results associated with simulating an actual storage tank, and model sensitivity analysis based on realistic parameter ranges.

#### 3.2.1 Alpha Tank Simulations

As discussed in Section 3.1, the parameters associated with the laboratory-scale column experiments were estimated using three different parameterizations for \( K_{Ls,y} a \). Using these three different parameterizations, the aeration model was included in the overall simulation model for representing the dynamics of a real-world storage tank using estimated flow rates, and averaged influent concentrations and air flow rates based on data provided by the utility (see Appendix D.1). Figures 3.10 and 3.11 present the simulated chloroform and bromoform dynamics for the North (non-aerated) and Middle (aerated) basins of the Alpha tank, respectively (results for bromodichloromethane and dibromochloromethane can be found in Appendix L.1).
These figures clearly show the impacts of the fill-drain cycles on the simulated concentration data.

Figure 3.10: Comparison of the Middle tank chloroform model performance using all three parameter estimation types. $K_{L,s,y} a$ values for cases “2” and “3” were calculated based on an air flow rate of 3.48 SCFM / diffuser. The plot features the absolute RMSE for each simulation where overall parameter cases “1” and “3” outperform case “2”.

Figure 3.10 demonstrates that the simulated tank results for chloroform adequately represent both the non-aerated and aerated basins of the Alpha tank. For the aerated basin, estimation cases 1 and 3 produced RMSE values of 1.5 and 2.0 µg/L, which were better than the case 2 estimates with an RMSE of 5.1 µg/L, which had a tendency to overestimate the removal via aeration. Figure 3.11 demonstrates that the simulated tank results for the non-aerated basin tended to (slightly) overestimate the observed concentrations (differences less than 0.2 µg/L). For the aerated basin, the parameter
Figure 3.11: Comparison of the Middle tank bromoform model performance using each parameter estimation method. $K_{L,s,y}$ values for cases “2” and “3” were calculated based on an air flow rate of 3.48 SCFM /diffuser. The plot features the absolute RMSE for each simulation where overall parameter cases “2” outperforms cases “1” and “3”.

- Middle Tank Case 1 RMSE = 0.12568 µg/L
- Middle Tank Case 2 RMSE = 0.10182 µg/L
- Middle Tank Case 3 RMSE = 0.13422 µg/L
- North Tank RMSE = 0.13422 µg/L
estimates associated with cases 1 and 3 were similar (RMSE of approximately 0.13 µg/L) and were slightly outperformed by the case 2 estimates (RMSE of 0.1 µg/L). For all three cases, the differences between the observed and simulated data were very small.

Interestingly, the case 1 parameter estimates, which estimated $K_{Ls,y}a$ using all of the data independent of air flow rate, outperformed the case 2 estimates (dependent on $Q_g$) but were similar to the case 3 estimates (dependent on $Q_g$, and incorporating changes in $A$ and $V$). When evaluating the data from the tank study, the tank heights observed during the study ranged from 14 to 22 ft, which are typically greater than the depths used in the experimental studies. For cases 1 and 2, which do not explicitly include changes in $A$ and $V$ within the parameter estimation, the simulation results are extrapolated outside the range of the experimental data, which may lead to inaccurate results. Case 3, which accounts for $A$ and $V$, adequately accounted for the change in depth ($A/V$) and resulted in good estimated results. By evaluating the resulting values of $K_{Ls,y}a$, the greater depth in the observed data reduced the case 3 estimates of $K_{Ls,y}a$ (by decreasing $A/V$) toward a value that was similar to that of the case 1 parameter estimate for $K_{Ls,y}a$. Thus, the near equivalent performance of the case 1 and 3 estimates were a result of the ratio $A/V$ bring the case 3 estimates close to that of the case 1 estimates. Overall, these results suggest that the case 3 parameterization of the aeration model both adequately represented the observed data, and was robust with respect to water depths outside of the range of the laboratory-scale experimental study.

While the previous results produced reasonable simulation results, due to the lack of significant temporal data these results were based on averaged values of air flow rate, chlorine and THM concentrations. To evaluate the potential range of dynamic behavior, the interquartile range of air flow rate, and initial chlorine and THM concen-
tations were used to “bracket” the averaged simulations (see Section D.1 for details on the interquartile range). Figures 3.12 and 3.13 illustrate the simulation results for chloroform and bromoform based on the average boundary conditions (central line) as well as the variability in the boundary conditions (upper and lower bounds) (results for bromodichloromethane and dibromochloromethane are provided in Appendix L). For the chloroform results, the simulated data range bracket the majority of the observed data. For the bromoform results, incorporating the range extends the results to include the observed data that was previous overestimated. However, the simulated data tend to miss the potentially reduced bromoform values near the end of the observation time, although these differences are still relatively small. The absolute RMSE values included on each figure were estimated by comparing the average conditions (central line) to the actual data for the Middle and North tanks. For chloroform the RMSE values for the Middle and North tanks were 1.65 µg/L, and for bromoform the RMSE values were 1.43e-1 and 1.59e-1 µg/L, respectively.

As mentioned earlier, and prior to the start of the basin study, both tanks were aerated at equal airflow rates until similar water quality was reached. As expected, the Middle and North tank models “diverge” from the initial conditions due to the difference in aeration status. The attempt to “bracket” the observed data from the Alpha tank was performed to evaluate the range of behaviors associated with the sparsely observed range of operational measurements. While the current modeling approach provided reasonable estimates given the limited temporal resolution, one other component of the model that might be included is the removal due to the power addition from the in-tank mixers used to maintain a completely mixed tank. However, the additional mass transport from the in-line mixers was not included in the model due to: 1) the generally good representation of the observed data by the current model; and 2) the range of behavior, not explicitly included in the model, that would likely overwhelm the slight addition fitting the additional term might add to the simulated data (i.e.,
Figure 3.12: Middle vs. North tank results for the chloroform model with respect to LVVWD data using ‘real’ operational conditions. The upper bound for both simulated tanks represents the simulation case using high influent THM concentrations and a lower airflow rate and vice-versa for the lower bound. Influent concentrations and simulated airflow rates boundary conditions were based on the actual distributions of the LVVWD data provided in Appendix D.
Figure 3.13: Middle vs. North tank results for the bromoform model with respect to LVVWD data using ‘real’ operational conditions. The upper bound for both simulated tanks represents the simulation case using high influent THM concentrations and a lower airflow rate and vice-versa for the lower bound. Influent concentrations and simulated airflow rates boundary conditions were based on the actual distributions of the LVVWD data provided in Appendix D.
any improvements would likely not be statistically significant).

### 3.2.2 Aeration Model Sensitivity

In addition to the dynamic simulations performed above, a sensitivity analysis was performed associated with a steady-state solution of the tank system. Figure 3.14 illustrates the steady-state sensitivity analysis over a range of operational conditions that target the liquid flow rate (i.e., hydraulic retention time), airflow rate, and influent chlorine concentration. For each sub-figure, the results represent the variation of only one parameter where the ‘nominal’ case is a common point of reference, which was selected to be the average operational conditions associated with the Middle (aerated) basin. Additionally, the steady-state liquid flow rate for both the influent and effluent was based on the average influent tank flow rate from the observed LVVWD data. For all cases, the influent concentrations for chloroform, bromodichloromethane, dibromochloromethane, and bromoform were set at 29.4, 22.3, 15.8, 2.1 µg/L, respectively, where all other boundary conditions were similar to those in Section 2.2.4. Each figure includes results from several steady-state simulations using a range of realistic parameters.

The most sensitive parameter was the tank flow rate. Figure 3.14.a illustrates that increasing the flow rate through the tank resulted in larger THM concentrations. By altering the flow rate through the tank, the hydraulic residence time was also changed, which impacted the THM concentrations. As the non-zero flow rate increased, the hydraulic residence time decreased from 342 hours to 43 hours with a corresponding increase in the steady-state THM concentrations due to the reduction in contact time in the aeration basin. From a practical standpoint, the overall THM concentrations can change drastically during tank fill-drain cycles. These results suggest that if operations could be altered to reduce the flow through the Alpha tank to increase the
Figure 3.14: Steady-state sensitivity analysis of the Alpha tank system including model responses to different a) liquid flow rates (e.g. hydraulic retention time), b) airflow rates, and c) influent chlorine concentrations. For all cases, influent concentrations for chloroform, bromodichloromethane, dibromochloromethane, and bromoform were set at 29.4, 22.3, 15.8, 2.1 µg/L, respectively.
hydraulic residence a greater reduction in THM concentrations could be observed.

The next most sensitive parameter associated with steady-state THM concentrations was the air flow rate. Figure 3.14.b illustrates that increased the air flow rate increased subsequent THM removal, which is consistent with theory as both the bubble and surface mass transport removal mechanisms are functions of $Q_g$. Practically, increasing the air flow rate could be an appropriate remedy to reduce THM concentrations, but the increased air flow rates would result in a greater energy expense from the blowers, which would result in a trade-off to be made by the utility.

Figure 3.14.c illustrates that the range of influent chorine concentrations can provide a further means to impact THM formation. As expected, a reduction in the influent chlorine concentration can provide some reduction in THM formation. The influent chlorine concentration was among the least sensitive parameter with significant changes observed only for chloroform. However, any changes to the influent chlorine concentration must continue to maintain a safe residual beyond the Alpha tank.

In general, the chloroform, bromodichloromethane, and dibromochloromethane were the most responsive to changes in tank operations. However, bromoform, as illustrated in Figure 3.14, for each sensitivity analysis was the least sensitive to parameter changes where the concentration at steady-state for nearly all cases was almost equal to the “nominal case” concentration.

Overall, the in-tank aeration system model demonstrated the ability to “closely” predict THM concentrations within a dynamical tank environment. Therefore, the model can be used to understand the fate of THMs within distribution system storage tanks. The application of the aeration tank model can help predict THM responses to changes in tank operation (i.e. liquid and air flow rates), understand the impacts of chlorination strategies, as well as serve as a design tool to help optimize THM control placement mechanisms. The model also has the flexibility to deal with changes in
water temperature, and accounts for changes in the tank surface area and tank volume throughout operation or if an aeration system is applied to a tank with disparate physical dimensions.

### 3.2.3 Surface Aeration

While THM removal is a function of both bubble and surface mass transport, the model results suggest that the greatest contributor associated with the overall mass transport for each THM was due to surface mass transport ($K_{La}a$). Using Equation 3.3, the contribution of the surface mass transport for all four THMs was almost exclusively governed by the surface transport term at roughly 97%. Thus, with bubble mass transport contributing only “slightly” to the overall mass removal rate, the utilization of fine bubble aeration as a removal mechanism could be compared to other removal process. As shown in Section 3.1.2, the surface aeration mass transfer process is a function of the power associated with mixing intensity. Thus, for the current tank conditions, in which surface aeration dominates, the use of the current model could be used to assess the incorporation of other mechanic mechanisms that could deliver similar “power” to the system and, potentially, deliver the same removal efficiency. These analyses would allow for the evaluation of the performance and energy trade-offs for the different technologies.

### 3.3 Results for System Wide Impacts

The following section presents and describes the results in two parts. The first section provides the system wide characteristics associated with the Alpha tank and the water quality distributions without the effects of aeration, while the second section the details the potential system wide impacts on the entire LVVWD SWM section.
3.3.1 System-wide water quality characteristics

With respect to system operation and hydraulics, Figure 3.15 presents the average percentage of water at each node that came from the Alpha tank system. These results were generated by using a trace analysis with EPANET 2.0, which specified the Alpha tank as the tracer source, and run with a simulation duration of 500 hours. The resulting average percentages were reported in hourly time steps from all nodes over the final 24 hours of the 500 hour simulation. Over half of the water network nodes receives more than 75% of the daily demand from the Alpha tank, most exclusively, pressure zone 2. Nodes receiving 60% to 80% of the water from the Alpha tank in most cases are located in the Northern section of pressure zone 1. Roughly half of the demand of the Northern part of pressure zone 1 is provided from pressure zone 2 where a pressure reducing valve bridges the zones and regulates the pressure head.

To represent the spatial distribution of water quality data for the system-wide model without the effects of aeration, Figure 3.16 presents the mean total THM concentrations for all nodes over the final 24 hours of the non-aerated 500 hour simulation. In general, the total THM concentrations are higher in pressure zone 2 due to longer residence times in the system, which is due, in part, to the residence time in both the Alpha and Delta tanks. In the Northern section of pressure zone 1, elevated levels of total THMs can be observed due to a combination of higher water age from within pressure zone 1 as well as flow from pressure zone 2. Within the SWM, roughly 550 nodes were modeled to have no demand; therefore, over a 500 hour simulation the initial chlorine concentrations decreased to zero resulting in maximum total THM formation. Figure 3.17 includes a spatial representation of the average free chlorine
Figure 3.15: Spatial plot of the quartile distribution of nodes receiving x percent of water from the Alpha tank.
concentrations at each node over the last 24 hours of any of the four simulations. Since pressure zone 2 was subject to higher water age than pressure zone 1, free chlorine concentrations within the water network are reflected such that zone 2 generally has lower mean free chlorine concentrations than zone 1.

Figure 3.18 provides empirical cumulative distribution function (ECDF) plots for the four individual THMs using the hourly concentrations from each node for the final 24 hours of the non-aerated simulation \((n = 148704)\). As expected (since there is only formation), the individual THM ECDFs follow a similar pattern consisting of three “typical” regions of concentrations. The first region, associated with ECDF values of approximately 0 – 0.2 represent areas fed almost exclusively from the Bravo Reservoir. The second region, associated with ECDF values of approximately 0.2 – 0.5, generally represents the northern portion of Pressure Zone 1, which also receives some water from the Alpha tanks. The third region is associated with ECDF values of about 0.7 – 0.9, which generally represents the Pressure Zone 2 region.

Figure 3.19 illustrates the ECDF plot of the hourly free chlorine concentrations in the system for each node over the last 24 hours of the simulation. As with the THM concentrations, there are three regions of chlorine concentration observed from the ECDF. These regions are generally centered around chlorine concentrations of approximately 0.4, 0.57 and 0.68 mg/L, which also correspond the regions of decreasing total THM concentrations. The lower end of the concentration range, approximately 0.15 mg/L, are the result of dead-end or very low demand nodes.

### 3.3.2 System-wide water quality impacts through aeration

The objective of the following analyses was to evaluate the potential impact that aeration might have on a system-wide basis relative to the non-aerated scenario. The aerated simulations were performed with only the Alpha tank systems being aerated
Figure 3.16: LVVWD system wide model TTHM spatial results without the effects of aeration. Node concentrations are the mean TTHM concentrations over the final 24 hours of the non-aerated 500 hour simulation. The discretization is divided into quintiles where the “light” nodes represent the lower concentrations and the “dark” nodes are the higher concentrations.
Figure 3.17: LVVWD system wide model free chlorine spatial results without the effects of aeration. Node concentrations are the mean free chlorine concentrations over the final 24 hours of each 500 hour simulation. The discretization is divided into quintiles where the “light” nodes represent the lower concentrations and the “dark” nodes are the higher concentrations.
Figure 3.18: ECDF plots for the four THMs including the hourly concentrations from each node for the final 24 hours of the non-aerated simulation ($n = 148704$).
Figure 3.19: ECDF plot for free chlorine comprised of the hourly concentrations from each node for the final 24 hours of the one of the four simulations \((n = 148704)\).

using the case 3 parameterization of \(K_{Ls,y}\) from section 2.1.4. Table 3.4 presents the \(K_{Ls,y}\) values resulting from the linear fit of the \(K_{Ls,y}\) from Table 3.3.

Table 3.4: \(K_{Ls,y}\) parameter calculations for EPANET-MSX water quality simulations for each per-diffuser airflow rate. \(K_{Ls,y}\) units are ft/min.

<table>
<thead>
<tr>
<th>SCFM / Diffuser</th>
<th>CHCl3</th>
<th>CHBrCl2</th>
<th>CHBr2Cl</th>
<th>CHBr3</th>
</tr>
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<td>3.838</td>
<td>3.211e-1</td>
<td>1.695e-1</td>
<td>9.078e-2</td>
<td>5.795e-2</td>
</tr>
</tbody>
</table>

Figure 3.20 illustrates the spatial distribution of the average total THM reduction for each node using the average air flow rate. Pressure zone two received the greatest reduction in average total THM concentration, which is expected since pressure zone two is heavily influenced by the Alpha tank (Figure 3.15). Areas in the northern part of pressure zone 1 still receive a significant benefit because there is a mixture of water coming from the Alpha tanks and the Bravo reservoir. The southern region of pressure zone 1 received little to no benefit given that most of the water comes
directly from the Bravo reservoir.

In addition to simulating aeration in the Alpha tank using the averaged air flow rate, two additional simulations were performed using half of the average, and twice of the average air flow rate. Figure 3.21 presents the ECDF plots for non-aerated and each of the three aerated simulations for the four individual THM species. These results suggest, as expected, that increasing the air flow rate in the Alpha tank results in a decrease in the THM concentrations that are impacted by the Alpha tank. Using hypothesis testing, results from: 1) a Kolmogorov-Smirnov two-sample test ($p < 0.05$, $n = 148704$ pairs) that compared the distribution of THM concentrations in each of the aerated simulations to the non-aerated, and 2) a Wilcoxon Rank Sum paired test that compared the median of the differences between the aerated and non-aerated concentrations to zero, both indicated that aeration had a statistically significant impact on the THM concentrations.

Figure 3.22 clearly illustrates the relationship between the reduction in absolute total THM concentration as a function of the percentage of water arriving at each node from the Alpha tank. These results show a very strong correlation between removal and fraction of Alpha tank water at a given node. Figures 3.23 and 3.24 show the same plots after reducing the air flow rate by half or doubling the air flow rate, respectively. The only meaningful difference between the plots area that reducing the air flow rate resulted in a 20% decrease in total THM reduction and doubling the flow rate resulted in a 20% increase in total THM reduction. Among these three plots there are three densely populated zones along the x-axis including A) ~ 0 to 20%, B) ~ 45 to 80%, and C) ~ 90 to 100% where, the regions tend to be more pressure zone specific. Envelope “A” typically represents the nodes that receive little to no new system flow for the entirety of the simulation or nodes that were not affected by the Alpha aeration tank. Envelope “B,” for the most part, represents the nodes in the
Figure 3.20: Absolute total THM spatial reduction for the LVVWD SWM section using the normal aeration rate. Each color represents a range of TTHM removal in µg/L. The discretization is divided into quintiles where the “light” areas are subject to the least concentration TTHM removal and the “dark” nodes represent the areas subject to higher TTHM concentration removal.
Figure 3.21: ECDF plots comparing the effectiveness of the LVVWD network non-aerated against three aeration scenarios using the Kolmogorov-Smirnov two sample test for each THM. Each CDF illustrates the all hourly results for the last 24 hour of the simulations at every node. The null hypothesis can be rejected for each aeration scenario against the non aerated scenario (p < 0.05, n = 148704).
northern part of pressure zone 1 (the lower of the two zones) where the nodes receive a mixture of Alpha tank and Bravo reservoir water. Finally, the “C” envelope, for the most part, is representative of the nodes within pressure zone 2. As illustrated, “C” nodes receive nearly 100% of the water supply from the Alpha tank where the most significant THM removal occurred.

Figure 3.22: Absolute THM reduction vs. Node supply percentage from the Alpha aeration tank (n = 6196 points). The simulations compared were the non-aerated and the normal rate aeration. The y-axis represents the difference in the average concentration at a node over the last 24 hours of the 500 hour simulations.
Figure 3.23: Absolute THM reduction vs. Node supply percentage from the Alpha aeration tank (n = 6196 points). The simulations compared were the non aerated and the half the normal aeration rate. The y-axis represents the difference in the average concentration at a node over the last 24 hours of the simulations.
Figure 3.24: Absolute THM reduction vs. Node supply percentage from the Alpha aeration tank (n = 6196 points). The simulations compared were the non aerated and the twice the normal aeration rate. The y-axis represents the difference in the average concentration at a node over the last 24 hours of the simulations.
3.4 Discussion

Aeration systems to control THMs, and likely many other VOCs, within large distribution systems can be a part of an overall strategy to enable a public water supplier to meet MCL levels. Tank systems, provided their large storage capacities and increased water age, may be excellent locations to employ DBP control strategies such as aeration. For larger water networks, the potential need for booster chlorination can challenge a water utility’s ability to meet disinfectant residual levels while satisfying by-product regulations. While altering system demands or the underlying infrastructure may not be feasible, from a practical and/or economical perspective, alternative solutions, such as aeration, may provide utilities more flexibility in satisfying future conditions. The current study demonstrated that the aeration model, which was developed at the laboratory-scale, worked well for representing a real set of system data, which would suggest additional opportunities for using such models in an evaluation and/or decision making framework.
Chapter 4

Summary and Conclusions

Utilities face multiple challenges in providing adequate water quality to the consumer tap. One such challenge is the trade-off required to maintain an adequate disinfectant residual while satisfying disinfectant by-product regulations. Modeling the fate of THMs within distribution systems can provide utilities with the tools necessary to predict water quality performance throughout the network, highlight key areas of concern, and allow the investigation of alternative methods to satisfy their objectives. The progression of knowledge for the current study was divided into three phases with the intent to model, validate, and assess system-wide effects of an in-tank fine bubble aeration THM removal strategy. The first phase was to estimate mass transport parameters and model the associated dynamics for each THM under varying operational conditions in a controlled laboratory environment. Secondly, using the estimated parameters from the first phase, the model was evaluated by simulating the dynamics of our partner utility’s 20 MG aeration basin and comparing the modeled THM concentrations to the observed data. Finally, the aeration model was included into a system-wide distribution network model to assess system-wide impacts that the tank aeration strategy might have on THM control within a distribution system.
The experimental design was intended to test the aeration model against a number of realistic operational conditions. The first-order model included both bubble and surface mass transport and required the estimation of two parameters. Using the laboratory experimental data, both model parameters were numerically estimated using a two dimensional search algorithm to minimize the root mean square error. With respect to the bubble mass transport term, two generalizations could be made: 1) the THM gas phase concentrations within the bubble rapidly reached equilibrium with the liquid phase; and 2) bubble mass transport alone was not sufficient for representing THM removal within the experimental studies. Thus, the surface mass transport, for the most part, dictated the total mass transport from the liquid phase. The surface mass transport term was parameterized in three different manners: 1) assumed constant for all experimental conditions; 2) assumed dependent on the airflow rate; and 3) assumed dependent on airflow rate while accounting for changes to the ratio of surface area to reactor volume. Based only on the experimental results, allowing the surface mass transport term to be a function of airflow rate appeared important.

The aeration model, developed with laboratory scale data, was included as part of a model to represent the changes in tank volume as well as chlorine decay and THM formation within a storage tank. The complete model was used to simulate observed conditions from our partner utility’s storage tank that included an aeration process to compare the experimental data to the model predicted data as an evaluation step. The model was applied to the Alpha aeration basin by using an effective tank surface area that assumed all of the mass transport was restricted to 1 foot diameter theoretical columns around each aeration membrane which was similar to the reactor dimensions used to estimate the transport coefficients. The effective area modeling strategy demonstrated that allowing the surface mass transport to vary with airflow rate and accounting for the ratio of surface area to tank volume was able to ‘closely’
represent the observed THM concentrations under dynamic tank operations. Potential limitations of the effective surface modeling approach include the fact that not all mass transport is likely contained within the theoretical columns and that additional surface mass transport might be occurring across the overall tank gas-liquid interfacial area.

The Alpha tank aeration model was then applied to our partner utility’s distribution system model to evaluate the system-wide impacts when using aeration as a THM control strategy within a centralized storage tank. With respect to the routine operation of the water network, the inclusion of the THM control strategy indicated a significant reduction in THM concentrations in the areas influenced by the Alpha tank system, and that increasing the airflow rate further reduced THM concentrations. Simulation results also illustrated a strong linear correlation between the absolute total THM reduction with respect to the percentage of water at a given location received from the Alpha tank.

Accurate water quality models enable greater predictability of the dynamics within a distribution system. Air-stripping is an effective way to remove THMs from distribution system tanks and can play a role as part of a THM management strategy. Modeling the impact that a bubble aeration system has on the removal of THMs within a distribution system can support the optimization of balancing water quality regulations and economics.
Chapter 5

Future Work

Potential future topics that could build upon the current study include:

1. Investigating the direct impact of tank mixing to model THM removal vs. mixing power.

2. Comparing the effectiveness and energy demand of DBP control through bubble aeration against other DBP control methods.

3. Evaluating optimization algorithms to support placement, design, and operation of future planning and implementation of a DBP aeration control strategy.
6 References


Harrison, J. (1999). *Point-of-entry (POE) point-of-use (POU) water treatment overview. Providing safe drinking water in small systems: technology, operations, and economics.*, chapter 5, page 293. CRC.


Appendix A

Justification of Completely Mixed Reactor Assumption

The following appendix describes the bubble rise velocity and the justification for complete reactor mixing.

A.1 Bubble Rise Velocity

Estimating bubble rise velocity using the principles of Stoke’s law is an iterative process depending on specific bubble parameters. Typically, laminar flow is assumed initially and tested against the Reynold’s number. For a sphere traveling through fluid, three flow regimes can be considered: laminar (Re ≤ 1), turbulent (Re ≥ 700), or transitional (1 ≤ Re ≤ 700) (Crowe et al., 2005). Parameters for the case of a bubble with a 2-mm diameter are as follows:

\[ \rho_{\text{water } 20^\circ C} = 9.9823e-1 \text{ g/cm}^3 \]
\[ \rho_{\text{air } 20^\circ C} = 1.185e-3 \text{ g/cm}^3 \]
\[ \eta_{\text{water } 20^\circ C} = 1.0087e-2 \text{ g/cm-sec} \]
g = 981 cm/sec

Bubble diameter (D) = 0.2 cm

Assuming laminar flow for bubble rise velocity (i.e., the bubble reaches terminal velocity rapidly), Stoke’s Law for laminar flow is:

\[ V_t = -\frac{D^2(\rho_{\text{air}} - \rho_{\text{water}})g}{18\eta} \]

where the negative sign accounts for a “rising bubble”, with a result of

\[ V_t = 215 \text{ cm/sec} \]

\[ Re = \frac{\rho V_t D}{\eta} = 4262 \]

where Re should be less than 1 for a sphere in laminar flow conditions.

Now, for turbulent flow, Stoke’s Law is as follows:

\[ V_t^2 = |3.0303D(S_g - 1)g| \]

where, \( S_g = \frac{\rho_{\text{air}}}{\rho_{\text{water}}} \), and

\[ V_t = 24.36 \text{ cm/sec} \]

\[ Re = 482 \]

And since Re should be greater than 700 the conditions are not turbulent.

Now, for transitional flow, Stoke’s Law is as follows:

\[ V_t = \sqrt{\frac{4D|(S_g - 1)|g}{3f_D}} \]

\[ f_D = \frac{24}{Re} + \frac{3}{\sqrt{Re}} + 0.34 \]

where the above equations, along with the equation for Re, were solved simultaneously to determine that \( f_D = 5.264 \)

\[ V_t = 22.26 \text{ cm/sec} \]

\[ Re = 441 \]

thus \( 1 \leq Re \leq 700 \) so the flow is in the transitional regime, and the bubble rise velocity is 22.26 cm/sec.
A.2 Complete Mixing

The experimental verification of the completely mixed assumption was conducted with chloroform and bromoform, the lightest and heaviest of the four THMs, respectively, in two separate experiments. The sampling regime is presented in Table A.1, where nine samples were taken along the height of the column at each of four time steps, excluding $t_0$. For both experiments, the sample sets were collected at 15, 30, 60, and 120 minutes, elapsed time. A greater number of samples were collected towards the bottom of the column and more sparsely toward the top of the column (see Table A.1). The first experiment was conducted with a chloroform and bromoform spike to 75 and 50 $\mu$g/L, respectively, with an air flow rate of 2 SCFM and water height of 11 ft. The second experiment was conducted with a bromoform spike of 50 $\mu$g/L, with an air flow rate of 2 SCFM and water height of 11 ft.

Results for the first experiment are presented in Figure A.1 for chloroform and Figure A.2 for bromoform. Results from the second experiment, bromoform only, are presented in Figure A.3. The following plots illustrate normalized THM concentrations, over five time steps, specific to the ten sampling locations. By qualitative observation, no unique spatial distribution of the concentration pattern existed across multiple time steps, thus the reactor was assumed to be completely mixed.
Table A.1: Sampling locations for verifying reactor assumptions. Each sampling position is denoted by ‘X’. Experiments were performed with a water height of 11 feet, and air flow rate of 2 SCFM.

<table>
<thead>
<tr>
<th>Height (ft)</th>
<th>Time (mins)</th>
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<td></td>
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<tr>
<td>11.5</td>
<td>D</td>
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The table shows the sampling locations for different depths and times, with each sampling position denoted by ‘X’.
Figure A.1: Reactor mixing assumption experiment 1; initial chloroform concentration of 75 µg/L, air flow rate of 2 SCFM, and water height of 11 ft. Each sampling depth is denoted by a disparate marker.
Figure A.2: Reactor mixing assumption experiment 1; initial bromoform concentration of 50 µg/L, air flow rate of 2 SCFM, and water height of 11 ft. Each sampling depth is denoted by a disparate marker.
Figure A.3: Reactor mixing assumption experiment 2; initial bromoform concentration of 50 µg/L, air flow rate of 2 SCFM, and water height of 11 ft. Each sampling depth is denoted by a disparate marker.
Appendix B

Henry’s Constant Regression

The Henry’s constants for THMs are functions of temperature and were modeled by Nicholson et al. (1984). The online EPA Henry’s Constant Calculator (USEPA, 2010) was used in conjunction with the THM models by Nicholson et al. (1984) over the temperature range of [5°C, 35°C] to transform the Henry’s constants to dimensionless values. Dimensionless Henry’s Constant models were computed by running exponential regressions on each THM as shown in Figure B.1.
Figure B.1: Henry’s Constant regressions for each THM converted from \([\text{m}^3 \text{ atm mol}^{-1}]\) from research by Nicholson et al. (1984) over temperature range \([5^\circ \text{C}, 35^\circ \text{C}]\) to dimensionless values by use of the EPA Henry’s Constant Converter (USEPA, 2010).
Appendix C

MATLAB code for Parameter Estimation

C.1 Code Preface and Description

The parameter estimation program was written to estimate the model parameters using one to multiple data sets and operational conditions using the first order model of Equation 2.4. Through the many scripts presented below, the program receives the raw experimental concentration data as well as operating conditions (e.g. air flow rate, liquid volume, and depth) as input, while the user establishes the transport coefficient ranges for the 2-dimensional matrix of transport values. The program finds the total RMSE value using all of the experimental data over a pre-defined range of parameter estimates. Next, the model finds the minimum RMSE value from the matrix, which is used to determine the best set of transport coefficients for representing the experimental data.
C.2 Example Progressive Scripts

C.2.1 Master Data Entry

This script is used to combine the the raw_data structure into the normalized_data structure.

```matlab
% this script is to combine the the raw_data structure into the normalized_data structure.
load raw_data;
load normalized_data;

%for i = 9:9
    temp = data_function(['dataset13.csv']);
    save('temp','temp');
    raw_data(temp.experimentnumber) = temp;
    save('raw_data','raw_data');

load temp
normalized_data(temp.experimentnumber) = normalfunction(temp.experimentnumber);
%end

save('raw_data','raw_data');
save('normalized_data', 'normalized_data')
clear

Reads Excel .csv file and stores in structures

function run = data_function(filename)
    %% Data entry
    %% Read Excel file and store in Structure for each THM

    % function entry experiment number
    % filename = 'trialdataset1.csv'

    % User Specified Experimental Run Number.
```
%experimentnumber = input('Experimental run number ?: ');
i = experimentnumber;

%AautoImport experimental number structure
experimentnumber = csvread(filename, 0, 1,[0,1,0,1]);
i = experimentnumber;
run.experimentnumber = i;
%Number of sample time steps
%import airflow rate SCFM
run.scfm = csvread(filename, 35, 0,[35,0,35,0]);
%import water height
run.height = csvread(filename, 37, 0,[37,0,37,0]);
%import initial concentration
run.iniconc = csvread(filename, 39, 0,[39,0,39,0]);
run.timesteps = input('Input the number of sample time steps (excluding t0): ');  
TS = experirun.timesteps + 1;
%Aautoimport timesteps
run.timeintervals = csvread(filename,2,0,[2,0,2,run.timesteps]);
%Aauto Import Data for each THM
%Number of sample sample positions
run.sampling = input('Input the number of sample positions at each timestep (excluding t0): ');  
col = run.timesteps;
%Chloroform
rowstart = 3; %specify this value
row = rowstart - 1 + run.sampling;
run.chloroform = csvread(filename,rowstart,0,[rowstart,0,row,col]);
clear row
%bromodichloromethane
rowstart = 11; %specify this value
row = rowstart - 1 + run.sampling;
run.dichloro = csvread(filename,rowstart,0,[rowstart,0,row,col]);
clear row
%Dibromochloromethane
rowstart = 19; %specify this value
row = rowstart - 1 + run.sampling;
run.dibromo = csvread(filename,rowstart,0,[rowstart,0,row,col]);
clear row
%Bromoform
rowstart = 27; %specify this value
row = rowstart - 1 + run.sampling;
run.bromoform = csvread(filename,rowstart,0,[rowstart,0,row,col]);
clear row
Function to normalize all data and store the information in data structures

function temp = normalfunction(run)
    %average the real values
    load raw_data
    load temp
    %%Chloroform
    i = 1; k = 1;
    while i < length(raw_data(run).chloroform(:,1))
        if raw_data(run).chloroform(i,1) > 0
            temp.chcl3(k) = raw_data(run).chloroform(i,1);
            k = k + 1;
        else
            end
            i = i + 1;
        end
        %Chloroform normalizing
        temp.nchloroform = raw_data(run).chloroform / mean(temp.chcl3);
        %Setting the initials normalized concentrations to ones
        temp.nchloroform(:,1) = 1;
        clear i
        clear k
    %%dichloro
    i = 1; k = 1;
    while i < length(raw_data(run).dichloro(:,1))
        if raw_data(run).dichloro(i,1) > 0
            temp.chcl2br(k) = raw_data(run).dichloro(i,1);
            k = k + 1;
        else
            end
            i = i + 1;
    end
    %dichloro normalizing
    temp.ndichloro = raw_data(run).dichloro / mean(temp.chcl2br);
    %Setting the initials normalized concentrations to ones
    temp.ndichloro(:,1) = 1;
    clear i
    clear k
    %%dibromo
    i = 1; k = 1;
while i < length(raw_data(run).dibromo(:,1))
    if raw_data(run).dibromo(i,1) > 0
        temp.chclbr2(k) = raw_data(run).dibromo(i,1);
        k = k + 1;
    else
        end
    i = i + 1;
end
% dichloro normalizing
temp.ndibromo = raw_data(run).dibromo / mean(temp.chclbr2);
% Setting the initials normalized concentrations to ones
temp.ndibromo(:,1) = 1;
clear i
clear k
% % bromoform
i = 1; k = 1;
while i < length(raw_data(run).bromoform(:,1))
    if raw_data(run).bromoform(i,1) > 0
        temp.chbr3(k) = raw_data(run).bromoform(i,1);
        k = k + 1;
    else
        end
    i = i + 1;
end
% dichloro normalizing
temp.nbromoform = raw_data(run).bromoform / mean(temp.chbr3);
% Setting the initials normalized concentrations to ones
temp.nbromoform(:,1) = 1;
clear i
clear k

C.2.2 Plot Data Manager

% Plot data manager
% this script pulls the normalized_data data and passes it through the
% function data_plot and stores the new values in the plot_data structure.
% The plot_data structure is a structure with 20 fields including the
% regression analysis for the data
load plot_data
load normalized_data
for i = 1:13 % data manager range specifiable here
plot_data(i) = dataplot(i);
end

save('plot_data', 'plot_data')
clear

%%places all the runs in columns in order in ...
%%[ runnumber, SCFM, Height, Co]
load experimental_titles
load normalized_data
%make temp into function later******
temp = zeros(1,length(normalized_data));
pH = zeros(1,length(normalized_data));

%User specifies list of temp and pH up to current knowledge
templist = [17,23,23,19,23,17,23,23,21.5,23,26,22.3,25.5];% oC
pHlist = ...
[7.9,7.69,8.17,7.92,7.56,8.23,7.56,7.55,7.52,7.39,7.93,8.13,7.97];%pH

for i = 1:length(normalized_data)
    if i > length(templist)
        temp(i) = NaN;
    else
        temp(i)=templist(i);
    end
end

for i = 1:length(normalized_data)
    if i > length(pHlist)
        pH(i) = NaN;
    else
        pH(i)=pHlist(i);
    end
end

temp = [17,23,23,19,23,17,23,23,23,0, 0, 0, 0];
pH = [7.9,7.69,8.17,7.92,7.56,8.23,7.56,7.55,7.55,20,0 ,0, 0, 0];
maxrun = length(templist);

A = zeros(maxrun,6);

for i = 1:maxrun
    A(i,1) = normalized_data(i).experimentnumber;
    A(i,2) = normalized_data(i).scfm;
    A(i,3) = normalized_data(i).height;
A(i,4) = normalized_data(i).iniconc;
A(i,5) = temp(i);
A(i,6) = pH(i);
end

experimental_titles = A;

save('experimental_titles', 'experimental_titles')

% Adding Henry's Constants to Experimental_titles.m

load experimental_titles
load henrys_constant

maxrun = 13;

for i = 1:maxrun
    henrys_constant(i).H = henrys_function(experimental_titles(i,5));
end

save('henrys_constant', 'henrys_constant')

function henrys_constant = henrys_function(temperature)

    %% Henry's Constant creator given temperature of THM

    load experimental_titles
    T = temperature;
    H(1) = 0.0375*exp(0.0574*T); % chloro
    H(2) = 0.0199*exp(0.0574*T); % dichloro
    H(3) = 0.0109*exp(0.0574*T); % dibromo
    H(4) = 0.005*exp(0.0627*T); % bromo
    henrys_constant = H;

end

Contents

- Run Cases Chloroform
- Creating single Data Array with all data from experiments selected
- Creating time array
- Model Data for each run
Parameter finding / optimizing
- RMSE minimum and parameter values
- Save Data

Run Cases

load henrys_constant
load normalized_data
load model_data

%%**********SAVE CASE NUMBER**********
save_case = 7; %**********

%*****UPDATE THIS EVERY RUN**********
% cases to compare in vector form
model_data(save_case).data_sets = [5,6,7,12];
model_data(save_case).k_s_chloroform = 0.015:0.0001:0.025; %0.0000001;%
model_data(save_case).k_b_chloroform = 3:0.001:4.1;
model_data(save_case).k_s_dichloro = 0:0.0001:0.02; %0:0.001:0.050;
model_data(save_case).k_b_dichloro = 1.7:0.001:2.5;
model_data(save_case).k_s_dibromo = 0.005:0.0001:0.007; %0:0.001:0.01;
model_data(save_case).k_b_dibromo = 0.8:0.001:2.5;
model_data(save_case).k_s_bromoform = 0.0003:0.001:0.05; %0:0.001:0.006;
model_data(save_case).k_b_bromoform = 0.4:0.001:0.7;

num_thm_species = 4;
for thmspecies = 1:num_thm_species
    switch thmspecies
    case 1
        thm = 'chloroform';
        % Building Henry's array for various temperatures
        C = [];
        for i = 1:length(model_data(save_case).data_sets)
            c = henrys_constant...
            (model_data(save_case).data_sets(i)).H(thmspecies);
            num = numel(normalized_data(model_data...
            (save_case).data_sets(i)).(genvarname(['n' thm])));
            C = [C; c*ones(num,1)];
        end
        H = C;
        clear C c num
    case 2
        thm = 'dichloro';
C = []; 
for i = 1:length(model_data(save_case).data_sets) 
    c = henrys_constant... 
        (model_data(save_case).data_sets(i)).H(thmspecies);
    num = numel(normalized_data(model_data...
        (save_case).data_sets(i)).(genvarname(['n' thm])));
    C = [C; c*ones(num,1)]; 
end 
H = C; 
clear C c num 

case 3 
    thm = 'dibromo'; 
    C = []; 
    for i = 1:length(model_data(save_case).data_sets) 
        c = henrys_constant... 
            (model_data(save_case).data_sets(i)).H(thmspecies);
        num = numel(normalized_data(model_data...
            (save_case).data_sets(i)).(genvarname(['n' thm])));
        C = [C; c*ones(num,1)]; 
    end 
    H = C; 
clear C c num 

case 4 
    thm = 'bromoform'; 
    C = []; 
    for i = 1:length(model_data(save_case).data_sets) 
        c = henrys_constant... 
            (model_data(save_case).data_sets(i)).H(thmspecies);
        num = numel(normalized_data(model_data...
            (save_case).data_sets(i)).(genvarname(['n' thm])));
        C = [C; c*ones(num,1)]; 
    end 
    H = C; 
clear C c num 
end 

Creating a single data array with all data from the experiments selected 

%establishing data array length for all the selected data sets 
sum = 0; 
for i = 1: length(model_data(save_case).data_sets) 
    temp =...
normalized_data(model_data(save_case).data_sets(i)).sampling...
* length(normalized_data(model_data(save_case).data_sets...
  (i)).timeintervals);
sum = sum + temp;
end

% fitting all the data into an array column by vertical concatenation
data = zeros(sum,1);
i=1;
temp1 = reshape(normalized_data(model_data(save_case).data_sets...
  (1)).(genvarname(['n' thm])),numel(normalized_data(model_data...
  (save_case).data_sets(1)).(genvarname(['n' thm]))),1);
for i = 2:length(model_data(save_case).data_sets)
  temp2 = reshape(normalized_data(model_data(save_case).data_sets...
    (i)).(genvarname(['n' thm])),numel(normalized_data(model_data...
    (save_case).data_sets(i)).(genvarname(['n' thm]))),1);
  temp1 = vertcat(temp1,temp2);
end
data = temp1;

Creating a time array

% setting up time arrays and placing them into a column vector
% initial
    a = normalized_data(model_data(save_case).data_sets...
        (1)).timeintervals;
    for j = 1:normalized_data(model_data(save_case).data_sets...
        (1)).sampling -1
        b = normalized_data(model_data(save_case).data_sets...
            (1)).timeintervals;
        a = vertcat(a, b);
    end
    A = reshape(a,numel(a),1);
% Setting up total time array
for i = 2:length(model_data(save_case).data_sets)
    a = normalized_data(model_data(save_case).data_sets...
        (i)).timeintervals;
    for j = 1:normalized_data(model_data(save_case).data_sets...
        (i)).sampling -1
        b = normalized_data(model_data(save_case).data_sets...
            (i)).timeintervals;
        a = vertcat(a, b);
    end
    B = reshape(a,numel(a),1);
A = vertcat(A, B);
Model Data for each run

% places SCFM into a vertical array
C = []; for i = 1:length(model_data(save_case).data_sets)
    c = normalized_data(model_data(save_case).data_sets(i)).scfm;
    num = numel(normalized_data(model_data(save_case).data_sets(i)).genvarname([’n’ thm]));
    C = [C; c*ones(num,1)];
end

% height
D = []; for i = 1:length(model_data(save_case).data_sets)
    d = normalized_data(model_data(save_case).data_sets(i)).height;
    num = numel(normalized_data(model_data(save_case).data_sets(i)).genvarname([’n’ thm]));
    D = [D; d*ones(num,1)];
end
D = D*pi() / 4;

% Model is an (i,2) matrix [SCF, Height]
model = horzcat(C,D);

Parameter estimation / optimization

counter = 1;
model_data(save_case).([’Z’ thm]) = zeros(length(model_data...
    (save_case).genvarname([’k_s_’ thm])), length(model_data...
    (save_case).genvarname([’k_b_’ thm])));
elements = numel(model_data(save_case).genvarname([’Z’ thm]));
for i = 1:length(model_data(save_case).genvarname([’k_s_’ thm]))
    for j = 1:length(model_data(save_case).genvarname([’k_b_’ thm]))
        model_data(save_case).([’Z’ thm])(i,j) = model_function...
            (model, H, data, model_data(save_case).genvarname...
            ([’k_s_’ thm])(i), model_data(save_case).genvarname...
            ([’k_b_’ thm])(j), t);
        counter = counter + 1;
    end
end
disp([’THM ’ num2str(thmspecies) ’/’ num2str(num_thm_species)...’:
    ’ num2str(counter) ’/’ num2str(numel(model_data...
    (save_case).([’Z’ thm]))), ’ percent complete = ’ num2str...
(counter*100/numel(model_data(save_case).([‘Z’ thm]))));
end

%% Plotter

% surfl(model_data(save_case).((genvarname([‘k_b’ thm]))),
% model_data(save_case).((genvarname([‘k_s’ thm]))),Z);
% colormap(spring)
% shading interp
%
axis([-0.01 0.01 -0.01 0.01 0 4]);
% xlabel(‘model_data(save_case).((genvarname([‘k_b’ thm]))’);
% ylabel(‘model_data(save_case).((genvarname([‘k_s’ thm]))’);
% zlabel(‘RMSE’);

end

Minimum RMSE and parameter values

num_thm_species = 4;
for thmspecies = 1:num_thm_species
    switch thmspecies
    case 1
        thm = ’chloroform’;
    case 2
        thm = ’dichloro’;
    case 3
        thm = ’dibromo’;
    case 4
        thm = ’bromoform’;
    end
    [model_data(save_case).([thm ‘m_rmse’]) model_data...
        (save_case).([thm ‘x’])] = min(model_data...
        (save_case).((genvarname([‘Z’ thm]))));
    [model_data(save_case).([thm ‘m_rmse’]) model_data...
        (save_case).([thm ‘y’])] = min(model_data...
        (save_case).((genvarname([‘Z’ thm]))));
end
disp([’For combined experiments: ’ num2str(model_data...
    (save_case).data_sets)]);
disp([’k_s = ’ num2str(model_data(save_case).((genvarname...
    ([’k_s’ thm])))(model_data(save_case).([thm ‘x’]))(model_data...
    (save_case).([thm ‘y’])))));
end

Model Function

% Model from Monteith.
function err = model_function(model, H, data, k_sf, k_bf, t)
    err = 0;
    for i = 1:length(data)
        temp = exp(-model(i,2) * k_sf + model(i,1) * H(i)... * (1 - exp(- k_bf * model(i,2) / model(i,1)/H(i))))... *t(i)/model(i,2);
        err = err + (temp - data(i))^2;
        if sqrt(err/i) > .4
            err = NaN;
            break;
        end
    end
    err = sqrt(err/i);
end
Appendix D

Alpha Tank Modeling: Supporting Information

D.1 Alpha Tank Flow Kinetics

The Alpha tank depth to volume relationships are illustrated in Figures D.1 and D.2. Figure D.1 presents the depth to volume relationship when all three compartments of the Alpha tank are operational. Figure D.2 presents the depth to volume relationship when only the North and Middle compartments of the Alpha tank are operational. A regression line was fit through the data for depths greater than 8 ft for use in the modeling as the observed depths were never outside the linear region of the depth to volume relationship.

Figure D.3 presents the estimated flows from using the available SCADA data. The top plot of Figure D.3 presents the observed and model predicted tank depths at one-hour time steps. The middle plot of Figure D.3 shows the estimated “inflow” data from the Alpha tank; a negative value indicates flow is leaving the tank back towards pressure zone 1. The bottom plot of Figure D.3 shows the estimated “outflow” data from the Alpha tank, which was based on the available pumping data.

Data pertaining to the airflow rate, $Q_g$, are presented in Figure D.4. The top plot of Figure D.4 presents a histogram of the air flow data, which suggests the air flows
were either "low" or "high." The bottom plot of Figure D.4 presents the temporal measurements of air flow (symbols) and periods of unknown air flow rate (lines). The 25th and 75th percentile air flow rates were 4621.5 and 5792.0 SCFM were used to represent the boundary conditions of the sensitivity analysis.

\[ \text{Volume} = 256973.25 \times D - 1e6 \]

Figure D.1: Alpha tank volume to depth linear regression for depths beyond 10 ft considering the entire 40 MG tank.
Figure D.2: Alpha tank volume to depth linear regression for depths beyond 10 ft considering the Middle and North tanks, only (20MG total capacity).
Figure D.3: Alpha tank flow and depths over time during the Alpha basin study. The top plot illustrates the model predicted and observed tank depths during the study period; the middle plot illustrates the “back-calculated” influent flow rate based on Equation 2.5; and the bottom plot depicts the measured effluent flow rate from Alpha.
Figure D.4: The top plot illustrates the histogram for the airflow measurements taken within the study time frame whereas the bottom plot illustrates the measured airflow rates over time. The ‘unknown’ values are for illustrative purposes. The average airflow rate during the study was 5268 SCFM with a standard deviation of 706.4 SCFM, represented as the dotted lines above and below the average.
D.2 Chlorine Decay and THM Formation Modeling: Supporting Information

The following section includes the modeling and parameter estimation methods for chlorine decay and THM formation rates using data provided by LVVWD.

D.2.1 Chlorine Decay and THM Formation Models

Four bottle tests were conducted by LVVWD from two sample sets taken from both the Middle and North basins of the Alpha tank system for quantification and parameter estimation of chlorine decay and THM formation. Initial samples were analyzed for chlorine and THM concentrations from each batch followed by additional samples analyzed at predefined time steps per batch. From both the Middle and North basins, samples were analyzed 4 and 7 days after the initial sampling time for the first batches of water, while the second batches were analyzed at 1, 2 and 7 days after the initial sample.

Chlorine decay is represented by the second-order model from Boccelli et al. (2003) as follows:

\[
\frac{dC_A}{dt} = -k_AC_AC_B \quad \frac{dC_B}{dt} = -k_BC_AC_B \tag{D.1}
\]

where \(C_A\) is the chlorine concentration (mg/L), \(C_B\) is the fictive species concentration of reactants in the liquid phase (mg/L), \(k_A\) and \(k_B\) are the reaction rates (L / (mg-t)) for the reactant species and \(t\) is time.

Unlike the first-order model, the second-order model better represents the fast and slow decay following the initial, very rapid decay. According to Boccelli et al. (2003), Clark and Sivaganesan (2002), in most cases the second-order chlorine decay model offers increased predictability, particularly for post-chlorinated waters leaving a clear well. Furthermore, research by Boccelli et al. (2003) suggests that the second order
reactive species model, described in Equation D.1, can outperform the first order model regardless of the initial and/or booster chlorination operations.

The analytical solution to Equation D.1, from Boccelli et al. (2003), using parameter substitutions for the unknown, fictive species is as follows:

\[ C_A(t) = \frac{C_{A,0} - \alpha}{1 - (\alpha/C_{A,0}) \exp[-(C_{A,0}/\alpha - 1)\beta t]} \]  

(D.2)

where \( C_{A,0} \) and \( C_{B,0} \) are the initial chlorine and fictive species concentrations, \( \alpha = aC_{B,0}/b \), \( \beta = k AC_{B,0} \), and the ratio \( a/b \) represents the stoichiometric reaction coefficients for chlorine and liquid phase reactants. Parameters \( \alpha \) and \( \beta \) were estimated using experimental chlorine decay data.

THM formation rates depend on chlorine decay rates in post-treated waters leaving the treatment plant. Independent of the reaction order of chlorine decay, THM formation can be modeled as a linear function with respect to chlorine demand (Boccelli et al., 2003, Clark, 1998) as follows:

\[ THM_y(t) = Tyx(t) + M_y, \]  

(D.3)

where \( T \) is a fitting parameter associated with the formation of THM \( y \), \( x(t) \) is the chlorine demand at time \( t \) (i.e. the difference between initial chlorine dose at \( t = 0 \) and remaining chlorine in the liquid phase at time \( t \)), and \( M \) is the initial THM concentration at \( t = 0 \).

D.2.2 Chlorine Decay and THM Formation Rate Estimation

The data from all four bottle tests were used together for the parameter estimation of the second-order chlorine decay model (Equation D.2). Based on the observed data, the initial chlorine concentrations for the four sample sets were specified as 1.2 mg/L. Using Excel solver, the sum of squared error was minimized between the model (Equation D.2) and the data by varying the \( \alpha \) and \( \beta \) parameters where results were
11.391e3, and 7.372e-2, respectively. According to Boccelli et al. (2003), as $\alpha \to \infty$, $\beta \to k_A$, which is approximated by the current parameter estimates, the second-order model reduces to the simple first-order model, shown in Equation 2.13. The final $k_A$ value for the resulting first-order model was estimated to be 3.07e-3 hr$^{-1}$.

THM formation parameters were also estimated using the four experimental data sets as discussed above. The resulting chlorine concentrations observed at time $t$ (corresponding to THM formation sampling times) were subtracted from the initial chlorine dose to calculate the chlorine demand at time $t$, $x(t)$. The parameters $T$ and $M$ from model Equation D.3 were estimated for each THM by minimizing the sum of squared error between the model predicted values and the observed THM concentrations using Excel solver. Table D.1 illustrates the results for THM formation parameters using the LVVWD experimental data sets. The predominantly chlorinated THMs form the most with respect to a unit chlorine decay, while the bromoform tends to form very little with respect to chlorine decay since there was likely lower concentrations of bromine in the water.

Table D.1: Parameter estimates for THM formation assuming a linear formation with respect to chlorine decay.

<table>
<thead>
<tr>
<th></th>
<th>CHCl$_3$</th>
<th>CHCl$_2$Br</th>
<th>CHClBr$_2$</th>
<th>CHBr$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_y$ (µg/L/mg/L)</td>
<td>57.87</td>
<td>14.28</td>
<td>4.67</td>
<td>1.51</td>
</tr>
<tr>
<td>$M_y$ (µg)</td>
<td>25.25</td>
<td>17.46</td>
<td>13.13</td>
<td>2</td>
</tr>
</tbody>
</table>

D.2.2.1 Chlorine and THM Influent Concentration Variability

Figures D.5 – D.9 present the distributions of chlorine and individual THM species to demonstrate the variability of the influent concentrations for use with the continuous flow model dynamics. The distributions of influent THM concentrations, for the most part, concentration distributions were not normally distributed so, in an effort
to retain consistency between the modeled compounds, the 25\textsuperscript{th} and 75\textsuperscript{th} percentiles were also used as appropriate boundary conditions to bracket the observed LVVWD data.

Figure D.5: Chlorine influent concentration histogram. The ‘unknown’ values are for illustrative purposes. The 25\textsuperscript{th} and 75\textsuperscript{th} percentiles are 0.61 and 0.81 mg/L, respectively
Figure D.6: Chloroform influent concentration histogram. The ‘unknown’ value is for ‘illustrative’ purposes. The 25<sup>th</sup> and 75<sup>th</sup> quantiles are 28 and 31 µg/L, respectively.
Figure D.7: Bromodichloromethane influent concentration histogram. The ‘unknown’ value is for ‘illustrative’ purposes. The 25th and 75th quantiles are 21 and 23 µg/L, respectively.
Figure D.8: Dibromochloromethane influent concentration histogram. The ‘unknown’ value is for ‘illustrative’ purposes. The 25th and 75th quantiles are 15 and 16 $\mu g$/L, respectively.
Figure D.9: Bromoform influent concentration histogram. The ‘unknown’ value is for ‘illustrative’ purposes. The $25^{th}$ and $75^{th}$ quantiles are 2.0 and 2.2 µg/L, respectively.
D.3 Modeling description

In general, the data sets provided by LVVWD, such as flow rates, were provided in one hour time steps and were assumed constant during that time period, which is consistent with typical distribution system modeling assumptions. Therefore, the model was solved as a series of $n$ one hour blocks. The initial conditions for any given hour were either specified by the user, for $t_0$, or from the model using the data from the end of the previous hour to represent the initial conditions at the next time step $t_{n+1}$.

A vector of initial conditions was passed through the model including the total mass of each THM ($\mu$g), the total mass of free chlorine (mg), and the total tank volume (L). The second vector of values passed through the model function included influent and effluent flow rates (L/hr) for the individual one hour time blocks, and a third vector of constants was passed to the model function that remained unchanged during the simulation, which included Henry’s constants, $K_{L_s,y,a}$ (or $K_{L_s,y}$) and $K_{L_b,y,a}$ values, $\psi$, influent concentrations for each THM, and chlorine decay and THM formation rates.

Since both tanks operate hydraulically similar, the influent and effluent flow rates associated with Alpha tank system were divided in half giving both the Middle and North tanks equal flow. The inflow data to the Alpha tank system was not measured, therefore a script was written to calculate the inflow rates over time by using the hourly change in tank volume and effluent pumping rates to ensure the total tank volume at every hour was consistent with observed data. If the supply pumps to the Alpha tank system were off, water was allowed to flow back out of the Alpha supply tank towards the source. Thus, if a negative inflow rate was passed through the model function, the concentration removal rate was handled by a logic argument that established that the concentration leaving the tank was equal to the concentration within the tank.

The following subsections present the scripts used in the tank modeling portion of
D.3.1 Middle Tank Input Script

```matlab
%clc
%clear
%close all
%% Bkgrd
%the purpose of this script is to setup all the values to pass through the
%ode solver. The mass and volumes are considered separate but within the
%model function masses are dependent on the volume since the influent mass
%rate is passed as a concentration rate.

%Solving and data management:
%Data sets for flow rates were privided from LVVWD as hourly tank effluent
%flow rates along with hourly changes in tank depth. The influent flow rate
%was back calculated using dV_in/dt = dV_tank/dt + dV_out/dt. These data were
%provided in KGPD (thousand gallon per day), and converted to Liter per
%hour. ALL COMMON UNITS ARE AS FOLLOWS: Liters; Hours; Mass.

%The code is designed to solve the an ODE for a 1 hour time block since
%flow data is provided in hourly blocks. Therefore, a timestep is
designated not for the ODE solver but for the hourly stepping process to
%solve an ODE. The code handles time stepping using an index value which
%is the start time and end time is the start time + 1 hours. Each
%hourly solution set get concatonated

%Initial Script Setup Constants, Definitions, and etc.
options = odeset('RelTol',1e-5,'AbsTol',1e-5);
galVol = 7.4805195; %Gal/ft^3
LiterVol = 28.316847; %Liter/ft^3
LiterGal = 3.7854; %Liter/Gal
L_temp = 15.14; %\degree Celsius

%Initial Liquid Volume for half the alpha tank system
height = 20.79;%
IniVol = (128912*height - 544330)*LiterVol/2;
% we are considering 1/4 of the whole tank

%Initial Concentrations Should be taken from Data
IniConc(1) = 17; %ppb dichloro
IniConc(2) = 2; %ppb bromo
IniConc(3) = 14; %ppb dibromo
```
IniConc(4) = 21.2; % ppb chloro
IniConc(5) = 0.83; % ppm chlorine

Ini(1) = IniVol; % Liters % volume in the tank
Ini(2) = IniConc(1)*IniVol; % mass in the tank
Ini(3) = IniConc(2)*IniVol; % mass in the tank
Ini(4) = IniConc(3)*IniVol; % mass in the tank
Ini(5) = IniConc(4)*IniVol; % mass in the tank
Ini(6) = IniConc(5)*IniVol; % mass in the tank

% Flows were reported from LVVWD in KGpD flow that Alpha tank system
load alpha_inflowrate % KGpD
load alpha_outflow % KGpD
delta_FLOW_in = (alpha_inflowrate(9:end,2))*1000*LiterGal/24/2;% Liter/hour
delta_FLOW_out = (alpha_outflow(9:end,2))*1000*LiterGal/24/2;% Liter/hour
delta_FLOW = horzcat(delta_FLOW_in,delta_FLOW_out);

Qg = 5268.4;% SCFM Change the value here if so desired
Num_diff = 1512;

SurfArea = 210*320;% ft^2
Psi = Num_diff*pi/4/SurfArea;

Hyd_res_inf = 3.3; % hrs
k_cl = 0.00307; % hr^{-1} Chlorine decay rate
DI_ClConc = 0.71; % ppm
DI_InfAlpha = DI_ClConc*exp(-k_cl*Hyd_res_inf);
deltaCL = DI_ClConc - DI_InfAlpha;
% formation (ppb/ppm)
dichForm = 14.28; % dichloro
bromForm = 1.51; % bromo
dibrForm = 4.67; % dibromo
chloForm = 57.87; % chloro

% Do not change parameters beyond this point
% Passing the constants through the model

v1(1) = Qg * LiterVol * 60; % SCFM -> liter per hour 5268.4
v1(2) = Psi;
% dichloro
v1(3) = (Qg/Num_diff*3.63e-2+3.02e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(4) = 2.119 * 60; % 1/hr (kb)
v1(5) = 22.2+deltaCL*dichForm; % ppb (influent conc)
v1(6) = henrys_function(L_temp,1); % Henrys % bromo
v1(7) = (Qg/Num_diff*1.08e-2+1.65e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(8) = 0.599 * 60; % 1/hr (kb)
v1(9) = 2.1+deltaCL*bromForm; % ppb (influent conc)
v1(10) = henrys_function(L_temp,2); % Henrys
% dibromo
v1(11) = (Qg/Num_diff*1.86e-2+1.94e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(12) = 1.193 * 60; % 1/hr (kb)
v1(13) = 15.8+deltaCL*dibrForm; % ppb (influent conc)
v1(14) = henrys_function(L_temp,3); % Henrys
% chloro
v1(15) = (Qg/Num_diff*7.08e-2+4.94e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(16) = 3.992 * 60; % 1/hr (kb)
v1(17) = 29.1+deltaCL*chloForm; % ppb (influent conc)
v1(18) = henrys_function(L_temp,4); % Henrys
% aeration plates in this tank
v1(19) = Num_diff; % plates
v1(20) = DI_InfAlpha; % ppm chlorine influent conc
v1(21) = k_cl; % hr^-1
% thm
v1(22) = dichForm; % dichloro
v1(23) = bromForm; % bromo
v1(24) = dibrForm; % dibromo
v1(25) = chloForm; % chloro
% power
v1(26) = 0; % L/ft^2-hr (kp)
v1(27) = 0; % L/ft^2-hr (kp)
v1(28) = 0; % L/ft^2-hr (kp)
v1(29) = 0; % L/ft^2-hr (kp)
v1(30) = SurfArea;

% initializing the mass and time arrays and ODE solver timestep items
mass_vol = [];
time = [];
t_start = 0; % hour
t_delt = 1; % hour
t_stop = t_start + t_delt; % hour
indexA = 1;
for i = 1:length(delta_FLOW)
% collect initial time block depths
depths(indexA,1) = (2*Ini(1)/LiterVol+544330) / 128912;
% 4*1/4tankvol = m H+1e6
% ode function
% New initial conditions, equal to final conditions from previous solution set
data_end = length(t);
Ini(1) = m_v(data_end,1); %Litters %volume in the tank
Ini(2) = m_v(data_end,2); %mass in the tank
Ini(3) = m_v(data_end,3); %mass in the tank
Ini(4) = m_v(data_end,4); %mass in the tank
Ini(5) = m_v(data_end,5); %mass in the tank
Ini(6) = m_v(data_end,6); %mass in the tank

% concatenating matrix of values
mass_vol = vertcat(mass_vol,m_v(1:data_end-1,:));
time = vertcat(time,t(1:data_end-1,:));

clear t m_v % clearing memory space

% updating time steps
  t_start = indexA;
  t_stop = t_start + t_delt;

  indexA = indexA + 1; % helps display what iteration this solver is on
end

%% Validation Extras
D.3.2 North Tank Input Script

% clc
% clear
% close all
% % Bkgrd
The purpose of this script is to setup all the values to pass through the ODE solver. The mass and volumes are considered separate but within the model function masses are dependent on the volume since the influent mass rate is passed as a concentration rate.

Solving and data management:
Data sets for flow rates were provided from LVVWD as hourly tank effluent flow rates along with hourly changes in tank depth. The influent flow rate was back calculated using \( \frac{dV_{in}}{dt} = \frac{dV_{tank}}{dt} + \frac{dV_{out}}{dt} \). These data were provided in KGPD (thousand gallon per day), and converted to Liter per hour. ALL COMMON UNITS ARE AS FOLLOWS: Liters; Hours; Mass.

The code is designed to solve the an ODE for a 1 hour time block since flow data is provided in hourly blocks. Therefore, a timestep is designated not for the ODE solver but for the hourly stepping process to solve an ODE. The code handles time stepping using an index value which is the start time and end time is the start time + 1 hours. Each hourly solution set get concatenation.

clear Ini IniConc

%Initial Script Setup Constants, Definitions, and etc.
options = odeset('RelTol',1e-5,'AbsTol',1e-5);
galVol = 7.4805195; %Gal/ft^3
LiterVol = 28.316847; %Liter/ft^3
LiterGal = 3.7854; %Liter/Gal
L_temp = 15; %^oCelcius

%Initial Liquid Volume for half the alpha tank system
height = 20.79; %15.47;
IniVol = (128912*height - 544330)*LiterVol/2;

%Initial Concentrations Should be taken from Data
IniConc(1) = 16; %ppb dichloro
IniConc(2) = 1.94; %ppb bromo
IniConc(3) = 13; %ppb dibromo
IniConc(4) = 19.4; %ppb chloro
IniConc(5) = 0.82; %ppm chloro

Ini(1) = IniVol; %Liters %volume in the tank
Ini(2) = IniConc(1)*IniVol; %mass in the tank
Ini(3) = IniConc(2)*IniVol; %mass in the tank
Ini(4) = IniConc(3)*IniVol; %mass in the tank
Ini(5) = IniConc(4)*IniVol; %mass in the tank
Ini(6) = IniConc(5)*IniVol; %mass in the tank
%Flows were reported from LVVWD in KGpD flow that Alpha tank system
load alpha_inflowrate %KGpD
load alpha_outflow %KGpD
delta_FLOW_in = (alpha_inflowrate(9:end,2))*1000*LiterGal/24/2;%Liter/hour
delta_FLOW_out = (alpha_outflow(9:end,2))*1000*LiterGal/24/2;%Liter/hour
delta_FLOW = horzcat(delta_FLOW_in,delta_FLOW_out);

Qg = 0; %SCFM %Change the value here if so desired
Num_diff = 1512;

SurfArea = 210*320;%ft2
Psi = 0;

Hyd_res_inf = 3.3; %hrs
k_cl = 0.00307; %hr^-1 Chlorine decay rate
DI_ClConc = 0.71; %ppm
DI_InfAlpha = DI_ClConc*exp(-k_cl*Hyd_res_inf);
deltaCL = DI_ClConc - DI_InfAlpha;
%formation (ppb/ppm)
dichForm = 14.28; %dichloro
bromForm = 1.51; %bromo
dibrForm = 4.67; %dibromo
chloForm = 57.87; %chloro

%% Do not change parameters beyond this point
%% Passing the constants through the model
v1(1) = Qg * LiterVol *60; % SCFM -> liter per hour 5268.4
v1(2) = Psi; %
%dichloro
v1(3) = (Qg/Num_diff*3.63e-2+3.02e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(4) = 2.119 * 60; % 1/hr (kb)
v1(5) = 22.2+deltaCL*dichForm; % ppb (influent conc)
v1(6) = henrys_function(L_temp,1); % Henrys
%dibromo
v1(7) = (Qg/Num_diff*1.08e-2+1.65e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(8) = 0.599 * 60; % 1/hr (kb)
v1(9) = 2.1+deltaCL*dibrForm; % ppb (influent conc)
v1(10) = henrys_function(L_temp,2); % Henrys
%chloro
v1(11) = (Qg/Num_diff*1.86e-2+1.94e-2) * LiterVol * 60; % L/ft^2-hr (ks)
v1(12) = 1.193 * 60; % 1/hr (kb)
v1(13) = 15.8+deltaCL*dibrForm; % ppb (influent conc)
v1(14) = henrys_function(L_temp,3); % Henrys
\[ v1(15) = \frac{(Q_{g}/\text{Num}_{\text{diff}})*7.08e-2+4.94e-2}{\text{LiterVol}} \times 60; \text{ L/ft}^2\cdot\text{hr (ks)} \]

\[ v1(16) = 3.992 \times 60; \text{ 1/hr (kb)} \]

\[ v1(17) = 29.1 + \text{delta}_{\text{CL}} \times \text{chlo}_{\text{Form}}; \text{  ppb (influent conc)} \]

\[ v1(18) = \text{henrys}_{\text{function}}(L_{\text{temp}},4); \text{ Henrys} \]

% aeration plates in this tank

\[ v1(19) = \text{Num}_{\text{diff}}; \text{ plates} \]

\[ v1(20) = \text{DI}_{\text{InfAlpha}}; \text{ ppm chlorine Influent conc} \]

\[ v1(21) = k_{\text{cl}}; \text{  hr}^{-1} \]

%thm

\[ v1(22) = \text{dich}_{\text{Form}}; \text{  dichloro} \]

\[ v1(23) = \text{brom}_{\text{Form}}; \text{  bromo} \]

\[ v1(24) = \text{dibr}_{\text{Form}}; \text{  dibromo} \]

\[ v1(25) = \text{chlo}_{\text{Form}}; \text{  chloro} \]

% power

\[ v1(26) = 0; \text{ L/ft}^2\cdot\text{hr (kp)} \]

\[ v1(27) = 0; \text{ L/ft}^2\cdot\text{hr (kp)} \]

\[ v1(28) = 0; \text{ L/ft}^2\cdot\text{hr (kp)} \]

\[ v1(29) = 0; \text{ L/ft}^2\cdot\text{hr (kp)} \]

\[ v1(30) = \text{SurfArea}; \]

% initializing the mass and time arrays and ODE solver timestep items

\[ \text{mass}_{\text{vol}} = []; \]

\[ \text{time} = []; \]

\[ \text{depths} = []; \]

\[ t_{\text{start}} = 0; \text{ hour} \]

\[ t_{\text{delt}} = 1; \text{ hour} \]

\[ t_{\text{stop}} = t_{\text{start}} + t_{\text{delt}}; \text{ hour} \]

\[ \text{indexA} = 1; \]

\[ \text{for} \ i = 1: \text{length(\text{delta}_{\text{FLOW}})} \]

\[ \% \text{collect initial time block depths} \]

\[ \text{depths(indexA,1)} = (2 \times \text{Ini}(1) / \text{LiterVol} + 544330) / 128912; \]

\[ \% \text{ode function} \]

\[ [t, m_{\text{v}}] = \text{ode}45(@\text{Cont}_{\text{model2}},... \]

\[ [t_{\text{start}} t_{\text{stop}}],\text{Ini},\text{options},\text{delta}_{\text{FLOW}}(i,:),v1); \]

\[ \% \text{New initial conditions, equal to final conditions from previous} \]

\[ \% \text{solution set} \]

\[ \text{data}_{\text{end}} = \text{length}(t); \]

\[ \text{Ini}(1) = m_{\text{v}}(\text{data}_{\text{end}},1); \text{  Litters  volume in the tank} \]

\[ \text{Ini}(2) = m_{\text{v}}(\text{data}_{\text{end}},2); \text{  mass in the tank} \]

\[ \text{Ini}(3) = m_{\text{v}}(\text{data}_{\text{end}},3); \text{  mass in the tank} \]

\[ \text{Ini}(4) = m_{\text{v}}(\text{data}_{\text{end}},4); \text{  mass in the tank} \]
Ini(5) = m_v(data_end,5); %mass in the tank
Ini(6) = m_v(data_end,6); %mass in the tank

concatenating matrix of values
mass_vol = vertcat(mass_vol,m_v(1:data_end-1,:));
time = vertcat(time,t(1:data_end-1,:));

clear t m_v %clearing memory space

%updating time steps
    t_start = indexA;
    t_stop = t_start + t_delt;

    indexA = indexA + 1; %helps display what iteration this solver is on
end

%%
clear Y_north
    Y=[];
    Y_north(:,1) = mass_vol(:,2) ./ mass_vol(:,1); %dichloro
    Y_north(:,2) = mass_vol(:,3) ./ mass_vol(:,1); %bromo
    Y_north(:,3) = mass_vol(:,4) ./ mass_vol(:,1); %dibromo
    Y_north(:,4) = mass_vol(:,5) ./ mass_vol(:,1); %chloro
    Y_north(:,5) = mass_vol(:,6) ./ mass_vol(:,1); %chlorine

    %plot(time,Y,'-')

D.3.3 Continuous Flow Model

Within the model function, the liquid flow rate was calculated for each individual hourly time block. The overall mass rates were estimated with the inclusion of mass flow rates within the liquid phase (in and out), chlorine decay and THM formation reactions, and through bubble and surface phase transport. The mass rate in (+) was equal to the product of the liquid inflow rate and the influent concentration, and included the formation of THMs as a function of chlorine decay. The mass rate out (-) was equal to the product of liquid outflow rate and tank concentration plus the mass rate though bubble and surface aeration (Middle tank), where the tank concentration was the quotient of the current total system mass and the current system liquid
volume. After each block was solved, the time vector was concatenated with the previous vector and likewise for the volume and mass data array. Finally, the script calculated the THM and free chlorine concentrations by dividing each mass at time $t$ by the respective tank volume.

```matlab
function dC_dt = Cont_model2(~,Init,delta_flow,v1)
% v1(1) = Qg * LiterVol *60; % SCFM -> liter per hour 5268.4
% v1(2) = 0.0164; %
% %dichloro
% v1(3) = (Qg/Num_diff*3.63e-2+3.02e-2) * LiterVol * 60; % L/ft^2/hr (ks)
% v1(4) = 2.119 * 60; % 1/hr (kb)
% v1(5) = 22.2+0.0714; % ppb (influent conc)
% v1(6) = henrys_function(L_temp,1); % Henrys
% %bromo
% v1(7) = (Qg/Num_diff*1.08e-2+1.65e-2)* LiterVol * 60; % L/ft^2/hr (ks)
% v1(8) = 0.599 * 60; % 1/hr (kb)
% v1(9) = 2.1+0.0076; % ppb (influent conc)
% v1(10) = henrys_function(L_temp,2); % Henrys
% %dibromo
% v1(11) = (Qg/Num_diff*1.86e-2+1.94e-2)* LiterVol * 60; % L/ft^2/hr (ks)
% v1(12) = 1.193 * 60; % 1/hr (kb)
% v1(13) = 15.8+0.0234; % ppb (influent conc)
% v1(14) = henrys_function(L_temp,3); % Henrys
% %chloro
% v1(15) = (Qg/Num_diff*7.08e-2+4.94e-2)* LiterVol * 60; % L/ft^2/hr (ks)
% v1(16) = 3.992 * 60; % 1/hr (kb)
% v1(17) = 29.1+0.2894; % ppb (influent conc)
% v1(18) = henrys_function(L_temp,4); % Henrys
% %aeration plates in this tank
% v1(19) = Num_diff; %plates
% v1(20) = 0.707; %ppm chlorine Influent conc
% v1(21) = 0.00307; %hr
% %thm
% v1(22) = 14.28; %dichloro
% v1(23) = 1.51; %bromo
% v1(24) = 4.67; %dibromo
% v1(25) = 57.87; %chloro
% %power
% v1(26) = 0.2336; %dichloro L/ft^2-hr (kp)
% v1(27) = 1.1149; %bromo L/ft^2-hr (kp)
% v1(28) = 0.0161; %dibromo L/ft^2-hr (kp)
% v1(29) = 0.7344; %chloro L/ft^2-hr (kp)
% v1(30) = AREA; %top surface area ft2
%% Volume change
v_in = delta_flow(1);  %liters/hour inflow rate
v_out = delta_flow(2); %liters/hour outflow rate
Flow_rate = v_in - v_out;

%% find liquid height for k_b section
LiterVol = 28.316847;  %Liter/ft^3

halfA = (4*Init(1)/LiterVol+1e6) / 256973;

h_vol = tempA(1)*pi/4*LiterVol;

%% if aeration is not used i.e. Q_g = 0;
if v1(1) == 0
    v1(1) = 1; % model would divide by zero...
    v1(2) = 0; % just removes the rate term by setting psi = 0
end

%% chlorine decay rate
if v_in < 0
    v1(20) = Init(6)/Init(1);
end

M_rate(5) = -v1(21)*Init(6) + v_in*v1(20) - v_out *Init(6)/Init(1);

%% THM dichloro
if v_in < 0
    v1(5) = Init(2)/Init(1);
end

M_rate(1) = v_in * v1(5) - v_out * Init(2)/Init(1)... - v1(26)*v1(30)*Init(2)/Init(1)...
 - v1(2)*(v1(3)*Init(2)/Init(1)*v1(30) ...) + v1(1)*(1-exp((-v1(4)*h_vol)/((v1(1)/v1(19)))...) *v1(6)))*v1(6)*Init(2)/Init(1))...
 + Init(6)*v1(21)*v1(22);

%% THM bromo
if v_in < 0
    v1(9) = Init(3)/Init(1);
end

M_rate(2) = v_in * v1(9) - v_out * Init(3)/Init(1)... - v1(27)*v1(30)*Init(3)/Init(1)...
 - v1(2)*(v1(7)*Init(3)/Init(1)*v1(30) ...) + v1(1)*(1-exp((-v1(8)*h_vol)/((v1(1)/v1(19)))...
*v1(10)))*v1(10)*Init(3)/Init(1). . .
+ Init(6)*v1(21)*v1(23);

%%% THM dibromo
if v_in < 0
    v1(13) = Init(4)/Init(1);
end
M_rate(3) = v_in * v1(13) - v_out * Init(4)/Init(1)...”
- v1(28)*v1(30)*Init(4)/Init(1)...”
- v1(2)*v1(11)*Init(4)/Init(1)*v1(30) . . .
+ v1(1)*(1-exp((-v1(12)*h_vol)/(v1(1)/v1(19))...”
*v1(14)))*v1(14)*Init(4)/Init(1)...”
+ Init(6)*v1(21)*v1(24);

%%% THM chloro
if v_in < 0
    v1(17) = Init(5)/Init(1);
end
M_rate(4) = v_in * v1(17) - v_out * Init(5)/Init(1)...”
- v1(29)*v1(30)*Init(5)/Init(1)...”
- v1(2)*v1(15)*Init(5)/Init(1)*v1(30) . . .
+ v1(1)*(1-exp((-v1(16)*h_vol)/(v1(1)/v1(19))...”
*v1(18)))*v1(18)*Init(5)/Init(1)...”
+ Init(6)*v1(21)*v1(25);

%%% Returns
dC_dt(1,1)=Flow_rate;
dC_dt(2,1)=M_rate(1);
dC_dt(3,1)=M_rate(2);
dC_dt(4,1)=M_rate(3);
dC_dt(5,1)=M_rate(4);
dC_dt(6,1)=M_rate(5);

end
Appendix E

System Wide Impacts: Supporting Information

E.1 LVVWD System Wide Mode Stationary Point

Based on results from several points hydraulically “far” from the BR supply reservoir, shown in Figure E.1, at approximately 400 hours the system nodes illustrated convergence toward a stationary pattern. Each simulation time span was extended by another 100 hours to reach a total length of 500 hours.

E.2 EPANET-MSX input file

The aeration model presented in Equation 2.4 was implemented in an EPANET-MSX script. THM formation kinetics were modeled as described in Section 2.2.3.3. Constants used within the model include reactor surface area $A$ of 268800 ft$^2$ and a value of $\psi$ equal to 1.78e-2 representing the aerated surface area using the number of diffusers times the theoretical 1 ft diameter area divided by the total surface areas.
Figure E.1: Demonstration of stationarity for the LVVWD network over a 500 hours simulation. Initial chlorine dosage was 0.71 µg/L from Bravo (supply tank for the system). Each node is located hydraulically “far” from the supply point. Node 9816 is the furthest of the two tanks from the supply point where the water age is some of the highest in the system.
of the tank. Hourly results were stored in an “.rpt” file by MSX. The data from the “.rpt” file were extracted using scripts created in Python 2.7.2 to convert the data into a format usable by MATLAB. Results from the simulations were analyzed with respect to a system-wide scale to evaluate the spatial reduction of THMs using aeration as a control strategy, and at a node-by-node level comparing THM reduction to the percentage of water demand received from the Alpha tank system.

[TITLE]
Multi-Species Analysis - Las Vegas Valley Water District, Las Vegas, Nevada

[OPTIONS]
RATE_UNITS HR ;Reaction Rates are Concentration (Mass/L)/Hour
SOLVER RK5 ;runge-kutta 5th order
TIMESTEP 60 ;1 min solution time step
RTOL 1.0e-4 ;Relative concentration tolerance
ATOL 1.0e-4 ;Absolute concentration tolerance

[SPECIES]
BULK HOCL MG ;Free Chlorine
BULK CHCL3 UG ;Chloroform
BULK CHL2BR UG ;Bromodichloromethane
BULK CHLBR2 UG ;Dibromochloromethane
BULK CHBR3 UG ;Bromoform
BULK VOLUME FT3
BULK DEPTH FT

[COEFFICIENTS]
;TEMP = 288.29 -> 15.14C pH between 8.0-8.5

;Dimensionless Henry’s constant for THMS converted from (Nicholson 1984)
PARAMETER H_CHCL3 8.942e-2 ;Henrys = 0.0375*exp(0.0574*temperature)
PARAMETER H_CHCL2BR 4.745e-2 ;Henrys = 0.0199*exp(0.0574*temperature)
PARAMETER H_CHCLBR2 2.599e-2 ;Henrys = 0.0109*exp(0.0574*temperature)
PARAMETER H_CHBR3 1.292e-2 ;Henrys = 0.005*exp(0.0627*temperature)

;airflow rate, constant at 11639.5 SCFM
PARAMETER Q_G 19.775603e6 ;LITER HOUR

;slope of THM formation vs total chlorine decay (UG/MG)
PARAMETER DF_CHCL3 57.87 ;Chloroform Formation
PARAMETER DF_CHCL2BR 14.28 ;Bromodichloromethane Formation
PARAMETER DF_CHCLBR2 4.67 ;Dibromochloroform Formation
PARAMETER DF_CHBR3 1.51 ;Bromoform Formation slope

;Parameters for mass transport in the model for THM removal
;each Ks is a function of airflow rate per diffuser Qair total / # diffusers
; KS = (M * Qtot/#diffusers + b) * 60 * 28.3168 -> L/ft2-hr
chloroform m = 7.08e-2 b = 4.94e-2
; dichloro  $m = 3.63 \times 10^{-2}$  $b = 3.02 \times 10^{-2}$
; dibromo  $m = 1.86 \times 10^{-2}$  $b = 1.94 \times 10^{-2}$
; bromoform  $m = 1.08 \times 10^{-2}$  $b = 1.65 \times 10^{-2}$

PARAMETER $KS_{CHCl3}$ 314.83  ; $ks$ all units are in L/ft2-hr
PARAMETER $KB_{CHCl3}$ 239.52  ; $kb$ hr^-1
PARAMETER $KS_{CHCl2Br}$ 169.73
PARAMETER $KB_{CHCl2Br}$ 127.14
PARAMETER $KS_{CHClBr2}$ 93.62
PARAMETER $KB_{CHClBr2}$ 71.58
PARAMETER $KS_{CHBr3}$ 63.20
PARAMETER $KB_{CHBr3}$ 35.94

; chlorine decay rate 1st order (regression from data)
PARAMETER $K_{CL}$ 0.0031  ; hr

; With respect to the model for THM removal
PARAMETER $PSI_{MULT}$ 0
CONSTANT $airp$ 6064
CONSTANT $LiterVol$ 28.3168
CONSTANT $Asurf$ 256973

[TERMS]
  $a_1$  $DF_{CHCl3} \times K_{CL} \times HOCL$  ; formation of chloroform
  $a_2$  $DF_{CHCl2Br} \times K_{CL} \times HOCL$  ; formation of dichloro
  $a_3$  $DF_{CHClBr2} \times K_{CL} \times HOCL$  ; formation of dibromo
  $a_4$  $DF_{CHBr3} \times K_{CL} \times HOCL$  ; formation of bromoform

; surface mass transport
  $a_7$  $PSI_{MULT} \times KS_{CHCl3} \times CHCl3 \times Asurf/(V \times LiterVol)$
  $a_8$  $PSI_{MULT} \times KS_{CHCl2Br} \times CHCl2Br \times Asurf/(V \times LiterVol)$
  $a_9$  $PSI_{MULT} \times KS_{CHClBr2} \times CHClBr2 \times Asurf/(V \times LiterVol)$
  $a_{10}$  $PSI_{MULT} \times KS_{CHBr3} \times CHBr3 \times Asurf/(V \times LiterVol)$

; bubble mass transport assume $f_y = 1$ for all cases
  $a_{11}$  $PSI_{MULT} \times Q \times H_{CHCl3} \times CHCl3/(V \times LiterVol)$
  $a_{12}$  $PSI_{MULT} \times Q \times H_{CHCl2Br} \times CHCl2Br/(V \times LiterVol)$
  $a_{13}$  $PSI_{MULT} \times Q \times H_{CHClBr2} \times CHClBr2/(V \times LiterVol)$
  $a_{14}$  $PSI_{MULT} \times Q \times H_{CHBr3} \times CHBr3/(V \times LiterVol)$

[PIPES]
  RATE  CHCl3  a1
  RATE  CHCl2Br  a2
  RATE  CHClBr2  a3
  RATE  CHBr3  a4
  RATE  HOCL  $-K_{CL} \times HOCL$

FORMULA VOLUME 0
FORMULA DEPTH 0

[TANKS]
  RATE  CHCl3  a1 - $a_7 - a_{11}$
  RATE  CHCl2Br  a2 - $a_8 - a_{12}$
RATE  CHCLBR2  a3 - a9 - a13
RATE  CHBR3      a4 - a10 - a14
RATE  HOCL       -K_CL*HOCL

FORMULA VOLUME $V
FORMULA DEPTH $Y

[PARAMETER]
TANK 9849 PSI_MULT 0.0185
TANK 9816 PSI_MULT 0

[SOURCES]
CONCEN  9839 HOCL 0.71
CONCEN  9839 CHCL3 29
CONCEN  9839 CHCL2BR 22
CONCEN  9839 CHCLBR2 16
CONCEN  9839 CHBR3 2

[QUALITY]
GLOBAL HOCL 0.71
GLOBAL CHCL3 29
GLOBAL CHCL2BR 22
GLOBAL CHCLBR2 16
GLOBAL CHBR3 2

[REPORT]
NODES ALL ;Report results for all nodes
LINKS None
SPECIES HOCL YES 3 ;Chlorine
SPECIES CHCL3 YES 3 ;Chloroform
SPECIES CHCL2BR YES 3 ;dichloro
SPECIES CHCLBR2 YES 3 ;dibromo
SPECIES CHBR3 YES 3 ;bromoform
SPECIES DEPTH YES
SPECIES VOLUME YES
Appendix F

MSX Validation

F.1 Introduction

This section presents the numerical validations of the EPANET-MSX input files compared to known analytical solutions or approximations from an equivalent MATLAB script for different aerated tank systems. EPANET-MSX v1.2 was used in conjunction with 4 example networks with tank aeration systems associated with static and dynamic hydraulics. Operating temperatures were held at 15.14°C for each comparison.

F.2 Test 1: Column Reactor

Test 1 was setup to validate the THM removal from a static tank with no inflow or outflow (equivalent to the laboratory-scale column). The tank was 1 ft in diameter, with a water depth of 11 ft and initial concentrations of 150 µg/L for each THM species and 0 mg/L for free chlorine. $\psi$ was set at 1, assuming only one diffusor plate, and the aeration rate was set to 2 SCFM (3398 L/hr). MSX results were normalized
to the initial concentrations \( (C_0) \) and compared to normalized “hand calculations based on the analytical solution to the first order equation as follows:

\[
\frac{C_t}{C_o} = \exp \left( - \left( \frac{k_s A + Q_g H f}{V} \right) \psi t \right) \tag{F.1}
\]

where

\[
f = 1 - \exp \left( \frac{-K_b a V}{Q_g H} \right) \tag{F.2}
\]

where \( k_s \) represents the surface mass transport coefficient (Liter/ft\(^2\)-t), \( A \) represents the liquid top surface area (ft\(^2\)), \( Q_g \) is the airflow rate (Liter/t), \( H \) is Henry’s constant (dimensionless), \( f \) is the percent saturation of one bubble or “bubble efficiency” (dimensionless), \( V \) is the liquid volume (Liter), \( \psi \) is the percent of top surface subject to aeration (dimensionless) and, \( K_b a \) is the bubble mass transport coefficient t\(^{-1}\).

The simulation time was 4 hours. Figure F.1 illustrates the comparison of the normalized MSX v1.2 results to the analytical solutions based on equation F.1. The maximum relative RMSE value was 3.8e-3 indicating that the errors between the numerical solutions of EPANET-MSX and the analytical solutions were negligible, successfully validating the EPANET-MSX results.

\[\text{F.3 Test 2: Draining Tank, Without THM Formation}\]

Test 2 was setup to validate the THM removal through aeration from a tank with only outflows. The tank was 100 ft in diameter with an initial water depth of 50 ft and initial concentration of 150 µg/L for each THM and 0 mg/L of free chlorine. \( \psi \) was set to 0.1 and aerated at 2 SCFM (3398L/hr) per diffusor. The tank contained 1000 diffusors and was aerated at a total rate of 3398000 L/hr. Results generated by MSX were compared to MATLAB approximations using the Runge-Kutta 4,5
Figure F.1: Comparisons of individual THMs between EPANET-MSX v1.2 simulation results and analytical calculations based on Equation F.1.
ordinary differential equation solver. The simulation duration was 15 hours and the constant effluent flow rate was set to 1200 GPM.

![Graphs showing concentration over time for Chloroform, Bromodichloromethane, Dibromochloromethane, and Bromoform.](image)

**Figure F.2**: Results for each THM comparing the MSX v1.2 simulation results and the hand calculations based on the Runge-Kutta 4,5 solution.

Figure F.2 illustrates the comparison between the EPANET-MSX solution and the MATLAB approximations. Similar to the Test 1 case, the absolute errors between the results from EPANET-MSX v1.2 and Runge-Kutta 4,5 solution were small with a maximum absolute RMSE value of 3.91e-1 for bromoform. Overall, the results from EPANET-MSX 1.2 matched the MATLAB approximations suggesting a successful validation.
F.4 Test 3: Draining Tank, With THM Formation

Test 3 was setup to validate the THM removal through aeration from a tank with no inflows only outflows and including THM formation through chlorine decay. The operating conditions were setup the same as Test 2, only the initial THM concentrations were set to 50 µg/L and the initial chlorine concentration was set to 1 mg/L. Results generated by EPANET-MSX were compared to solutions based on MATLAB approximations using the Runge-Kutta 4,5 ode solver. The simulation duration was 15 hours with a the constant effluent flow rate was set to 1200 GPM.

Figure F.3: Results for each THM comparing the MSX v1.2 simulation results and the hand calculations based on the Runge-Kutta 4,5 solution.

Figure F.3 illustrates the comparison between the EPANET-MSX solution and the
MATLAB approximations. Similar to the Test 1 and Test 2 case, the absolute errors between the results from EPANET-MSX and the Runge-Kutta 4,5 solution were small with a maximum absolute RMSE value of 1.11e-1 for bromoform. Overall the results from EPANET-MSX v1.2 match the MATLAB approximations very closely suggesting a successful validation.
F.5 Test 4: Flow Through Tank, With THM Formation and Disparate Source Water Quality

Test 4 was setup to validate the THM removal from a tank with a flow through system. The test network is illustrated in Figure F.4. The operating conditions were setup using simple controls where from simulation time 0 to 8 hours flow to tank 9 was supplied only by reservoir 2, and from hour 8 to hour 15 the flow was supplied only from reservoir 1. Both reservoirs supplied a different water quality – THM concentrations in reservoir 1 were set to 10 µg/L with a chlorine concentration of 1 mg/L while for reservoir 2 THM concentrations were 25 µg/L with a chlorine concentration of 1 mg/L. Both reservoirs provided a constant head of 75 ft and the initial depth for Tank 9 was set to 25 ft. The influent flow rate changed over time based on the EPANET hydraulic simulation results. The simulation was run for a 15 hour duration with a constant effluent flow rate from Tank 9 set to 3000 GPM. \( \psi \) was set to 0.1 with an air flow rate of 2 SCFM (3398L/hr) per diffusor. The tank contained 1000 diffusors and was aerated at a total rate of 3398000 L/hr. Results generated by EPANET-MSX were compared to MATLAB approximations using the Runge-Kutta 4,5 ode solver.

Figure F.5 illustrates the comparison between the MSX solution and the MATLAB approximations. Similar to the previous tests, the absolute errors between the EPANET-MSX v1.2 results and the MATLAB Runge-Kutta 4,5 solutions were small with a maximum absolute RMSE value of 5.31e-2 for bromoform. Overall, the results from EPANET-MSX v1.2 match the MATLAB approximations very closely suggesting a successful validation.
Figure F.4: Test 4 network; nodes 1 and 2 are reservoirs with a constant head of 75 ft, Tank 9 is the tank and Node 16 is the demand node for the effluent flow from Tank 9.

Figure F.5: Results for each THM comparing the MSX v1.2 simulation results and the hand calculations based on the Runge-Kutta 4,5 solution.
F.6 Summary

Overall the EPANET-MSX simulation results were consistent with the analytical or numerical approximations (from an established algorithm) based on the RMSE comparisons for a range of test systems. The results for Test 1 indicated that the EPANET-MSX aeration model functioned properly under simple conditions and was compared to the true analytical solution. Test two through four demonstrated that the EPANET-MSX solutions were numerically equivalent to the models developed using a standard numerical code available in commercial software. Overall, these tests have been performed to “validate the EPANET-MSX modeling framework for extension into network scale evaluation.”
Appendix G

Modeling Results for Reactor Experiments

G.1 Chloroform

Figures G.1, G.2, and G.3 provide the experimental data for chloroform in relation to the aeration model with case 1 parameterization for air flow rates of 1, 2, and 4 SCFM. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25\textsuperscript{th} and 75\textsuperscript{th} percentiles from each sampling point and time step. The model predictions associated with the chloroform experimental data has a root mean square error (RMSE) of 2.74\% while the range of RMSE is [1.04\%, 4.18\%] for the individual experimental runs. The parameter estimates were determined by using an enumeration approach by varying the $K_{Ls,CHCl_3}a$ and $K_{Lb,CHCl_3}a$ and selecting the parameter values where the RMSE between the experimental and model data was minimized. The parameter estimates of $K_{Ls,CHCl_3}a$ and $K_{Lb,CHCl_3}a$ for chloroform were 1.76e-2 min\textsuperscript{-1} and 3.99 min\textsuperscript{-1}. 
respectively.

Figure G.1: Results for chloroform from experiments performed at 1 SCFM. The figure includes the normalized mean chloroform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 1.76e-2 min\(^{-1}\) and 3.99 min\(^{-1}\) for \(K_{Ls,CHCl_3}\) and \(K_{Lb,CHCl_3}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure G.2: Results for chloroform from experiments performed at 2 SCFM. The figure includes the normalized mean chloroform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 1.76e-2 min⁻¹ and 3.99 min⁻¹ for $K_{Ls,CHCl_3}a$ and $K_{Lb,CHCl_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure G.3: Results for chloroform from experiments performed at 4 SCFM. The figure includes the normalized mean chloroform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 1.76e-2 min^{-1} and 3.99 min^{-1} for $K_{Ls,CHCl_3,a}$ and $K_{Lb,CHCl_3,a}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
G.2 Bromodichloromethane

Figures G.4, G.5, and G.6 provide the experimental data for bromodichloromethane in relation to the aeration model with case 1 parameterization for air flow rates of 1, 2, and 4 SCFM. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25\textsuperscript{th} and 75\textsuperscript{th} percentiles from each sampling point and time step. The model predictions associated with the chloroform experimental data has a root mean square error (RMSE) of 3.80\% while the range of RMSE is [0.883\%, 6.09\%] for the individual experimental runs. The parameter estimates were determined by using an enumeration approach by varying the $K_{Ls,CHBrCl_2}a$ and $K_{Lb,CHBrCl_2}a$ and selecting the parameter values where the RMSE between the experimental and model data was minimized. The parameter estimates of $K_{Ls,CHBrCl_2}a$ and $K_{Lb,CHBrCl_2}a$ for chloroform were 1.76e-2 min\textsuperscript{-1} and 3.99 min\textsuperscript{-1} respectively.
Figure G.4: Results for bromodichloromethane from experiments performed at 1 SCFM. The figure includes the normalized mean bromodichloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 1.02e-2 min$^{-1}$ and 2.12 min$^{-1}$ for $K_{Ls,CHBrCl_2}a$ and $K_{Lb,CHBrCl_2}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure G.5: Results for bromodichloromethane from experiments performed at 2 SCFM. The figure includes the normalized mean bromodichloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 1.02e-2 min$^{-1}$ and 2.12 min$^{-1}$ for $K_{Ls,CHBrCl_2a}$ and $K_{Lb,CHBrCl_2a}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure G.6: Results for bromodichloromethane from experiments performed at 4 SCFM. The figure includes the normalized mean bromodichloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of $1.02 \times 10^{-2}$ min$^{-1}$ and $2.12$ min$^{-1}$ for $K_{Ls,CHBrCl_2} a$ and $K_{Lb,CHBrCl_2} a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
G.3 Dibromochloromethane

Figures G.7, G.8, and G.9 provide the experimental data for dibromochloromethane in relation to the aeration model with case 1 parameterization for air flow rates of 1, 2, and 4 SCFM. Each plot shows the model presented and experimental data with respect to the two different initial chlorine concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25\textsuperscript{th} and 75\textsuperscript{th} percentiles from each sampling point and time step. The model predictions associated with the chloroform experimental data has a root mean square error (RMSE) of 5.05% while the range of RMSE is [1.14\%, 7.10\%] for the individual experimental runs. The parameter estimates were determined by using an enumeration approach by varying the $K_{Ls,CHBr_2Cl_a}$ and $K_{Lb,CHBr_2Cl_a}$ and selecting the parameter values where the RMSE between the experimental and model data was minimized. The parameter estimations for $K_{Ls,CHBr_2Cl_a}$ and $K_{Lb,CHBr_2Cl_a}$ were calculated to be $5.8e-3 \text{ min}^{-1}$ and $1.19 \text{ min}^{-1}$, respectively.
Figure G.7: Results for dibromochloromethane from experiments performed at 1 SCFM. The figure includes the normalized mean dibromochloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 5.8e-3 min\(^{-1}\) and 1.19 min\(^{-1}\) for \(K_{L_s,CHBr_2Cl_a}\) and \(K_{L_b,CHBr_2Cl_a}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure G.8: Results for dibromochloromethane from experiments performed at 2 SCFM. The figure includes the normalized mean dibromochloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 5.8e-3 min$^{-1}$ and 1.19 min$^{-1}$ for $K_{Ls,CHBr_2Cl}$ and $K_{Lb,CHBr_2Cl}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure G.9: Results for dibromochloromethane from experiments performed at 4 SCFM. The figure includes the normalized mean dibromochloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 5.8e-3 min\(^{-1}\) and 1.19 min\(^{-1}\) for \(K_{Ls,CHBr_2Cl}a\) and \(K_{Lb,CHBr_2Cl}a\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
G.4 Bromoform

Figures G.10, G.11, and G.12 provide the experimental data for bromoform in relation to the aeration model with case 1 parameterization for air flow rates of 1, 2, and 4 SCFM. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25th and 75th percentiles from each sampling point and time step. The model predictions associated with the chloroform experimental data has a root mean square error (RMSE) of 7.57% while the range of RMSE is [3.12%, 10.6%] for the individual experimental runs. The parameter estimates were determined by using an enumeration approach by varying the $K_{Ls, CHBr_3}$ and $K_{Lb, CHBr_3}$ and selecting the parameter values where the RMSE between the experimental and model data was minimized. The parameter estimations for $K_{Ls, CHBr_3}$ and $K_{Lb, CHBr_3}$ were calculated to be 4.1e-3 min$^{-1}$ and 5.99e-1 min$^{-1}$, respectively.
Figure G.10: Results for bromoform from experiments performed at 1 SCFM. The figure includes the normalized mean bromoform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 4.1e-3 min$^{-1}$ and 5.99e-1 min$^{-1}$ for $K_{Ls,CHBr_3}a$ and $K_{Lb,CHBr_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure G.11: Results for bromoform from experiments performed at 2 SCFM. The figure includes the normalized mean bromoform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 4.1e-3 min\(^{-1}\) and 5.99e-1 min\(^{-1}\) for \(K_{Ls,CHBr_3,a}\) and \(K_{Lb,CHBr_3,a}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure G.12: Results for bromoform from experiments performed at 4 SCFM. The figure includes the normalized mean bromoform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of $4.1 \times 10^{-3} \text{ min}^{-1}$ and $5.99 \times 10^{-1} \text{ min}^{-1}$ for $K_{L_s,CHBr_3,a}$ and $K_{L_b,CHBr_3,a}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Appendix H

Demonstrating the importance of $K_{Lb,y}a$ parameter estimation on model performance

Assuming $K_{Ls,y}a = 0$, the Matter-Müller et al. (1981) model only incorporates bubble mass transport. Therefore,

$$\frac{dC_{L,y}}{dt} = -\frac{Q_g f_y H_y C_{L,y}}{V_L}$$

(H.1)

where,

$$f_y = 1 - \exp(-K_{Lb,y}a V_L)$$

(H.2)

and,

$$f_y = 1 - RHS$$

(H.3)

$$RHS = \exp(-K_{Lb,y}a V_L)$$

(H.4)

Based on the experimental results from section [REF], as $f_y \to 1$, $RHS \to 0$, which, from a parameter estimation standpoint, for a given set of experimental conditions is equivalent to $K_{Lb,y}a \to \infty$. Therefore, if complete saturation of THM into the gas
Figure H.1: Figure to accompany proof for $K_{Lb,y,a}$ selection when $K_{Ls,y,a} = 0$

phase is achieved ($f_y = 1$) then estimating $K_{Lb,y,a}$ via numerical techniques is difficult because once $K_{Lb,y,a}$ reaches a value where $f_y \sim 1$ there is little “driving force” to change the model parameter any further. As an illustration, Figure H.1 demonstrates that as $K_{Lb,y,a}$ increases ($f_y \rightarrow 1$) the RMSE converges to a “constant” value. For the current application, a tolerance of four significant figures associated with the RMSE value was selected to terminate the estimation process associated with $K_{Lb,y,a}$. 
Appendix I

Complete Model Results for Reactor Experiments with $K_{LS,y} = 0$

I.1 Chloroform

Figures I.1, I.2, and I.3 provide the experimental data for chloroform in relation to the aeration model with $K_{LS,y}a = 0$. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25th and 75th percentiles from each sampling point and time step. The model predictions associated with the chloroform experimental data has a root mean square error (RMSE) of 9.64% while the range of RMSE is [4.02%, 16.1%] for the individual experimental runs. The parameter estimations were determined by using a factorial approach by varying the $K_{Lb,CHCl_3}a$ where the RMSE between the experimental and model data was minimized to get 3.791 min$^{-1}$. 
Figure I.1: Results for chloroform from experiments performed at 1 SCFM. The figure includes the normalized mean chloroform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min⁻¹ and 3.791 min⁻¹ for $K_{Ls,CHCl₃}$ and $K_{Lb,CHCl₃}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure I.2: Results for chloroform from experiments performed at 2 SCFM. The figure includes the normalized mean chloroform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min$^{-1}$ and 3.791 min$^{-1}$ for $K_{L_s,CHCl_3}$ and $K_{L_b,CHCl_3}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure I.3: Results for chloroform from experiments performed at 4 SCFM. The figure includes the normalized mean chloroform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min$^{-1}$ and 3.791 min$^{-1}$ for $K_{Ls,CHCl_3}$ and $K_{Lb,CHCl_3}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
I.2 Bromodichloromethane

Figures I.4, I.5, and I.6 provide the experimental data for bromodichloromethane in relation to the aeration model with $K_{LS,CHBrCl_2}a = 0$. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25th and 75th percentiles from each sampling point and time step. The model predictions associated with the bromodichloromethane experimental data has a root mean square error (RMSE) of 11.1% while the range of RMSE is [6.49%, 16.79%] for the individual experimental runs. The parameter estimations were determined by using a factorial approach by varying the $K_{LS,CHBrCl_2}a$ where the RMSE between the experimental and model data was minimized to get 1.98 min$^{-1}$. 
Figure I.4: Results for bromodichloromethane from experiments performed at 1 SCFM. The figure includes the normalized mean bromodichloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min\(^{-1}\) and 1.98 min\(^{-1}\) for \(K_{Ls,CHBrCl_2}a\) and \(K_{Lb,CHBrCl_2}a\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure I.5: Results for bromodichloromethane from experiments performed at 2 SCFM. The figure includes the normalized mean bromodichloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min\(^{-1}\) and 1.98 min\(^{-1}\) for \(K_{Ls,CHBrCl_2a}\) and \(K_{Lb,CHBrCl_2a}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure I.6: Results for bromodichloromethane from experiments performed at 4 SCFM. The figure includes the normalized mean bromodichloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min$^{-1}$ and 1.98 min$^{-1}$ for $K_{Ls,CHBrCl_2}a$ and $K_{Lb,CHBrCl_2}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
I.3 Dibromochloromethane

Figures I.7, I.8, and I.9 provide the experimental data for dibromochloromethane in relation to the aeration model with $K_{L,CHBr_2Cl^*} = 0$. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25th and 75th percentiles from each sampling point and time step. The model predictions associated with the dibromochloromethane experimental data has a root mean square error (RMSE) of 11.98% while the range of RMSE is [6.28%, 17.10%] for the individual experimental runs. The parameter estimations were determined by using a factorial approach by varying the $K_{L,CHBr_2Cl^*}$ where the RMSE between the experimental and model data was minimized to get $1.11 \text{ min}^{-1}$. 
Figure I.7: Results for dibromochloromethane from experiments performed at 1 SCFM. The figure includes the normalized mean dibromochloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min$^{-1}$ and 1.11 min$^{-1}$ for $K_{Ls,CHBr_2Cl} a$ and $K_{Lb,CHBr_2Cl} a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure I.8: Results for dibromochloromethane from experiments performed at 2 SCFM. The figure includes the normalized mean dibromochloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min\(^{-1}\) and 1.11 min\(^{-1}\) for \(K_{Ls,CHBr_2Cl}\) and \(K_{Lb,CHBr_2Cl}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure I.9: Results for dibromochloromethane from experiments performed at 4 SCFM. The figure includes the normalized mean dibromochloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min$^{-1}$ and 1.11 min$^{-1}$ for $K_{Ls,CHBr_2Cl}a$ and $K_{Lb,CHBr_2Cl}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
I.4 Bromoform

Figures I.10, I.11, and I.12 provide the experimental data for bromoform in relation to the aeration model with $K_{Ls,CHBr_3}a = 0$. Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25th and 75th percentiles from each sampling point and time step. The model predictions associated with the dibromochloromethane experimental data has a root mean square error (RMSE) of 14.95% while the range of RMSE is [9.77%, 23.52%] for the individual experimental runs. The parameter estimations were determined by using a factorial approach by varying the $K_{Lb,CHBr_3}a$ where the RMSE between the experimental and model data was minimized to get $6.15e-1$ min$^{-1}$.
Figure I.10: Results for bromoform from experiments performed at 1 SCFM. The figure includes the normalized mean bromoform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min\(^{-1}\) and 6.15e-1 min\(^{-1}\) for \(K_{Ls, CHBr_3}^a\) and \(K_{Lb, CHBr_3}^a\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure I.11: Results for bromoform from experiments performed at 2 SCFM. The figure includes the normalized mean bromoform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min\(^{-1}\) and 6.15e-1 min\(^{-1}\) for \(K_{L_s,CHBr_3}\) and \(K_{L_b,CHBr_3}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure I.12: Results for bromoform from experiments performed at 4 SCFM. The figure includes the normalized mean bromoform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and was estimated using Equation 2.3 and the value of 0 min$^{-1}$ and 6.15e-1 min$^{-1}$ for $K_{Ls,CHBr_3,a}$ and $K_{Lb,CHBr_3,a}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Appendix J

Impact of Power on Surface Mass Transport Rate $K_{Ls,y}a$
The following appendix illustrates the complete parameter estimation results for each experimental set for each THM. The $K_{Ls,y}a$ values per THM were estimated for each individual air flow rate (1, 2, and 4 SCFM). Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and $25^{th}$ and $75^{th}$ percentiles from each sampling point and time step.

J.1 Power Results for 1 SCFM

Figures J.1 – J.4 illustrate the model predicted concentrations to the experimental using the parameter estimations for each $K_{Ls,y}a$ value from the 1 SCFM experiments.
Figure J.1: Results for chloroform experiments at 1 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $1.55 \times 10^{-2}$ min$^{-1}$ and $3.99$ min$^{-1}$ for $K_{Ls,CHCl_3}a$ and $K_{Lb,CHCl_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure J.2: Results for bromodichloromethane experiments at 1 SCFM. This figure includes the normalized mean bromodichloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $8.40e-3 \text{ min}^{-1}$ and $2.12 \text{ min}^{-1}$ for $K_{L_s,CHBrCl_2a}$ and $K_{L_b,CHBrCl_2a}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the $25^{th}$ and $75^{th}$ percentiles, respectively.
Figure J.3: Results for dibromochloromethane experiments at 1 SCFM. This figure includes the normalized mean dibromochloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 4.50e-3 min⁻¹ and 1.19 min⁻¹ for $K_{Ls,CHBr_2Cl}$ and $K_{Lb,CHBr_2Cl}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure J.4: Results for bromoform experiments at 1 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $3.00e-3$ min$^{-1}$ and $5.99e-1$ min$^{-1}$ for $K_{Ls,CHBr_3}a$ and $K_{Lb,CHBr_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
J.2 Power Results for 2 SCFM

Figures J.5 – J.8 illustrate the model predicted concentrations to the experimental using the parameter estimations for each $K_{Ls,y}$ value from the 2 SCFM experiments.

Figure J.5: Results for chloroform experiments at 2 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 1.87e-2 min⁻¹ and 3.99 min⁻¹ for $K_{Ls,CHCl_3,a}$ and $K_{Lb,CHCl_3,a}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure J.6: Results for bromodichloromethane experiments at 2 SCFM. This figure includes the normalized mean bromodichloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $1.10e^{-2}$ min$^{-1}$ and 2.12 min$^{-1}$ for $K_{Ls,CHBrCl_2}$ and $K_{Lb,CHBrCl_2}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure J.7: Results for dibromochloromethane experiments at 2 SCFM. This figure includes the normalized mean dibromochloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 6.70e-3 min$^{-1}$ and 1.19 min$^{-1}$ for $K_{Ls,CHBr2Cl}a$ and $K_{Lb,CHBr2Cl}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure J.8: Results for bromoform experiments at 2 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $4.80e-3 \text{ min}^{-1}$ and $5.99e-1 \text{ min}^{-1}$ for $K_{Ls,CHBr_3}a$ and $K_{Lb,CHBr_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
J.3 Power Results for 4 SCFM

Figures J.9 – J.12 illustrate the model predicted concentrations to the experimental using the parameter estimations for each $K_{Ls,y}a$ value from the 4 SCFM experiments.

Figure J.9: Results for chloroform experiments at 4 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 3.76e-2 min$^{-1}$ and 3.90 min$^{-1}$ for $K_{Ls,CHCl_3}a$ and $K_{Lb,CHCl_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure J.10: Results for bromodichloromethane experiments at 4 SCFM. This figure includes the normalized mean bromodichloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 2.11e-2 min\(^{-1}\) and 2.12 min\(^{-1}\) for \(K_{L_s,CHBrCl_2a}\) and \(K_{L_b,CHBrCl_2a}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure J.11: Results for dibromochloromethane experiments at 4 SCFM. This figure includes the normalized mean dibromochloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 1.15e-2 min\(^{-1}\) and 1.19 min\(^{-1}\) for \(K_{Ls,CHBr_2Cl,a}\) and \(K_{Lb,CHBr_2Cl,a}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure J.12: Results for bromoform experiments at 4 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $7.30e^{-3}$ min$^{-1}$ and $5.99e-1$ min$^{-1}$ for $K_{Ls,CHBr_3}$ and $K_{Lb,CHBr_3}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Appendix K

Results for Surface Mass Transport Rate $K_{Ls,y}$: Parameter Estimation

Case 3

The following section includes the “case 3” parameter estimation results for each experiment. The RMSE values along with model solving boundary conditions are included on each figure. The $K_{Ls,y}$ values per THM were estimated for each individual air flow rate (1, 2, and 4 SCFM). Each plot shows the model presented and experimental data with respect to the two different initial THM concentrations [columns] and water depth [rows]. The experimental data presented on each plot includes the average and 25$^{th}$ and 75$^{th}$ percentiles from each sampling point and time step.
K.1 Power Results for 1 SCFM

Figures K.1 – K.4 illustrate the model predicted concentrations to the experimental using the parameter estimations for each $K_{Ls,y}^a$ value from the 1 SCFM experiments.

Figure K.1: Results for chloroform experiments at 1 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $1.39e^{-2}$ ft/min and $3.99$ min$^{-1}$ for $K_{Ls, CHCl_3}$ and $K_{Lb, CHCl_3}^a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure K.2: Results for bromodichloromethane experiments at 1 SCFM. This figure includes the normalized mean bromodichloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 7.40e-2 ft/min and 2.12 min\(^{-1}\) for \(K_{Ls,CHBrCl_2}\) and \(K_{Lb,CHBrCl_2,a}\), respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25\(^{th}\) and 75\(^{th}\) percentiles, respectively.
Figure K.3: Results for dibromochloromethane experiments at 1 SCFM. This figure includes the normalized mean dibromochloromethane experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 4.0e-2 ft/min and 1.19 min⁻¹ for $K_{Ls,CHBr_2Cl}$ and $K_{Lb,CHBr_2Cl}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure K.4: Results for bromoform experiments at 1 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 1 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $2.71 \times 10^{-2}$ ft/min and $5.99 \times 10^{-1}$ min$^{-1}$ for $K_{Ls,CHBr_3}$ and $K_{Lb,CHBr_3}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
K.2 Power Results for 2 SCFM

Figures K.5 – K.8 illustrate the model predicted concentrations to the experimental using the parameter estimations for each $K_{Ls,y}a$ value from the 2 SCFM experiments.

![Graphs showing chloroform experiments results](image)

Figure K.5: Results for chloroform experiments at 2 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $1.63e-1$ ft/min and $3.99$ min$^{-1}$ for $K_{Ls,CHCl_3}$ and $K_{Lb,CHCl_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure K.6: Results for bromodichloromethane experiments at 2 SCFM. This figure includes the normalized mean bromodichloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 9.18e-2 ft/min and 2.12 min⁻¹ for $K_{L_s,CHBrCl_2}$ and $K_{L_b,CHBrCl_2}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure K.7: Results for dibromochloromethane experiments at 2 SCFM. This figure includes the normalized mean dibromochloromethane experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $5.37e-2$ ft/min and $1.19$ min$^{-1}$ for $K_{Ls, CHBr_2Cl}$ and $K_{Lb, CHBr_2Cl}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the $25^{th}$ and $75^{th}$ percentiles, respectively.
Figure K.8: Results for bromoform experiments at 2 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 2 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 3.83e-2 ft/min and 5.99e-1 min⁻¹ for $K_{Ls,CHBr_3}$ and $K_{Lb,CHBr_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
## K.3 Power Results for 4 SCFM

Figures K.9 – K.12 illustrate the model predicted concentrations to the experimental using the parameter estimations for each $K_{Ls,y}$ value from the 4 SCFM experiments.

**Figure K.9:** Results for chloroform experiments at 4 SCFM. This figure includes the normalized mean chloroform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $3.42 \times 10^{-1}$ ft/min and $3.99$ min$^{-1}$ for $K_{Ls,CHCl_3}$ and $K_{Lb,CHCl_3}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure K.10: Results for bromodichloromethane experiments at 4 SCFM. This figure includes the normalized mean bromodichloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 1.79e-1 ft/min and 2.12 min⁻¹ for $K_{Ls,CHBrCl_2}$ and $K_{Lb,CHBrCl_2}$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25th and 75th percentiles, respectively.
Figure K.11: Results for dibromochloromethane experiments at 4 SCFM. This figure includes the normalized mean dibromochloromethane experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using 9.48e-2 ft/min and 1.19 min$^{-1}$ for $K_{Ls,CHBr_2Cl}$ and $K_{Lb,CHBr_2Cl}^a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{th}$ and 75$^{th}$ percentiles, respectively.
Figure K.12: Results for bromoform experiments at 4 SCFM. This figure includes the normalized mean bromoform experimental data plotted over time at 4 SCFM with the model. The model is shown as a line and is estimated using Equation 2.3 using $5.95e-2$ ft/min and $5.99e-1$ min$^{-1}$ for $K_{Ls,CHBr_3}$ and $K_{Lb,CHBr_3}a$, respectively. The middle bar indicates the average normalized concentration of a data set while the lower and upper bars represent the 25$^{{th}}$ and 75$^{{th}}$ percentiles, respectively.
Appendix L

Continuous Flow Model Results
Using Actual LVVWD Operational Conditions

The following appendix presents the continuous flow model results using actual operational conditions associated with bromodichloromethane and dibromochloromethane. The first section presents the comparison between the three $K_{L,s,y}$ parameter estimation cases and the latter section illustrates the results associated with the model performance using the $K_{L,s,y}$ case “3”.

L.1 Comparing Model Performance Using Each Parameter Estimation Method

Figures L.1 and L.2 provide the results for bromodichloromethane and dibromochloromethane, respectively, for comparing the three parameter estimation cases. Overall estimation
case “2” is typically outperformed by “1” and “3” and provided that case “1” excludes the means to represent surface mass transport rate at different airflow rates, case “3” was selected for use for the modeling of each THM.

![Graph showing RMSE values for Middle Tank cases 1, 2, and 3 for bromodichloromethane model performance using each parameter estimation method.](image)

**Figure L.1:** Comparison of the Middle tank bromodichloromethane model performance using each parameter estimation method. $K_{Ls,y}$ values for cases 2 and 3 were calculated based on an air flow rate of 3.48 SCFM / diffuser. The plot features the absolute RMSE for each simulation where overall parameter cases 1 and 3 outperform case 2.

### L.2 Alpha Simulations Mass Removal

The model results for bromodichloromethane and dibromochloromethane are illustrated in Figure L.3 and Figure L.4, respectively. In general the model predicted concentrations strongly represent the experimental data samples for each THM. Based
<table>
<thead>
<tr>
<th>Date</th>
<th>Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>04/14</td>
<td>6 µg/L</td>
</tr>
<tr>
<td>04/17</td>
<td>8 µg/L</td>
</tr>
<tr>
<td>04/20</td>
<td>10 µg/L</td>
</tr>
<tr>
<td>04/22</td>
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<td>04/28</td>
<td>16 µg/L</td>
</tr>
<tr>
<td>05/01</td>
<td>18 µg/L</td>
</tr>
</tbody>
</table>

Middle Tank Case 1 RMSE = 0.54742 µg/L
Middle Tank Case 2 RMSE = 1.5976 µg/L
Middle Tank Case 3 RMSE = 0.4799 µg/L
North Tank RMSE = 0.4799 µg/L

Figure L.2: Comparison of the Middle tank dibromochloromethane model performance using each parameter estimation method. $K_{Ls,y}$ values for cases 2 and 3 were calculated based on an air flow rate of 3.48 SCFM / diffuser. The plot features the absolute RMSE for each simulation where overall parameter cases 1 and 3 outperform case 2.
on the “central” simulations from each tank model, the absolute RMSE between the model predicted concentrations compared to the experimental are less than 1 µg/L for both bromodichloromethane and dibromochloromethane. Overall the model represents the LVVWD data ‘closely’.

![Graph showing concentration over time for North and Middle tanks](image)

![Graph showing concentration over time for North and Middle tanks](image)

Figure L.3: Middle vs. North tank results for the bromodichloromethane model with respect to LVVWD data using real operational conditions. The upper bound for both simulated tanks represents the simulation case using high influent THM concentrations and a lower airflow rate and vice-versa for the lower bound. Influent concentrations and simulated airflow rates boundary conditions were based on the actual data distributions supplied by LVVWD provided in Appendix D.
Figure L.4: Middle vs. North tank results for the dibromochloromethane model with respect to LVVWD data using real operational conditions. The upper bound for both simulated tanks represents the simulation case using high influent THM concentrations and a lower airflow rate and vice-versa for the lower bound. Influent concentrations and simulated airflow rates boundary conditions were based on the actual data distributions supplied by LVVWD provided in Appendix D.