Fall 2015

DEVELOPING A HORIZONTAL IN-LINE DIFFUSED AERATION SYSTEM FOR REMOVING TRIHALOMETHANES FROM WATER DISTRIBUTION MAINS

Meagan McCowan
University of New Hampshire, Durham

Recommended Citation
McCowan, Meagan, "DEVELOPING A HORIZONTAL IN-LINE DIFFUSED AERATION SYSTEM FOR REMOVING TRIHALOMETHANES FROM WATER DISTRIBUTION MAINS" (2015). *Master's Theses and Capstones*. 1050.
https://scholars.unh.edu/thesis/1050

DEVELOPING A HORIZONTAL IN-LINE DIFFUSED AERATION SYSTEM FOR REMOVING TRIHALOMETHANES FROM WATER DISTRIBUTION MAINS

BY

MEAGAN L MCCOWAN
BS in Environmental Engineering, University of New Hampshire, 2013

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Master of Science
In
Civil Engineering

September, 2015

This thesis/dissertation has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering by:

Thesis Director
M. Robin Collins, Ph.D., P.E.
Professor of Civil Engineering and Environmental Engineering

Thomas P. Ballestero, Ph.D., P.E.
Associate Professor of Civil Engineering and Environmental Engineering

James P. Malley, Jr., Ph.D.
Professor of Civil Engineering and Environmental Engineering

On May 5, 2015

Table of Contents

Acknowledgments

I would like to acknowledge the USEPA along with the DeRISK Center at UC Boulder for the partial funding of this research. I would like to thank my Advisor Dr. Robin Collins and the WTTAC staff for making this research a success, as well as the students, faculty and staff at Gregg Hall. I would also like to thank my family for their constant love and support.

List of Tables

List of Figures

List of Abbreviations

A:W	air to water
ANOVA	analysis of variance
DBP	disinfection byproduct
gpm	gallons per minute
HAA5	haloacetic acids
HILDA	horizontal in-line diffused aeration
ID	inner diameter
IDSE	initial distribution system evaluation
LRAA	local running annual average
MRT	mean residence time
NOM	natural organic matter
OD	outer diameter
psi	pounds per square inch
PVC	polyvinyl chloride
RAA	running annual average
RMS	root mean square
RO	reverse osmosis
scfm	standard cubic feet per minute
STDEV	standard deviation
THM	trihalomethane
TOC	total organic carbon
TTHM	total trihalomethanes
UV	ultraviolet
VOC	volatile organic carbon

ABSTRACT

DEVELOPING A HORIZONTAL IN-LINE DIFFUSED AERATION SYSTEM FOR REMOVING TRIHALOMETHANES FROM WATER DISTRIBUTION MAINS

BY

MEAGAN L MCCOWAN

University of New Hampshire, September 2015

This study collected removal data for four EPA regulated trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) for a pilot scale horizontal in-line diffused aeration (HILDA) system under various design and operational variables. Design variables included water flow rate, air to water (A:W) ratio, reactor length, pressure, trihalomethane (THM) speciation and mixer type.

A HILDA system that could remove THMs from a pressurized piping system was developed and an air-water mixing expression was used to model the treatment performance when using Komax static in-line mixers in the system. The models can be used to predict the mixing intensity needed to achieve a certain total THM removal in the system. Models for total THM removal were created for A:W ratios of 5:1, 10:1, and 20:1, with an influent THM speciation of approximately 70% chloroform and 10% each of the other three species, and at a temperature and pressure reasonably close to 20 °C and 40 PSI, respectively. Models were also developed for each THM species, allowing for the prediction of the needed mixing intensity even if the influent speciation varies. Once a value of mixing intensity is predicted, an air-water mixer configuration can be determined.

Adding turbulence is required in order to reach saturation THM removals especially at lower flow rates. Turbulence can be created by increasing the flow rate, increasing the A:W ratio, increasing the mixing length, decreasing the reactor diameter, or adding a static mixer into the system.

When using Komax static in-line mixers to facilitate air-water mixing, significant variables included air flow rate, water flow rate, and length, which had contributions to THM removal of 81.0%, 12.7%, and 3.3%, respectively, with a 3% contribution from error. When comparing systems at 25 PSI and 40 PSI for a 10:1 A:W ratio, pressure was found to have little contribution to the overall % removals of THMs.

1 Introduction

Disinfection byproducts (DBPs) are compounds that form when natural organic or inorganic constituents in a source water react with disinfectants during the drinking water treatment process. Specifically, Trihalomethanes (THMs) and Haloacetic acids (HAA5) are disinfection byproducts that form when natural organic matter (NOM) reacts with chlorine (USEPA, 2013). The reaction describing DBP formation can be seen in the following equation:

$$\boldsymbol{NOM + Cl_2 = DBPs} \tag{1.1}$$

THMs and HAA5 are suspected carcinogens and THMs may increase the risk of health problems in the liver, kidney, and central nervous system. Because of this, the total amount of THMs and HAA5 present in treated drinking water are a constant concern of the U.S. EPA. The total amount of regulated THMs (TTHMs) includes four different compounds: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. There are five regulated HAA5: dichloroacetic acid, trichloroacetic acid, chloroacetic acid, bromoacetic acid, and dibromoacetic acid (USEPA, 2013).

Originally, the EPA regulated total trihalomethanes to a level of 0.10 mg/L in an amendment to the National Interim Primary Drinking Water Regulations under the Safe Drinking Water Act (USEPA, 1981). This included requiring quarterly drinking water distribution system monitoring for at least four sites, with one being at the far end of the system and the other three at average hydraulic retention times in the system. The running annual average (RAA) for the entire system had to be less than 0.10 mg/L to be in compliance with EPA regulations (MWH, 2005).

In 1998, new regulations were added to the Safe Drinking Water Act. The Stage 1 Disinfectants and Disinfection Byproducts Rule was implemented in order to protect humans from potential health effects of disinfection byproducts. This rule includes the regulation of TTHMs to an annual average of 0.080 mg/L. The compliance deadline for large surface water systems was 2002 while the deadline for smaller surface water systems and groundwater systems was 2004 (USEPA, 1998). On top of the lower 0.080 mg/L TTHM regulation, the EPA passed the Stage 2 Disinfectants and Disinfection Byproducts Rule in 2005 which increased the monitoring regulations for TTHMs. This regulation requires drinking water treatment plants to sample their water at different locations along the distribution system over the course of the year in order to calculate their local running annual average (LRAA) for TTHMs. These sites must be those with the highest DBP concentrations in the system in accordance to the required Initial Distribution System Evaluation (IDSE). If this LRAA exceeds 0.080 mg/L at any point along the distribution system, then the treatment plant is not in compliance with the SDWA (USEPA, 2005). These more stringent THM regulations show the need for practical and cost effective solutions to control THMs in the distribution system.

1.1 THM Management Approaches

Several approaches exist for managing THMs for a drinking water treatment supply. Two of these approaches occur at the drinking water treatment plant and are used to help reduce the amount of THMs that are formed. The 1st method is to reduce the amount of organic matter in the water prior to disinfection. This can be achieved through enhanced coagulation, activated carbon adsorption, ion exchange, nanofiltration, reverse osmosis, and precipitatave softening (MWH, 2005). The 2nd method is to reduce the amount of chlorine contact time or replace the chlorine that is reacting with the natural organic matter with an alternate disinfectant. Contact time reduction can be performed by adding chlorine as far along the treatment process as possible, and by adding ammonia once the required disinfection contact time has been achieved. The ammonia and free chlorine will react to form combined chlorine, or chloramines, which will still form DBPs but will do so at a much slower rate (MWH, 2005). Alternative disinfectants include ozone, chloramines as discussed above, chlorine dioxide, ultraviolet (UV) treatment, or a combination of disinfectants. Using these disinfectants will prevent or reduce the formation of THMs, but could facilitate the production of other potentially harmful byproducts. Also, using ozone or UV as a disinfectant will not provide a residual in the distribution system (USEPA, 1981 & USEPA, 1999). While effective at reducing THM formation, changing or upgrading the water treatment plant to include these control techniques could be costly and negatively affect other plant processes.

Another method for dealing with THMs is to remove them after formation. This management method for THMs is typically called post treatment removal. Post treatment removal can be a cost effective solution for systems with THM problems since many THM problems occur at the far ends of the distribution system, meaning a much reduced amount of the water would require treatment.

1.2 Post Treatment of THMs

Post treatment of THMs can be achieved through the use of adsorption and aeration. Adsorption of THMs can be accomplished through the use of granular activated carbon (GAC) or powdered activated carbon (PAC). Studies have shown that PAC does not adsorb chloroform very well, but increases in performance as THM species contain more bromine. Data has also shown GAC to have a short service life and therefore may not be a viable treatment option on its own owing to the need to constantly regenerate the bed (USEPA, 1981).

Aeration of water after THM formation has been found to be a viable method. Both countercurrent packed towers and diffused aeration in open reactors can remove THMs, with packed towers typically able to remove more THMs than diffused aeration with the same ratio of air to water (USEPA, 1981). Research has also shown that spray aeration in storage tanks is another viable method of aeration (Brooke & Collins, 2011).

THM formation depends on the contact time of NOM and chlorine, therefore THMs can continue to form in the water distribution system after the water leaves the treatment plant. This means that some areas farther along in the distribution system will exceed THM regulations while areas earlier in the system will not (USEPA, 2006). These problematic areas in the system or THM "hot spots" require treatment to remove THMs. While post treatment can occur in tanks through the use of spray aeration, some communities may not have storage tanks located in a high THM level area along the distribution system, or may not have a storage tank at all. In these cases, pressurized in-line diffused aeration systems could be viable options because they could be placed at optimal sites along the distribution system, as depicted in Figure 1.1, and would only need to treat a reduced amount of water.

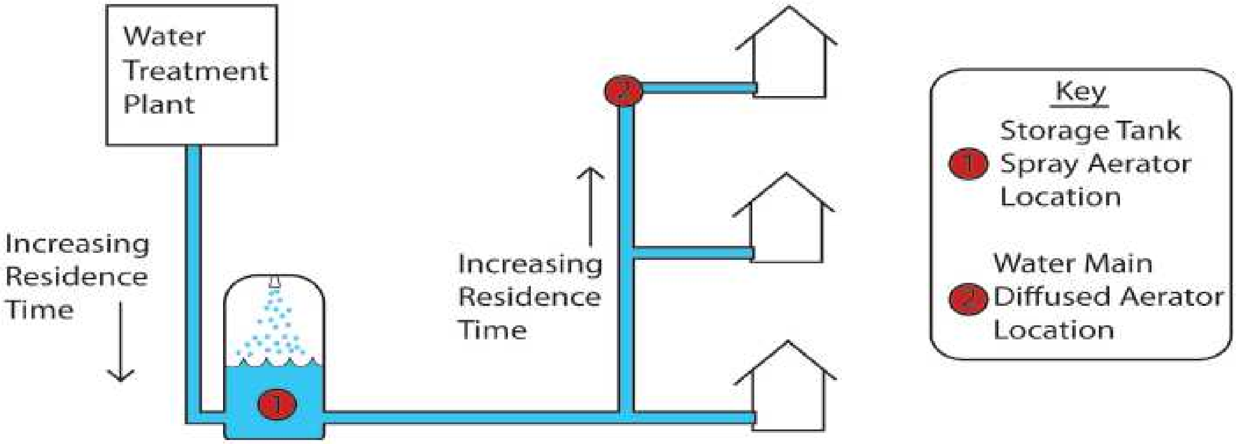


Figure 1.1 Distribution system with storage tank aeration (1) or diffused aeration (2)

1.3 Research Objectives

This research focuses on an aeration method to remove THMs from THM "hot spots" along the distribution system piping. While "hot spot" THM removal can be performed in storage tanks by spray or diffused aeration systems (Brooke & Collins, 2011), the proposed in-line method investigates the use of pressurized horizontal in-line diffused aeration (HILDA) systems. With this method, aeration can occur within the distribution pipeline without depressurizing the system, and could be beneficial to communities with limited space, without storage tanks in strategic locations to remove THMs, or in low demand sections of the system far from the water treatment plant.

There are two specific objectives of the study. The 1st objective is to develop the configuration of a reactor that sufficiently facilitates air and water mixing so that saturation, or optimal aeration, conditions may be achieved. The 2nd objective is the development of a model for predicting THM removal using horizontal pressurized diffused in-line aeration with consideration of the air to water (A:W) ratio and mixing intensity. The resulting model would help distribution system operators estimate the needed A:W ratio and size of the reactor needed to achieve a desired THM removal depending on the temperature, pressure, reactor configuration, and speciation of THMs in the water to be treated.

With consideration to relationships on how the A:W ratio, pressure, and temperature affect THM removals, predictions can be made for maximum % removal, or equilibrium removal of THMs when these parameters are altered. It is hypothesized that adequate mixing and interaction between air and water will be the driving force to achieve saturation removals in the horizontal pressurized aeration system. Therefore, a parameter that incorporates the flow, reactor length, reactor diameter and mixing efficiency should be able to quantify the interaction between air and water. This parameter could then be used to show what mixing configuration is needed to achieve saturation removals of THMs.

2 Literature Review

Chapter 2 covers topics related to aeration and mixing relevant to this thesis. Different aeration methods are discussed, followed by two-film theory and Henry's law which are used to explain aeration mechanisms. Previous work performed on the influence of temperature, pressure, and A:W ratio on THM removal will be presented, followed by information on quantifying mixing intensity which will later be used to help model THM removal.

2.1 Aeration: Overview and Methods

Aeration can be used to remove volatile substances from water, or add substances such as oxygen, ozone, or carbon dioxide (MWH, 2005). In this thesis, the removal of volatile organic carbons (VOCs) known as THMs will be investigated.

Some general aeration methods include thin-film or droplet air-water contact, diffused aeration, and mechanical aeration. Thin-film or droplet methods include packed towers, spray aerators, cascade aerators, and tray aerators. Packed tower aeration is a form that involves a tower filled with a packing media. Water is uniformly dispersed down from the top of the tower while air flows either cocurrent, countercurrent, or across the water. This allows for the air and water to contact and volatile compounds to be removed into the air as the water falls down through the packing media in the tower. Figure 2.1 shows an example of a packed tower aerator. Spray aerators use a nozzle to separate the water into droplets which come into contact with air as the droplets fall. Contaminants such as VOCs and those that cause taste and odor problems can be removed while the water droplet is in contact with the air. Spray aerators can be used in storage tanks as well as reservoirs. An example of a spray aerator in a tank can be seen in Figure 2.2.

Cascade aerators use a series of steps that the water can flow over, and tray aerators include a series of trays so that water can flow down over the sides from one tray to another (MWH, 2005).

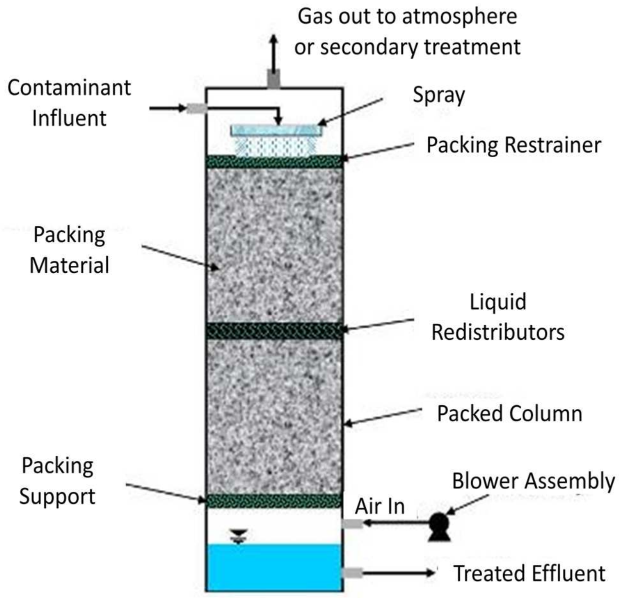


Figure 2.1Configuration of packed tower aerator, showing contaminant influent flowing from top though packing media with air being pumped up from the bottom and being released into the atmosphere (USEPA, 2014)

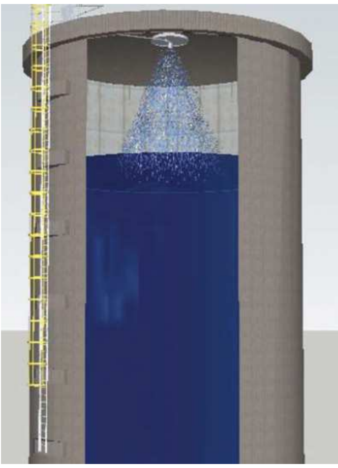


Figure 2.2 Spray aerator placed inside of storage tank (Brooke & Collins, 2011)

Diffused aeration typically involves bubbling air into a clearwell or tank in order to remove VOCs or add gasses to the water (MWH, 2005). A schematic of diffused aeration can be found in Figure 2.3.

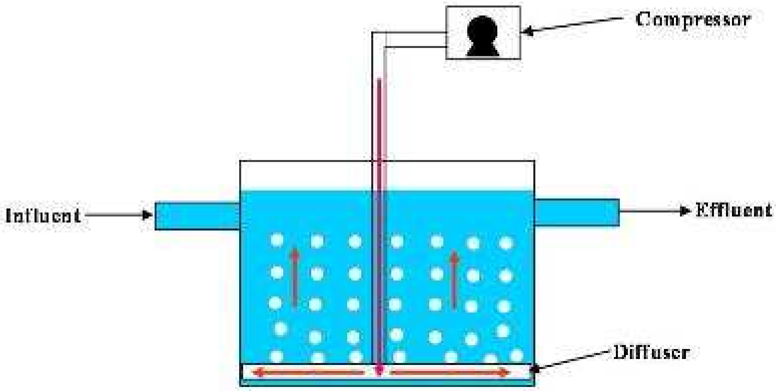


Figure 2.3 Diffused aeration device showing influent compressed air bubbling up through water through a diffuser (USEPA, 2014)

Mechanical aeration can be used if VOC removals less than 90% are needed. This type of aeration can be done at the water surface or below the water. Aerators can be placed at the surface in propeller or brush form, can have impellors that draw air into the system, or can disperse compressed air into the system with a rotating turbine (MWH, 2005). An example of a mechanical aerator can be found in Figure 2.4.

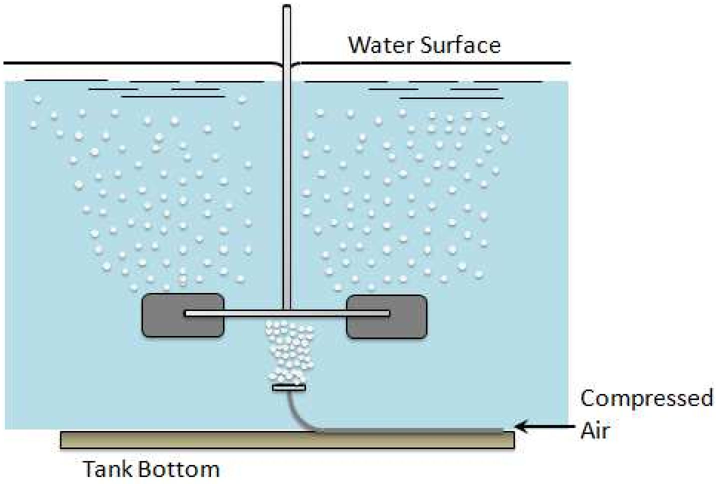


Figure 2.4 This mechanical aerator shows a turbine dispersing compressed air into the system (figure adapted from González, J.F., 1996)

2.2 Two Film Theory

Two film theory can be used to describe the stripping of volatile compounds from water to air, or the absorption of gasses from air to water. For stripping or absorption to occur, there exists a bulk air phase, a bulk liquid phase, an air film, a liquid film, and an air-water interface. In the case if air stripping, the concentration of the VOC in the bulk liquid phase is greater than that in the air-water interface, meaning the VOC will diffuse into the air-water interface. The VOC will partition at the air-water interface depending on its Henry's law constant. The concentration of the VOC is then greater at the interface than in the bulk air phase, so the VOC will then diffuse into the air (MWH, 2005). A visual representation of two film theory can be found in Figure 2.5, where:

- G_b=the concentration of volatile substance in bulk gas phase
- G_{awi}=the concentration of volatile substance in gas-phase of air-water interface
- G_e=the concentration of volatile substance in gas phase in equilibrium with bulk water phase
- L_b=the concentration of volatile substance in bulk liquid phase
- L_{awi} =the concentration of volatile substance in liquid phase of air-water interface
- L_e=the concentration of volatile substance in liquid phase in equilibrium with bulk air phase.

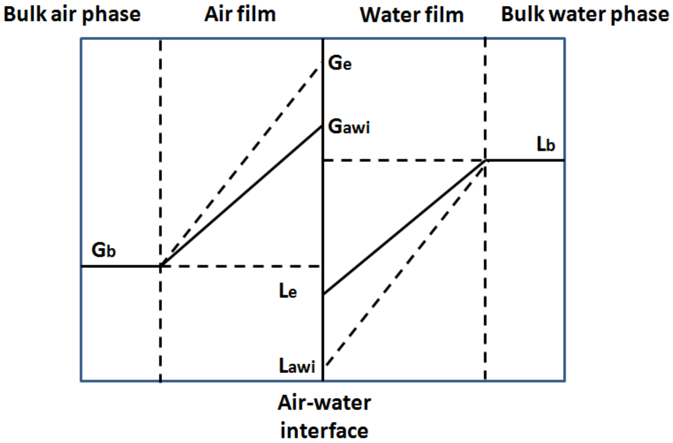


Figure 2.5 Two Film Theory showing bulk air phase, air film, water film, bulk water phase and air-water interface, along with the concentration gradients between the phases and films that are the driving force for air stripping (figure adapted from MWH, 2005)

2.3 Using Henry's Law to Describe Gas-Liquid Equilibrium

At equilibrium, chemical compounds such as VOCs can diffuse between the gaseous and liquid phases as seen in Equation 2.1.

$$VOC_{liquid} \leftrightarrow VOC_{gas} \tag{2.1}$$

Henry's Law describes the extent to which a chemical compound will be in the gaseous phase vs. the liquid phase when the two phases come into contact and diffusion occurs. The equation for Henry's Law can be seen in Equation 2.2 (MWH, 2005). Typically the equilibrium constant, H, does not depend on the concentration of the VOC in the liquid unless the concentration is greater than 0.01 mol/L. Also, air in the system should not affect H because VOC concentrations are minimal or are not present in the air (MWH, 2005).

$$\frac{\{VOC_{gas}\}}{\{VOC_{liquid}\}} = H \tag{2.2}$$

- $\{VOC_{gas}\}$ = the activity of the VOC in the air (mol/L of air)
- $\{VOC_{liquid}\}$ = the activity of the gas in the water (mol/L of water)
- H=the dimensionless equilibrium constant known as Henry's constant

Henry's law can be described in many other forms, both dimensionless as in Equation 2.2 and dimensioned. Common dimensionless forms can be found in Equations 2.3 and 2.4 (Staudinger & Roberts, 2000), while common dimensioned forms can be found in Equations 2.5 and 2.6 (Staudinger & Roberts, 2000).

$$H_{cc} = \frac{C_G}{C_L} \tag{2.3}$$

- C_G = concentration of compound in gas (mg/L or mol/L)
- C_L = concentration of compound in liquid (mg/L or mol/L)
- H_{cc} = Dimensionless Henry's law constant

$$H_{yx} = \frac{y}{x} \tag{2.4}$$

- y = molar fraction of compound in gas (mol/mol)
- x = molar fraction of compound in liquid (mol/mol)
- H_{yx} = Dimensionless Henry's law constant

$$H_{px} = \frac{yP_T}{x} \tag{2.5}$$

- y = molar fraction of compound in gas (mol/mol)
- P_T = total atmospheric pressure (atm)
- x = molar fraction of compound in liquid (mol/mol)
- H_{px} = Dimensioned Henry's law constant (atm)

$$H_{pc} = \frac{yP_T}{C_L} \tag{2.6}$$

- y = molar fraction of compound in gas (mol/mol)
- P_T = total atmospheric pressure (atm)
- C_L = concentration of compound in liquid (mg/L or mol/L)
- H_{pc} = Dimensioned Henry's law constant ($atm \cdot m^3/mol$)

Many times, Henry's law constant values for different compounds have already been determined and are available in the literature. If Henry's law constant values are not available, they can be determined using Equation 2.7 using vapor pressure and aqueous solubility data for the compound in question (MWH, 2005).

$$H_{cc} = \frac{P_v}{C_s} \tag{2.7}$$

- H_{cc} =Henry's law constant for compound based on concentration
- P_v =the vapor pressure of compound (atm)
- C_s =the aqueous solubility of compound (mol/L)

Values for H can also be obtained by measuring the concentration and pressure in a system at equilibrium or while an air and water exchange process at equilibrium is occurring (Mackay et al, 1981).

2.4 Correcting for Temperature and Pressure

Work performed by Zwerneman (2012) shows that Henry's law constant is dependent on pressure. This research determined a model that can be applied to Henry's law constant and change Henry's law constant accordingly depending on the pressure.

A 3 L 0.75 cm inner diameter (ID) and 0.75 m long PVC bench scale reactor was used for this study. Air was introduced through a diffuser stone and released through an air relief valve. For the different experiments, system pressure, aeration time, and A:W ratio were altered. Water spiked with THMs was run through the reactor and percent removals were found for different experiments. Henry's law constants were then calculated for the different THMs for different pressures using a method developed by Mackay et al. (1981) as seen in Equation (2.8):

$$ln\left(\frac{C_e}{C_0}\right) = -\left(\frac{H_{cc}Q_G}{V_L}\right)t \tag{2.8}$$

- $\frac{C_e}{C_0}$ = the ratio of the effluent concentration to the influent concentration of the volatile solution
- H_{cc} = the Henry's law constant
- Q_G = the flow rate of the air (L/min)
- V_L = the volume of the liquid (liters)
- t = the time (minutes)

The calculated Henry's Law constants then needed to be corrected for temperature. To do this, a form of van't Hoff's equation developed by Staudinger & Roberts, 2000 was used:

$$H_{cc,T} = \left(H_{cc,20°C}\right)\left[10^{-B\left(\frac{1}{T}-\frac{1}{293}\right)}\right] \tag{2.9}$$

- $H_{cc,T}$ = the temperature corrected Henry's law constant
- $H_{cc,20°C}$ = the Henry's law constant at 20 °C
- T = the temperature in °K
- B = the temperature dependant relationship constant which was experimentally determined along with $H_{cc,20°C}$ for each compound by Nicholson et al. (1984).

Values for B and $H_{cc,20°C}$ determined by Nicholson can be found in Table 2.1.

Table 2.1 Values for $H_{cc,20°C}$ and B (Nicholson et al, 1984)

Temperature Dependant Relations		
Compound	$H_{cc,20°C}\ x\ 10^{-3}$	B
$CHCl_3$	121	2131
$CHCl_2Br$	64.2	2135
$CHClBr_2$	35.2	2135
$CHBr_3$	18.0	2335

Zwerneman's data showed the relationship of pressure to Henry's law constant to be approximately second order, and can be estimated using Equation (2.10):

$$\frac{1}{H_{cc}} - \frac{1}{H_{cc,0}} = kP \tag{2.10}$$

- H_{cc} = the dimensionless Henry's law constant at system pressure
- $H_{cc,0}$ = the dimensionless Henry's law constant at atmospheric pressure.
- P = the system pressure (psi)
- k = the experimentally determined rate constant (psi^{-1})

Figure 2.6 shows % Removal vs. A:W ratio data for each THM species depending on the pressure of the system for a continuous reactor. % removals for each THM increased as A:W ratio increased and were higher for 25 psi than 50 psi. Also, % removals were highest for chloroform, and then decreased as more bromine was added. k values were determined for each THM using the second order plots of $\frac{1}{H_{cc}}$ vs. pressure. Table 2.2 shows the experimentally determined values of k for each THM.

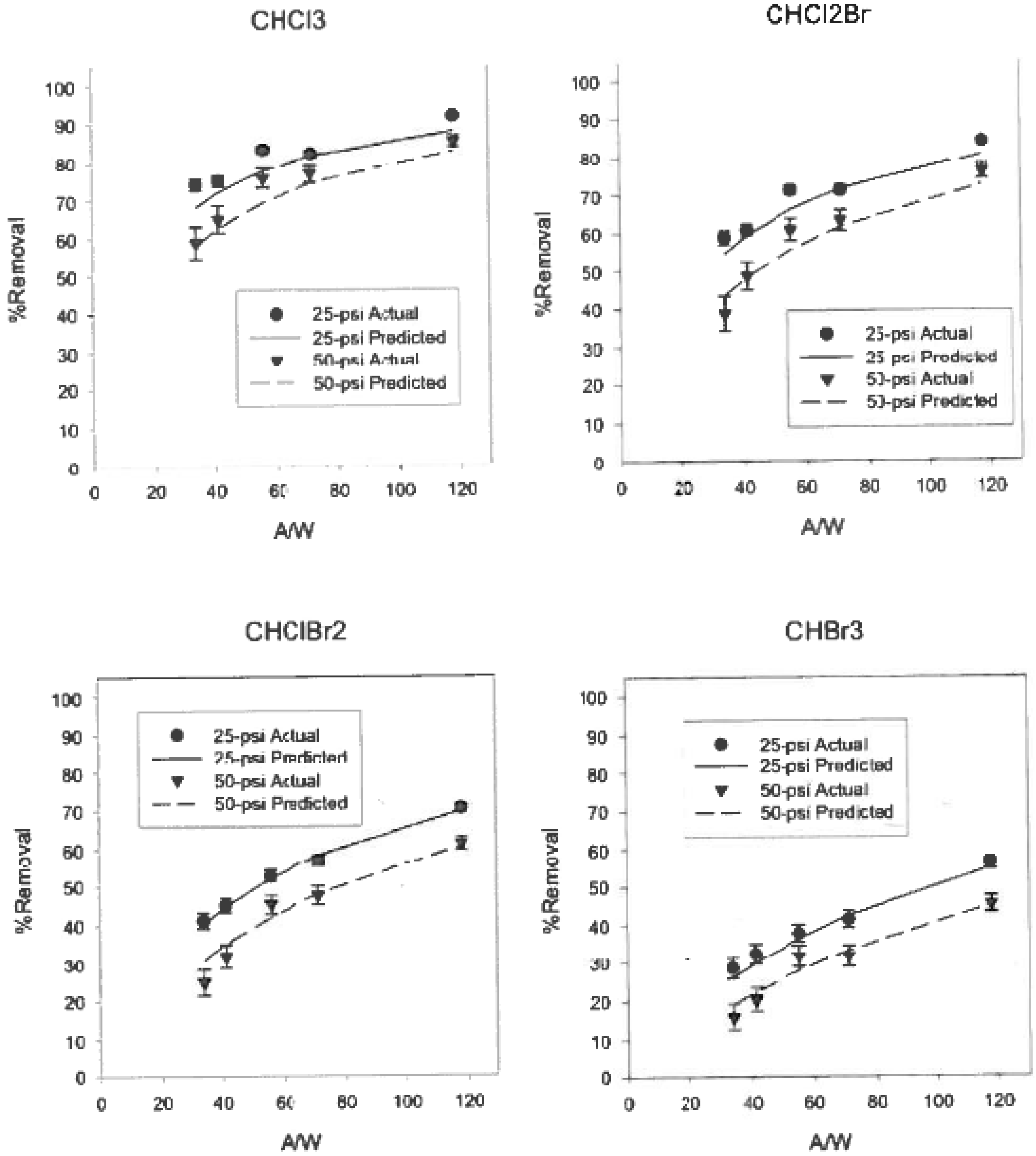


Figure 2.6 Influence of A:W ratios, operating pressures, and THM species on TTHM removals in continuous vertical pressurized diffused aeration reactor (Zwerneman, 2012)

Table 2.2 Experimentally determined second order rate constants for each THM species (Zwerneman, 2012)

Second Order Rate Constants (psig^{-1})	
$CHCl_3$	0.377
$CHCl_2Br$	0.674
$CHClBr_2$	1.21
$CHBr_3$	1.81

2.5 Predicting Steady State Equilibrium Removals

The work of Matter-Müller et al. (1981) provides a method which allows equilibrium contaminant removal values to be predicted. Neglecting pressure and volume changes in the air bubbles, the following equation can be used for the general gas transfer model for rising bubbles in a homogenous volume of liquid in order to predict the mass transfer rate of the contaminant out of the system.

$$F = Q_G H_{cc} L_b \left[1 - \exp\left(-\frac{K_{OL} a_i V_L}{H Q_G}\right)\right] \tag{2.11}$$

- F = the mass transfer coefficient of contaminant y out of an aeration system (g/s)
- Q_G = the gas flow in (m^3/s)
- H_{cc} = the Henry's law constant of compound y
- L_b = the bulk liquid concentration of compound y (g/ m^3)
- K_{OL} = the overall mass transfer coefficient (m/s)
- a_i = the interfacial area per unit volume of liquid in (m^2/m^3)
- V_L= the liquid volume in (m^3).

Assuming that aeration is the only mechanism removing the contaminant and that the system is at steady state, equation 2.12 shows a mass balance for a continuous flow reactor:

$$V_L \frac{dL_b}{dt} = Q_L\left(L_{b,i} - L_b\right) - F \tag{2.12}$$

- $\frac{dL_b}{dt}$ = the change in the bulk liquid concentration of compound over the change in time (g/(m^{3}s))
- Q_L = the liquid flow rate (m^3/s)
- $L_{b,i}$ = the influent concentration of compound y (g/m^3).

Subbing Equation (2.11) into Equation (2.12) yields:

$$\frac{L_b}{L_{b,i}} = \frac{1}{1 + \frac{H_{cc}Q_G}{Q_L}\left[1 - \exp\left(-\frac{K_{OL,}aV_L}{H_{cc}Q_G}\right)\right]} \tag{2.13}$$

If the expression $\frac{K_{OL}aV_L}{HQ_G}$ is much larger than 1, indicating equilibrium conditions with the gas completely saturated, then the simplified Equation (2.14) can be used to predict maximum contaminant removals. Predicted contaminant removals can be compared to observed removals in this study to determine if maximum removal, or equilibrium, has been achieved. As seen in Figure 2.6, actual and predicted % removals for the continuous flow reactor were similar, helping to confirm this prediction method.

$$\frac{L_b}{L_{b,i}} = \frac{1}{1 + \frac{Q_G H_{cc}}{Q_L}} \tag{2.14}$$

2.6 Vertical Diffused Aeration

Work performed by Cecchetti et al. (2013) investigated THM removal in a vertical pressurized pipe. The research consisted of a tracer study and a THM study in effort to relate THM removal to the mean residence time (MRT) of the system. The experimental apparatus, as seen in Figure 2.7, was vertical 6 inch PVC pipe, and reactor lengths of two and four feet were used.

For the tracer study, a salt solution was passed through the system, and a cumulative mass curve was developed to determine the MRT, when half of the solution had passed through. For the THM study, a spiked THM solution was run through the system, and percent THM removals were found for each reactor run where the flow ranged from 1-4 gpm. These percent removals were related to the corresponding MRT and also compared to predicted % removals. Predicted removals were calculated by correcting Henry's law constant for temperature, pressure, and using the approach of Matter-Müller et al. (1981). Each trial was run at a pressure of 40 psi, temperature of 10°C, A:W ratio of 10:1, and THM speciation of 70% $CHCl_3$, and 10% each of $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$. Table 2.3 shows the results of the study.

Figure 2.7 Vertical diffused aeration apparatus, where 1) is the influent water piping, 2) is the main reactor column, 3) is the effluent water piping, 4) are the air release valves and effluent airflow monitoring, 5) is the pressure and air inflow monitoring, and 6) is the flow meter

Table 2.3 Vertical Diffused Aeration THM Study Results

Run #	MRT (min)	Average Influent TTHM (ug/L)	Average Effluent TTHM (ug/L)	Standard Deviation (ug/L)	% Removal	Projected TTHM % Removals
1	30.0	237	164	3.88	31	26
2	15.6	237	160	3.88	33	26
3	11.5	237	173	3.88	27	26
4	10.8	237	160	0.30	33	26
5	8.1	237	166	0	30	26

Results of this study show that THM removals can be achieved within a MRT of 8.1 minutes. Further study would look at shorter MRT values to get a better estimate of when equilibrium is achieved in the system. Figure 2.8 is a graphical representation of the THM % removal data vs. MRT.

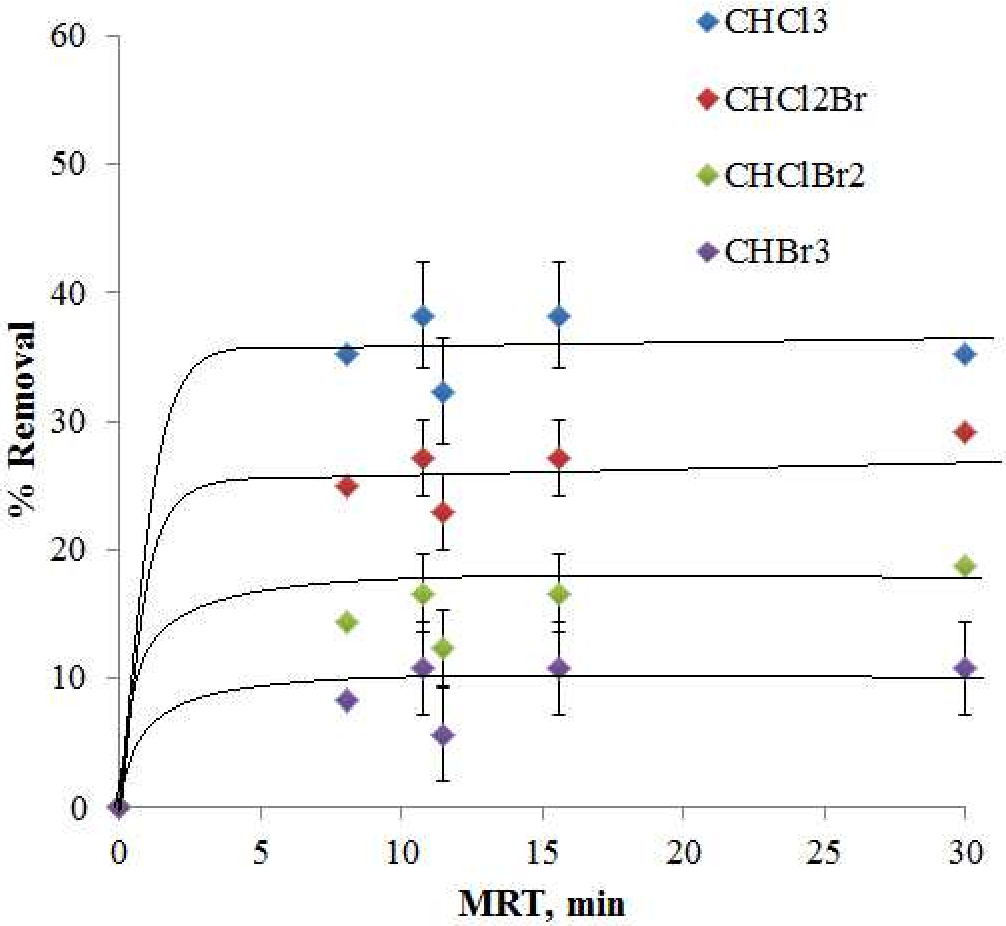


Figure 2.8 % Removal vs. MRT for THMs in a vertical diffused aeration system at 40 psi, 10:1 A:W ratio, temperature of 19°C, and THM speciation of 70% $CHCl_3$, and 10% each of $CHCl_2$ Br, $CHClBr_2$, and $CHBr_3$ (Cecchetti et al, 2013)

2.7 Turbulence and Mixing

Most drinking water treatment plants produce large water flows which are turbulent in the water distribution system. However, flow towards the ends of the distribution system may be less turbulent. In order to achieve saturation THM removals, it is hypothesized that more turbulence may be needed in the system to facilitate air and water mixing.

Turbulent flow is characterized by the time varying velocity components in the x, y, and z directions (Çengel & Cimbala, 2010). It consists of large eddies that impart their energy into smaller and smaller eddies as each eddy moves about. The initial energy of the large eddies could come from a mixer, pump, water falling over a weir, etc. Energy will keep being transferred to smaller eddies until the viscous force of the water overpowers the inertial force (MWH, 2005).

Mixing is widely used in drinking water treatment, mainly for coagulation and for homogeneously adding chemicals into the water such as chlorine for disinfection. Different types of mixers include centerline diffusers, venturi injectors, static mixers, axial pumped jets, lateral pumped jets, and conventional stirred tanks. While widely used, mixing is still considered something of an art, although tools do exist to aid in the design on mixing systems (MWH, 2005). Another option to increase turbulence is static mixing. Static mixers consist of rigid elements that change the flow when it comes in contact with the elements. Previously injected chemicals are mixed into the water as it passes through the elements. Advantages of static mixers include that they require only the space taken by the pipe, they do not have mechanical parts, and they do not use energy. However, static mixers consume energy from the fluid. (Jones et al. 2002).

Several methods can be used to describe the degree of turbulence or mixing in water. These methods can potentially be used in a model to determine the impact of increasing turbulence of %TTHM removals.

Reynolds number (Re) is commonly used measure for turbulence and is a ratio of the inertial forces and the viscous forces in the fluid. For flow in a circular pipe, Reynolds number is shown in Equation (2.15). The flow is considered laminar if $Re \leq 2300$, transitional if $2300 \leq Re \leq 4000$, and turbulent if $Re \geq 4000$ (Çengel & Cimbala, 2010). Reynolds number can be increased by increasing temperature, increasing flow rate, decreasing the pipe diameter, or adding a mixer.

$$Re = \frac{\mathrm{v}_{avg} D_h}{\nu} = \frac{p \mathrm{v}_{avg} D_h}{\mu} \tag{2.15}$$

Where:

- Re =Reynolds number
- v_{avg} = the average flow velocity ($\frac{m}{s}$)
- D_h = the hydraulic diameter of the pipe (m)
- ν = the kinematic viscosity of the liquid ($\frac{m^2}{s}$)
- p = the density of the fluid ($\frac{kg}{m^3}$)
- μ = the dynamic viscosity of the fluid ($\frac{kg}{m \cdot s}$)

Alternate equations similar to Reynolds number that can be used to describe mixing can be found in Equations (2.16) and (2.17).

$$Re_{Komax} = \frac{3157 Q_L S}{\mu D} \tag{2.16}$$

Where:

- Q_L = liquid flow (gpm)
- S = specific gravity of liquid
- μ =liquid viscosity (cp)
- D = pipe diameter (inches)

Equation (2.16) (Komax Systems, Inc. Triple Action Static Mixer) is typically used to determine the number of Komax static mixers needed for an application.

$$Re' = \mathrm{v}\frac{\sqrt{DL_m}}{\nu} \tag{2.17}$$

Where:

- v = water velocity (ft/s)
- D = pipe diameter (ft)
- L_m = mixer length (ft)
- ν = kinematic viscosity of water (ft^2/s)

Equation (2.17) (Ballestero, 2014) describes mixing while taking into account the length of the mixing unit. The numerator describes the momentum of the fluid in the vicinity of the mixer and the denominator describes the viscous resistance forces in that same vicinity.

The root-mean-square (RMS) velocity gradient, proposed by Camp and Stein in 1943, is a parameter that is widely used in the development of flocculation systems. For turbulent water, the RMS velocity gradient, as seen in Equation 2.19, is averaged over the entire mixing volume (MWH, 2005). While the RMS velocity gradient was designed for the use of flocculation basins, the value has become prominent in engineering to help describe different types of mixers.

$$G = \sqrt{\frac{P}{uV}} \tag{2.19}$$

- G = the RMS velocity gradient (s^{-1})
- P = the power input (W)
- u = the dynamic viscosity of the water in ($N \cdot \frac{s}{m^3}$)
- V = the volume in which the mixing occurs (m^3)

Another form of G used for baffled basins can be found in Equation (2.20) (MWH, 2005):

$$G = \sqrt{\frac{\rho g_a \Delta H}{\mu \theta}} \tag{2.20}$$

- p = the density of water ($\frac{kg}{m^3}$)
- g_a = acceleration due to gravity (9.81 m/s^2)
- ΔH = head loss through basin (m)
- u = the dynamic viscosity of the water ($N \cdot \frac{s}{m^3}$)
- θ = detention time (s)

3 Methods and Materials

Included in chapter 3 is the design of the experiment to determine how selected variables of flow, length, and A:W ratio would influence THM removals. A diagram of the experimental apparatus can be found, along with explanations of the different mixing methods. The procedures and quality control for running the apparatus are discussed, along with analytical methods

3.1 Experimental Apparatus

Experiments were performed in an experimental apparatus designed to simulate a 6-inch diameter water main with functions to control the selected design variables of flow, length and A:W ratio. The experimental apparatus consists of a 6-inch diameter, clear, schedule 40 polyvinyl chloride (PVC) pipe with an outer diameter (OD) of 6.625 inches and an (ID) of 6.065 inches. Figure 3.1 shows the pilot scale horizontal diffused reactor.

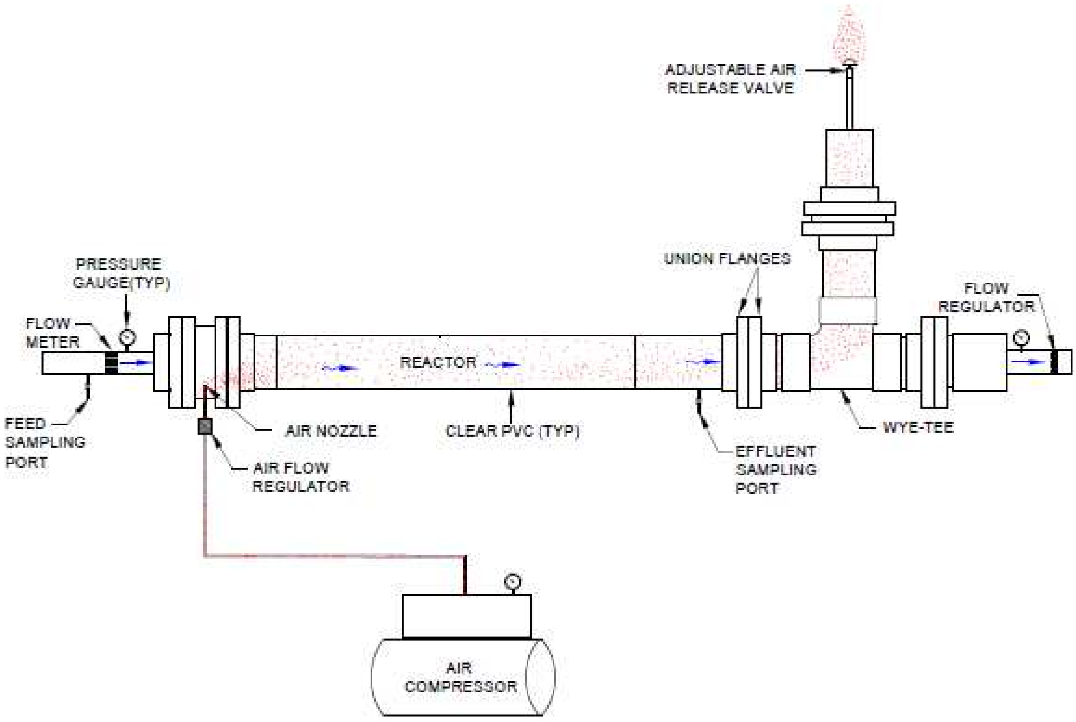


Figure 3.1 Horizontal diffused aeration reactor design, showing control devices and sampling locations (Prepared by WTTAC Staff)

Water entering as well as leaving the system is monitored by flow meters. Air is added into the system via air compressor or compressed air tank and exits the system through an air release valve. A mixing device can be placed in between the air inlet and outlet. Samples can be taken at ports placed before the air injection and after certain lengths of pipe. Air flow meters placed at the air inlet and air release valve show how much air is entering and leaving the system, and pressure gauges are placed at about 1/3 and 2/3 of the pipe to show the pressure of the system. An attempt was made to measure the pressure drop or head loss for the tubular piping array using a differential meter, however this was not successful and showed no pressure difference at 7.5 gpm. This could have been due to pressure differences that were too low, a problem with the meter, or due to that the air and water at the far end of the system were used as the restriction point affecting everything in front of that point making it hard to register the pressure difference.

3.2 A:W Mixing Reactor Configurations

Mixing devices for this study included a pipe array mixer, a pipe array mixer containing static inline mixers, DeltaPak ®, and Komax static inline mixers. All mixers fit inside the 6-inch diameter pipe, except for the Komax mixers, which are housed in 1.5 inch or 1 inch schedule 40 PVC pipe.

3.2.1 No Mixers

Figure 3.2 shows the experimental apparatus without any static mixers. A housing system was developed for two stainless steel number 8 fan nozzles with 90° spray radii manufactured by BETE. The nozzles were each twisted out at a 45° angle and the housing unit was placed at the bottom of the reactor for maximum air coverage.

Figure 3.2 Reactor design with no static mixers, double nozzle placed on bottom of reactor for optimal air coverage

3.2.2 Pipe Array Mixers

Figure 3.3 shows the pipe array mixer before it was placed in the system. It consists of 19 3/4-inch schedule 40 PVC pipes and 12 3/8-inch schedule 40 PVC pipes, as shown in the schematic in Figure 3.4. Gaps along the edges of the mixer were filled in with PVC in order to try and encourage the air and water to flow into the tubes. Figure 3.5 shows the mixer array placed in the system, and Figure 3.6 shows the array containing static inline mixers in the system. Using the recommendation from the manufacturer, BETE nozzle ss4.8 with a 35° spray angle was used for the pipe array mixers. The placement of the nozzle was due to visual observation of how well the air entered the piping system.

Figure 3.3 Pipe array static inline mixer before placement in pipe showing blocked surface area

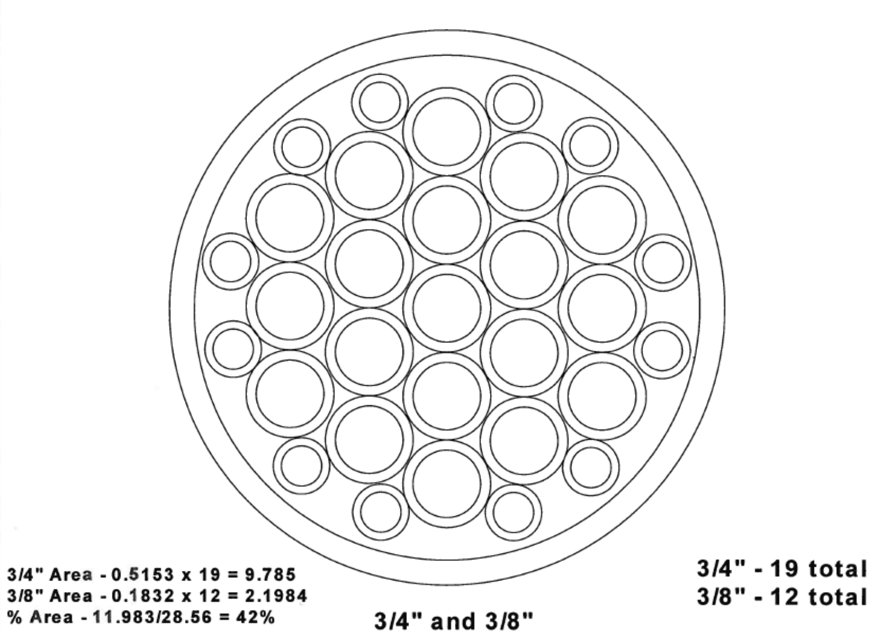


Figure 3.4 Cross-section schematic of pipe array mixer showing number and placement of 3/4-inch and 3/8-inch pipes along with calculation for % of area available.

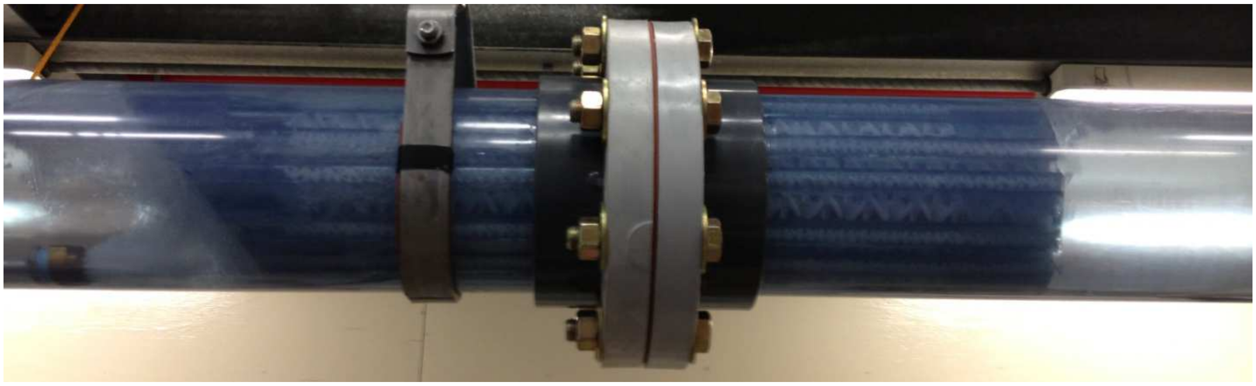


Figure 3.5 Static in-line mixer filled tube pipe array placed in pipe

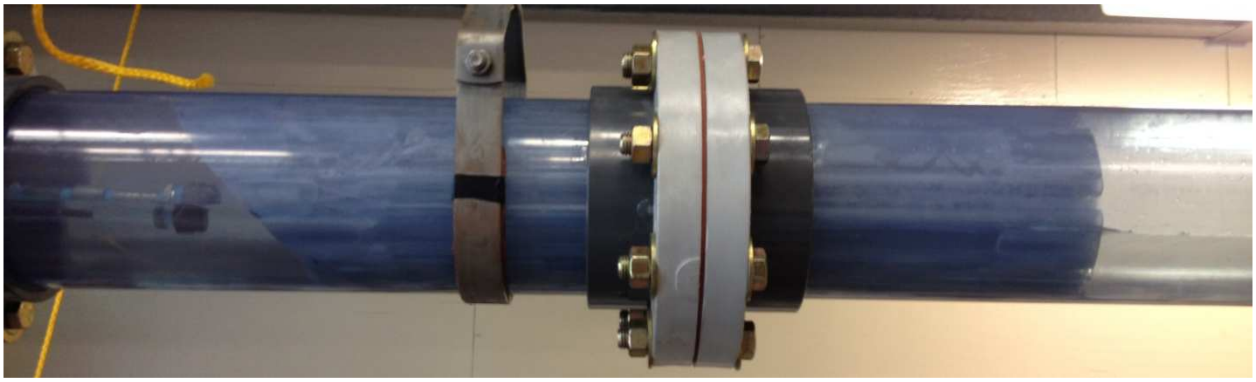


Figure 3.6 Empty tube pipe array static mixer placed in pipe

3.2.3 DeltaPak®

Delta Pak ® is a packing material usually used for mass transfer applications such as air stripping. The PVC is wound spirally to form small, long tubes (Delta Cooling Towers, Inc., 2015). DeltaPak® has much thinner walls and many small, long tubes compared to the pipe array mixer. While the pipe array without tubes has only about 42% of its surface area available, DeltaPak® has about 92% of its surface area available as shown in the calculations in appendix B. Figure 3.7 shows a cross-section of DeltaPak® while Figure 3.8 shows DeltaPak ® placed within the system. As with no mixers, two BETE nozzles with 90° spray radii were placed at 45° angles in a housing unit at the bottom of the pipe to try and cover the whole area of the pipe and get air through all of the tubes.

Figure 3.7 DeltaPak® cross-section showing small tubes formed from spirally wound PVC (Delta Cooling Towers, Inc., 2015)

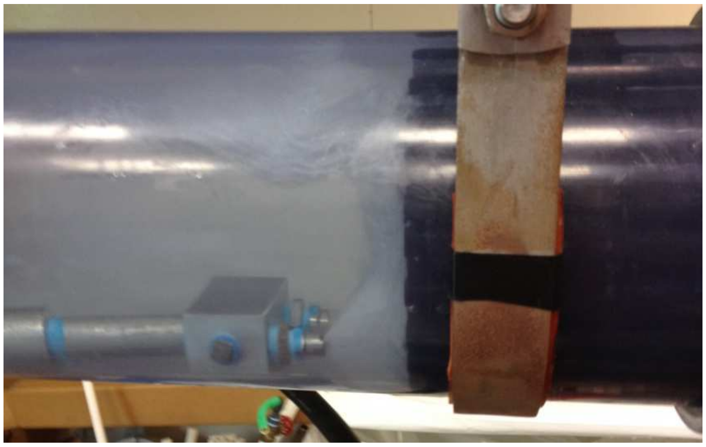


Figure 3.8 DeltaPak® placed in horizontal pipe

3.2.4 Komax Static Inline Mixers

Komax static inline mixers consist of rigid, stainless steel mixing elements inside of a schedule 40 PVC housing (Komax Systems, Inc. Static CPS Mixer). Figure 3.9 shows a Komax static inline mixer placed within the system. One stainless steel BETE fan nozzle number 8 with a 90° spray pattern was used for the Komax mixers and the air was injected vertically. Using one nozzle was sufficient as it was being injected into a much smaller pipe and was easily integrated into the mixing system.

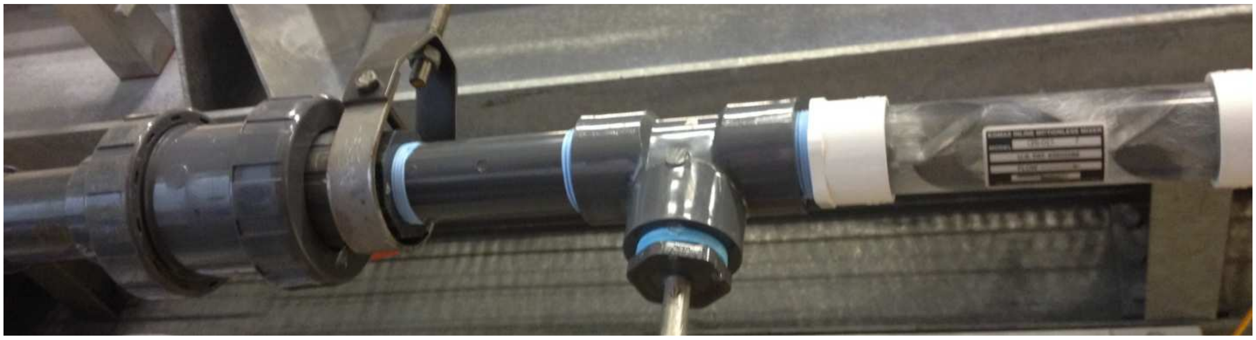


Figure 3.9 Komax static inline mixer placed in horizontal pipe

3.3 Experimental Approach

Phase 1: A reactor study was performed to explore the design of the reactor that could achieve saturation conditions in the horizontal orientation. The reactor study involved the use of no mixer, a pipe array mixer, a pipe array mixer containing static inline mixers, DeltaPak ®, and Komax static inline mixers. Trials consisted of running the reactor at different flow rates and A:W ratios for each mixer type, and determining how actual TTHM removals compared to predicted THM removals. From this study, the mixer with the best THM removals was selected.

Phase 2: A full factorial design for the selected mixer was performed in order to develop a model for THM removal in the water main-based diffused aeration system. Trials consisted of running the reactor at different flow rates, A:W ratios, and lengths. Six confirmation trials were used to confirm the model. The confirmation trials involved different flows, A:W ratios, lengths, and mixer diameters to achieve mixing intensity values that were expected to achieve saturation conditions. Factor levels for the final experiment (excluding the confirmation trials) can be found in Table 3.1.

Table 3.1 Factor levels for final experimental design using 1.5 inch komax static inline mixer: flow, A:W ratio, and length (runs to be performed at temperature of 20 °C, pressure of 40 psi, and influent speciation of 70% $CHCl_3$, 10% $CHCl_2Br$, 10% $CHClBr_2$, and 10% $CHBr_3$

Factor Levels			
Flow (gpm)	Velocity (ft/s)	A:W Ratio	Length (ft)
1	0.16	5	¾ 3
4	0.63	10	
7	1.1	20	

3.4 Statistical Methods

The data collected was analyzed using the statistical software JMP®. The data was found to follow a normal distribution fairly well, so a normal analysis of variance (ANOVA) could be carried out. The fit model platform was used to determine the significant factors, interactions between factors, and which factors were more significant than others. The nonlinear modeling platform in JMP® was used to fit models to the THM removal data.

3.5 Trihalomethane Stock Solution

A stock solution of THMs was created so that the reverse osmosis (RO) water used for each experimental challenge could be spiked with THMs and end up with similar concentrations of THMs. The target stock solution was a 1 g/L solution of methanol containing 70% chloroform, and 10% each of dibromochloromethane, bromodichloromethane, and bromoform. Methanol resulted in good THM conservation when used to make a similar THM stock solution by Zwerneman (2012) and Cecchetti et al. (2013). Once the stock solution was created, the solution was divided into 40 mL, 20 mL, or 250 mL containers with the same size opening and cap. Duplicate samples were sent for analysis so the actual concentration could be determined.

For each experimental challenge, the amount of water needed was predicted prior to the challenge and a conservative amount of water was spiked with the THM stock solution. The desired THM concentration was 250 ug/L with 70% chloroform and 10% of each of the other three THM species. A detailed procedure for the stock solution preparation and source water preparation can be found in Appendix C. In order to make sure this method produced adequate mixing, 4 samples were taken from the influent port during one set of experimental runs. These influent samples showed only a 3% difference between influent samples, showing that the mixing method is viable. The chemical reagents used to create the stock solution may be found in Table 3.2.

Table 3.2 Chemical Reagents Used in Stock Solution

Chemical Reagents			
Reagent	Abbreviation	Vendor	Grade
Chloroform	$CHCl_3$	Sigma-Aldrich	HPLC ≥99.9%
Bromodichloromethane	$CHCl_2Br$	Acros Organics	98+%
Dibromochloromethane	$CHClBr_2$	Alfa Aesar	98%
Bromoform	$CHBr_3$	Acros Organics	99+%
Methanol	$MeOH$	EMD	HPLC

3.6 Sampling Procedure

THM samples were collected in 40 mL (total organic carbon) TOC vials provided by Eastern Analytical. Samples were taken from the reactor sampling port through Cole-Parmer PharMed tubing attached to the port. The tube was inserted into the bottom of the sample vial and the vial was filled so that the tip was below the water surface. This was done to eliminate extra air being added into the sample which could cause added THM volatilization. The sample vials were filled until they were overflowing and then allowed to sit until all air bubbles had exited the sample. If necessary, the vials were tapped gently to encourage trapped air bubbles to escape. The samples were capped and then overturned to make sure there were no air bubbles in the vial. Samples were stored in the refrigerator at 0-6 °C and then transported to Eastern Analytical, Inc. in a cooler with ice packs. The step by step THM sampling procedure may be referenced in Appendix C.

3.7 Analytical Methods

All THM samples were sent to Eastern Analytical, Inc. in Concord, NH where they were analyzed for THMs using EPA Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. Eastern Analytical, Inc. is accredited through the National Environmental Laboratory Accreditation Conference, and is accredited in all New England states. The minimum detection limit for THMs is 0.05 ug/L and as required by the method, standards were run along with the samples to make sure THM values were read ±20%. These standards are 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4.

3.8 Quality Assurance/Quality Control

THM samples were collected in vials containing sodium thiosulfate, which prevents any chlorine from reacting with organic matter to produce added THMs. For THM sampling, at least two influent samples were taken for each challenge. Duplicate samples were taken for each effluent sample. Temperature was measured with two separate thermometers at the beginning and end of each sampling event. Table 3.3 summarizes the parameters measured along with the methods used, minimum detection limit, sample size, storage container, preservation needed, and maximum holding time for the sample.

Table 3.3 Analytical Methods, Sample Volumes, Containers, Preservations, and Holding Time

Analyte	Method	MDL	Sample Size Required	Container Type	Preservation	Holding Time
Temperature	Handheld meter	.5 °C	50 mL	glass or plastic	none	Analyze immediately on site
THMs	EPA 524.2	.05 ug/L	40 mL	glass	Sodium Thiosulfate	14 days

Three flow meters (one digital) were used for this study. The reactor was filled to check for major leaks before each run, and the air compressor was checked to make sure it is working correctly before each run. Compressed air tanks were used for runs that required more air than the compressor could provide or if the compressor was not working correctly. The pressure was monitored throughout sampling, with a goal of keeping at 40±1 psi for each experiment. For the most part this was achieved and psi ranges were documented for each experiment.

A set of control experiments were run alongside of the THM experiments. This set consisted of a full factorial control experiment, using a flow of 4 gpm, length of 3/4 ft., diameter of 1.5 inches, psi of 40, A:W ratio of 20:1 or 0:1, and using a mixer vs. not using a mixer. The goal of this experiment was to show what baseline THM removals could be obtained when using no mixer and no air and to show whether the air and mixer were significant in THM removal. Table 3.4 shows the factor levels for the control experiment.

Table 3.4 Factor Levels for Control Experiment

A:W Ratio	Mixer
20:1	Yes
0:0	No

4 Results and Discussion

Chapter 4 first discusses the exploration of methods to increase air and water mixing intensity and therefore the operating conditions required to reach saturation values of TTHM removal. A numerical modeling approach for predicting both TTHM and THM species removal under various operating conditions was developed. The chapter concludes with statistical analysis of the variables using JMP®, and a case study for predicting TTHM removals from a local distribution system.

4.1 Factors Influencing Achievement of Saturation Conditions in HILDA

Saturation conditions can be achieved in HILDA by reaching a required mixing intensity and duration in an appropriate reactor. Various reactor configurations were tested including baseline air/water flow, a tubular piping array, and static in-line mixers. All raw data can be found in Appendix D.

4.1.1 Influence of Air and Water Flow Rates

Three experimental trials shown in Table 4.1 were performed to determine the THM removal when the A:W ratio and flow rate were changed in the 6-inch pipe without the addition of any mixing devices.

Table 4.1 THM removal data for changing air and water flow rates in 6 inch pipe, n=8 (40 psi, 20 °C, and with a THM speciation of 68% $CHCl_3$, 10% $CHCl_2Br$, 11% $CHClBr_2$, and 11% $CHBr_3$- 9.9.2014)

Sample #	Flow (gpm)	A:W Ratio	Influent (ug/L)	Effluent Average (ug/L)	% Removal Actual	% Removal Predicted
1	7.5	10	236	198	16%	26%
2	5	20	222	156	30% ± 1%	38%
3	5	30	229	127	45%	49%

These THM removals were compared to predicted THM removals in order to determine if equilibrium conditions had been met. Equilibrium is considered met when the actual THM removals reach predicted removals. Predicted removals were found using the temperature, pressure, and mass balance equations developed by Staudinger & Roberts (2000), Zwerneman (2012) and Matter-Müller et al. (1981), respectively. An explanation of how removals were predicted can be found in Appendix E. For this sample set, the influent THM concentration increased as sampling progressed, so the corresponding influent samples were used for samples 1 and 2, and the influent value used for the second sample taken (sample 3) was an average of the first and third influent samples. This increasing influent THM values occurred for several sample sets. The mixing method was performed the same way for all sample sets, but it is possible that influent sample concentrations could have been affected by the temperature of the water, the type of bottle the THM solution was stored in, or the wait time between mixing and starting the experiment. As seen in Appendix F, increases were generally linear, so this assumption was made to calculate influent values for all sampling events that had increasing influent values. Appendix F explains how influent sample values were calculated and shows which values were used for each sample.

These trials illustrate that mixing of the air and water is needed to achieve optimal THM removal since no trial was able to achieve its predicted equilibrium removal. However, the difference between actual and predicted removals decreased as the A:W ratio increased. This is likely due to the larger volume of air added for higher A:W ratios as well as the extra turbulence that more air provides. This is confirmed in ***Wastewater Engineering Treatment Disposal and Reuse***, which shows that air flows in confined reactor volumes can increase mixing intensity (Tchobanoglous et al, 2002). Depending on the THM removal needed for a given situation, just adding a sufficient amount of air could be a viable option. For the purposes of this research, it was desired to develop a system that could provide the most THM removal possible per a variety of A:W ratios, therefore several mixing designs were explored.

4.1.2 Influence of Air-Water Reactor Configurations

Tubular Piping Arrays

As shown in the methods, a PVC pipe array was used in order to try and force air into contact with more water. The pipe array was built with a 45° angle at the air inlet with the idea that air would travel up and distribute more evenly into different pipes. Four experiments were performed and the results can be found in Table 4.2. The flow rates varied between 1 and 7 gpm while the A:W ratio remained constant at 10:1.

Table 4.2 TTHM Removal data for pipe array without static inline mixers, n=12 (40 psi, 21 °C, and influent THM speciation of 71% $CHCl_3$, 10% $CHCl_2Br$, 10% $CHClBr_2$, and 9% $CHBr_3$ – 5.30.14)

Sample #	Flow (gpm)	A:W Ratio	Influent (ug/L)	Effluent Average (ug/L)	% Removal	% Removal Predicted
1	1	10	254	229.5	10%±1%	25%
2	2	10	267	219.5	18%	25%
3	4	10	267	213.5	20%±4%	25%
4	7	10	281	195.5	30%	25%

Results showed that as flow rate increased, so did the % removal. However, the only configuration that was able to achieve saturation conditions of TTHMs in the air was at 7 gpm. Another drawback of the PVC pipe array was that it visually appeared to have increased head loss due to increased pipe sidewall friction. The % removal at 7 gpm was larger than the predicted. This could have been due to the increasing influent THM values causing the influent value to be too high, or error occurring during sampling or sample analysis.

DeltaPak®

Another channeling design selected was Delta-Pak®. Delta-Pak® was chosen as a reactor because it is made out of a spirally-wound, thin walled PVC material (Delta Cooling Towers, Inc., 2015) which has much thinner walls than the PVC pipe array, hopefully allowing for less resistance than the PVC pipe array, and more air and water interaction. The Delta-Pak® was placed horizontally in the pipe, and five experimental trials were performed. Flow rates were either 5 gpm or 7 gpm and A:W ratios were 10:1, 20:1, or 30:1 and the length of the reactor was 2 ft. Table 4.3 shows the results of the Delta-Pak® trials and Figure 4.1 shows a graphical representation of the DeltaPak® removal data.

Table 4.3 TTHM Removal Data for Delta-Pak® Configuration, n=16 (40 psi, 20 °C, and influent THM speciation of 64% $CHCl_3$, 11% $CHCl_2Br$, 13% $CHClBr_2$, and 12% $CHBr_3$ – 8.20.14)

Sample #	Mixer (Y/N)	Flow (gpm)	A:W Ratio	Influent Average (ug/L)	Effluent Average (ug/L)	% Removal	% Removal Predicted
1	Y	5	10	285.5	245	14 %±1%	24%
2	Y	5	20	285.5	194	32%±1%	37%
3	Y	5	30	285.5	166	42%±1%	46%
4	Y	7.5	10	285.5	237.5	17%±3%	24%
5	Y	7.5	20	285.5	205	28%±1%	37%
6	N	5	10	285.5	242	15%	24%

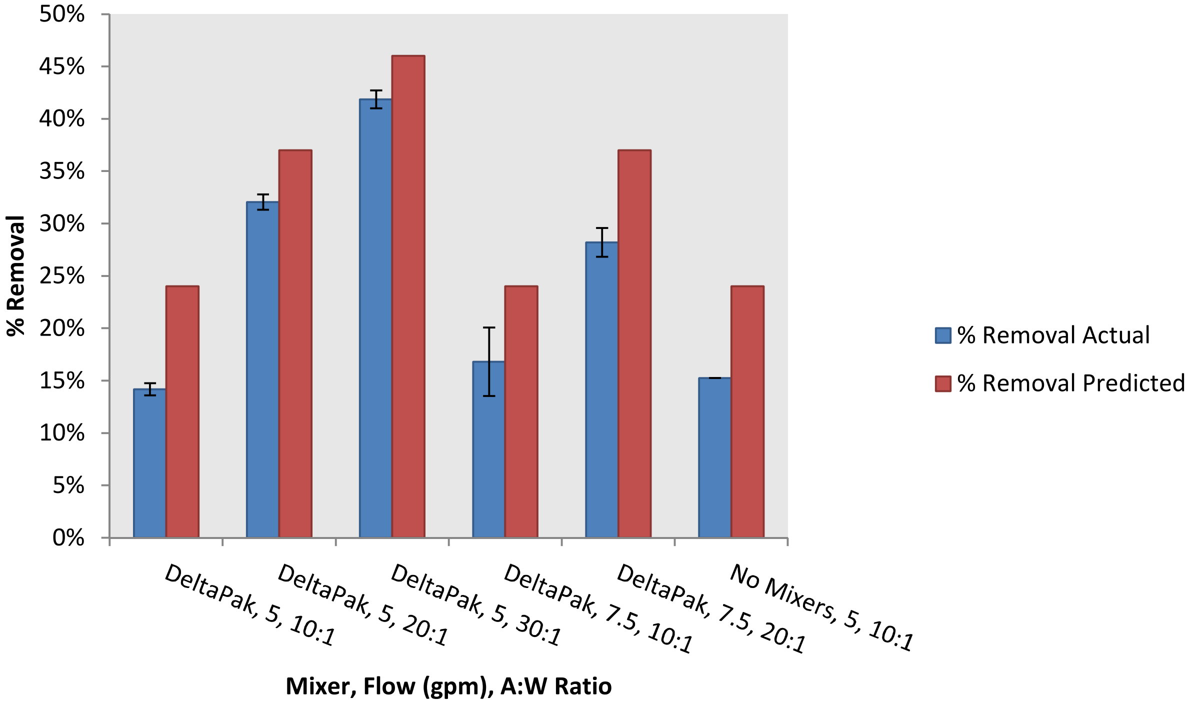


Figure 4.1 Experimental THM removals for Delta-Pak® reactor at various A:W ratios and comparison to use of no mixer

The data from the Delta-Pak® experiments show that typically, for 5 gpm, the difference between actual removal and predicted removal decreases as A:W ratio increases which was similar to the finding with no static mixers, again indicating that adding more air increases turbulence. The difference in removal for 10:1 was about 10%, 20:1 was about 5%, and for 30:1 was about 4%. When the flow rate is increased to 7.5 gpm, the difference in removal appears to increase from 7% at an A:W ratio of 10:1 to 9% at an A:W ratio of 20:1. However, factoring in the standard deviation of the 7.5 gpm runs leaves it uncertain as to whether the gap between actual and predicted THM removal increased or decreased. When comparing DeltaPak® vs. no mixers at 5 gpm at a 10:1 A:W ratio, it can be seen that there is no significant difference between the two. DeltaPak® has a removal of 14%±1% while no mixer has a removal of 15%, suggesting that the DeltaPak® mixer does not improve A:W interaction for this application and that the decrease in predicted and actual THM removal may be due to the amount of air added to the system. It should also be noted that the DeltaPak® is being used for a different situation than the packed tower media function it was designed for.

The pipe array and Delta-Pak® reactors were both considered tubular mixers. The idea was that the air and water would be forced into many tubes, therefore distributing the air along more of the water instead of the air travelling right to the top of the pipe. This, however, did not appear to be the case. The results indicate that even though the air was being separated into tubes, the air was moving to the top of each tube and not being mixed thoroughly enough to reach equilibrium removals. Apparently, as illustrated in Figure 4.2 with a comparison of % TTHM removal vs. the Reynolds number in the mixing reactor, more turbulence was needed along the length of the mixing system.

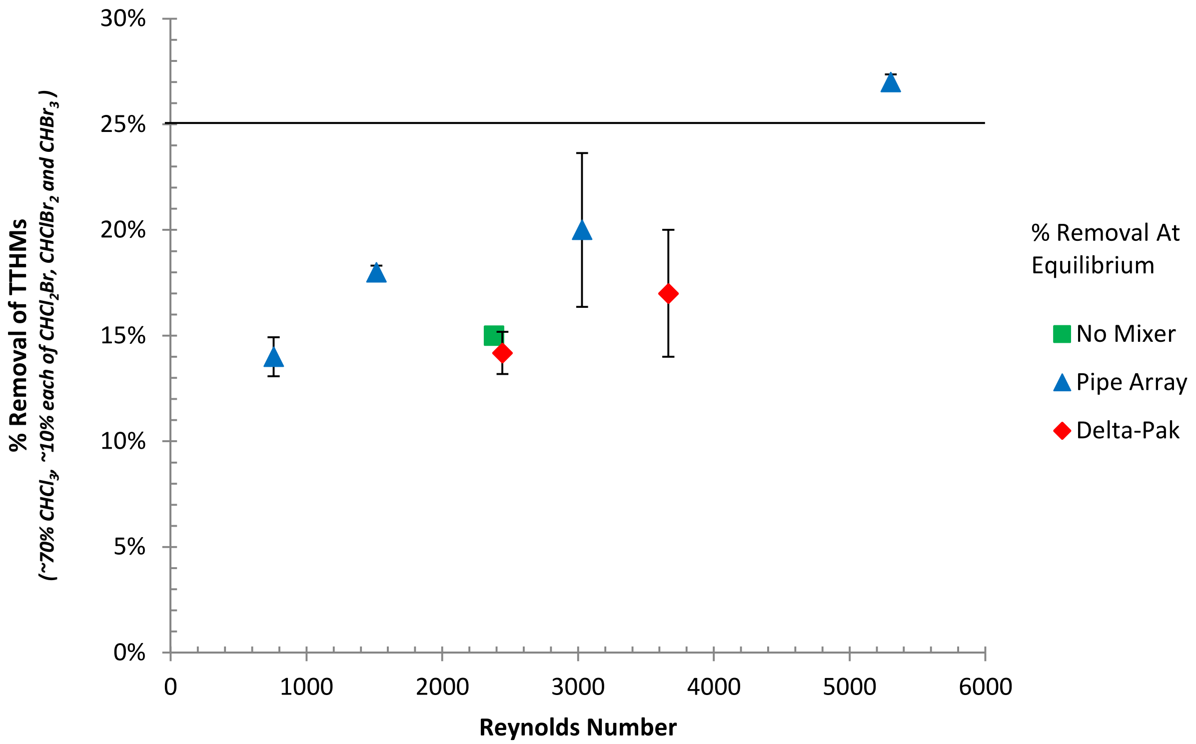


Figure 4.2 TTHM % Removal vs. Reynolds number at a 10:1 A:W ratio for no mixer, the pipe array, and DeltaPak® (Equilibrium at 25% is average of predicted removals for 10:1)

Reynolds number was calculated using the following equation:

$$Re = \frac{\mathrm{v} d_h}{v} \tag{4.2}$$

Where:

- v=velocity in pipe based on cross-sectional area (ft/s)
- d_h=hydraulic diameter (ft), which is equal to $\frac{4A}{p}$, where A= the cross-sectional area of the pipe (ft^2), and p= the wetted perimeter of the pipe (ft)
- v=kinematic viscosity ($\frac{\mathrm{ft}^2}{\mathrm{s}}$)

Reynolds numbers were calculated for the 6-inch pipe without mixers, with the pipe array, and with the Delta-Pak®. The cross-sectional area was corrected for each calculation depending on how much area of the 6-inch pipe was available depending on the reactor cross-sectional area. This means that for constant flow rates, the tubular pipe array would have the highest Reynolds number with only 40% of the total cross-sectional area available, Delta-Pak® would have the second highest with 92% available, and no mixer the lowest with 100% of the cross-sectional area available.

The depicted data shows that only one point, the tubular array at 7 gpm, was able to achieve equilibrium removals at a 10:1 A:W ratio, which was also the only point with a Reynolds number higher than 4000. This Reynolds number is often considered the number where flow in a pipe changes from transitional to turbulent (Çengel & Cimbala, 2010). Again, it appears that there is a correlation between increasing turbulence or Reynolds numbers and achieving equilibrium removals.

For this reason, additional methods of increasing turbulence, or Reynolds number, were explored. These methods could include decreasing pipe diameter, increasing the flow rate, increasing the temperature, or adding in-line mixers.

StaMixCo In-line Mixers

In order to see if saturation conditions could be achieved at all flow rates, StaMixCo static inline mixers were inserted in each smaller pipe along the 2 ft. length of the pipe array in order to promote maximum mixing. Visual observations showed that the air was having trouble entering the pipes, and that it was flowing around the reactor sides and to the top along the path of least resistance. Maximum removals were not achieved, but data still was collected in order to assess the mixer as summarized in Table 4.4. One influent and one effluent sample was taken for each setting.

Table 4.4 TTHM removal data for pipe array containing StaMixCo static mixers, n=8 (40 psi, 19 °C, and influent THM speciation of 71% $CHCl_3$, 10% $CHCl_2Br$, 10% $CHClBr_2$, and 9% $CHBr_3$- 5/15/14)

Sample #	Flow (gpm)	A:W Ratio	Influent (ug/L)	Effluent (ug/L)	% Removal	% Removal Predicted
1	4	10	225	202	10%	25%
2	2	10	238	202	15%	25%
3	1	10	225	213	5%	25%
4	0.5	10	238	226	5%	25%

The data shows a maximum of 15% removal at a 10:1 A:W ratio at a flow of 2 gpm. As the flow decreases, the % removal decreases to 5% at 1 gpm and 0.5 gpm, showing that the lower flow rates with less air entering into the piping system do not mix as well as higher flow rates with more air. It also confirmed the visual observation that air was not traveling through the pipes as desired and this is likely due to too much resistance from the in-line mixers placed inside of the small pipes.

Komax Static In-line Mixers

Since there was too much head loss associated with placing the static mixer inside the pipe array, another static inline mixer device was explored. Komax static in-line mixers were chosen as a method to increase turbulence in the air-water reactor. Turbulence was increased by using a mixer with a smaller cross-sectional area than the 6-inch diameter pipe, and by adding a static in-line mixer. A smaller surface area was suggested by Komax, Inc. (Kshirsagar, 2014), due to the relatively low flow rates that were being studied.

The mixer selected for testing was the 1.5-inch Komax CPS static in-line mixer. Preliminary visual observations showed the air entrained over the entire mixer length. An initial study was performed which varied air and water flow rates and length of the reactor. Table 4.5 shows the THM removal data for the initial Komax static in-line mixer experiments in the order of which they were taken. A graphical representation of the % TTHM removal vs. water flow for this initial data is shown in Figure 4.3.

Table 4.5 TTHM removal data for first Komax static in-line mixer challenge, n=26 (40 psi, 18 °C, and influent THM speciation of 70% $CHCl_3$, 10% $CHCl_2Br$, 11% $CHClBr_2$, and 9% $CHBr_3$ -10/1/14)

Sample #	Flow (gpm)	A:W Ratio	Length (ft)	Influent Average (ug/L)	Effluent Average (ug/L)	% Removal	% Removal Predicted
1	7	20	0.75	287	180	37% ± 4%	38%
2	7	10	0.75	287	225	21.7% ± 1%	24%
3	4	20	0.75	287	200	30.4%	38%
4	4	10	0.75	287	236	17.8% ± 1%	24%
5	1	20	0.75	287	222	22.7% ± 1%	38%
6	1	10	0.75	287	238	17.1% ± 4%	24%
7	7	10	3	287	229	20.5%	24%
8	4	20	3	287	184	35.3% ± 5%	38%
9	4	10	3	287	217	24.5% ± 1%	24%
10	1	20	3	287	201	30.0%	38%
11	1	10	3	287	231	19.8% ± 5%	24%

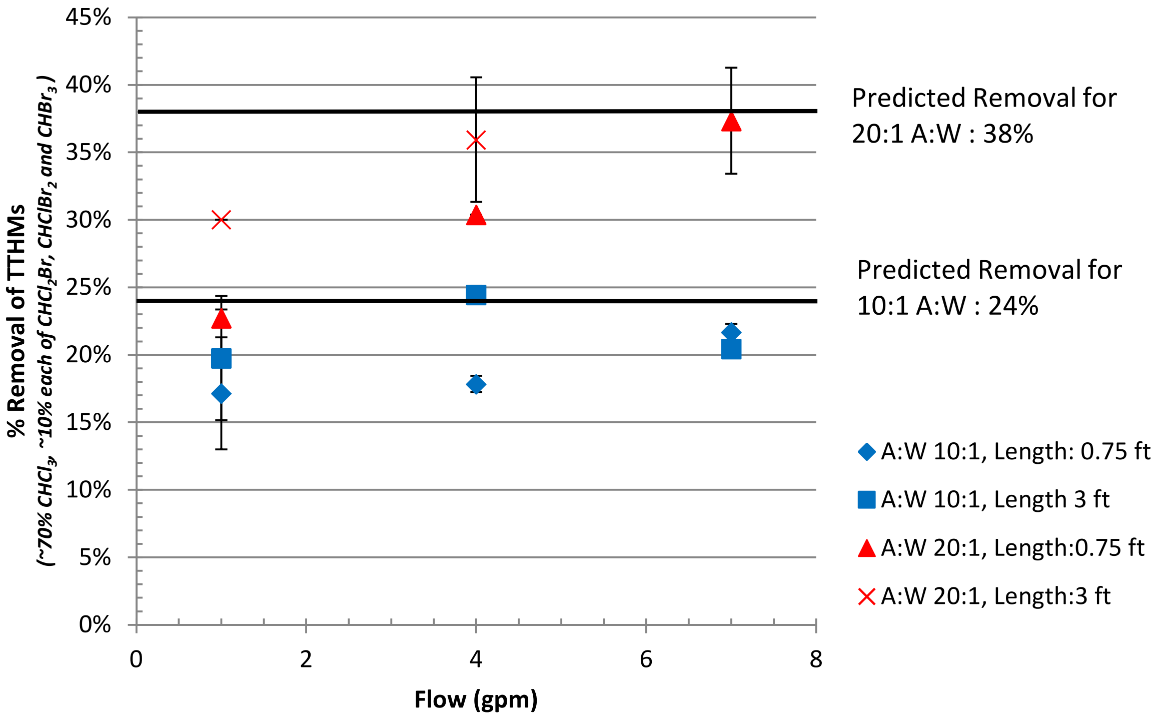


Figure 4.3 % TTHM Removal vs. Flow for Komax 1.5 inch static mixers at 10:1 and 20:1 A:W ratios, n=26 (saturation values based on average temperature and influent THM concentrations- 10.1.14)

In general, these initial results showed an upward removal trend as the flow increased. Removals also appeared to increase when length increased, except in the case of 10:1 at 7 gpm. The Komax mixers follow a trend of increasing removals with increasing flow rate, length, and A:W ratio, and also close removals to saturation conditions, except in the case of 7 gpm, for the 10:1 A:W ratio. Statistical assessment using JMP Pro 11 Software shown in Appendix G indicated that at a significance of 0.05, significant variables for this sampling event were flow and A:W ratio with p-values of 0.03 and 0.0005, respectively, while length was less significant at 0.1. While length was not found to be significant at a 0.05 significance level for this study, the p-value was still low and further study could better determine its impact. Overall, initial results were promising and the Komax mixers were chosen for additional evaluations.

4.2 Developing Air/Water Mixing Intensity Expressions

Before continuing experiments, it was desired to come up with a unifying expression that could be used to relate % THM removal to mixing or turbulence intensity. The initial Komax results indicated that both flow and length of the reactor were important in the % TTHM removal that could be achieved. Therefore, an expression including flow and reactor length could be used in order to predict the % THM removal for each A:W ratio. Four expressions were selected as potential candidates.

4.2.1 Ballestero Reynolds Number: Re’

- $Re' = \mathrm{v}\frac{\sqrt{d * L_m}}{\nu}$
    - v = velocity of water (ft/s)
    - d = pipe diameter (ft)
    - L_m = length of reactor (ft)
    - ν = kinematic viscosity (ft^2/s)

Re’ is a version of Reynolds number which was created to capture the magnitude of fluid momentum compared to resistance to flow. Figure 4.4 shows a graphical representation of % removal vs. Re’ at 10:1 and 20:1 A:W ratios. This unit appears to be a good description of when saturation values are achieved.

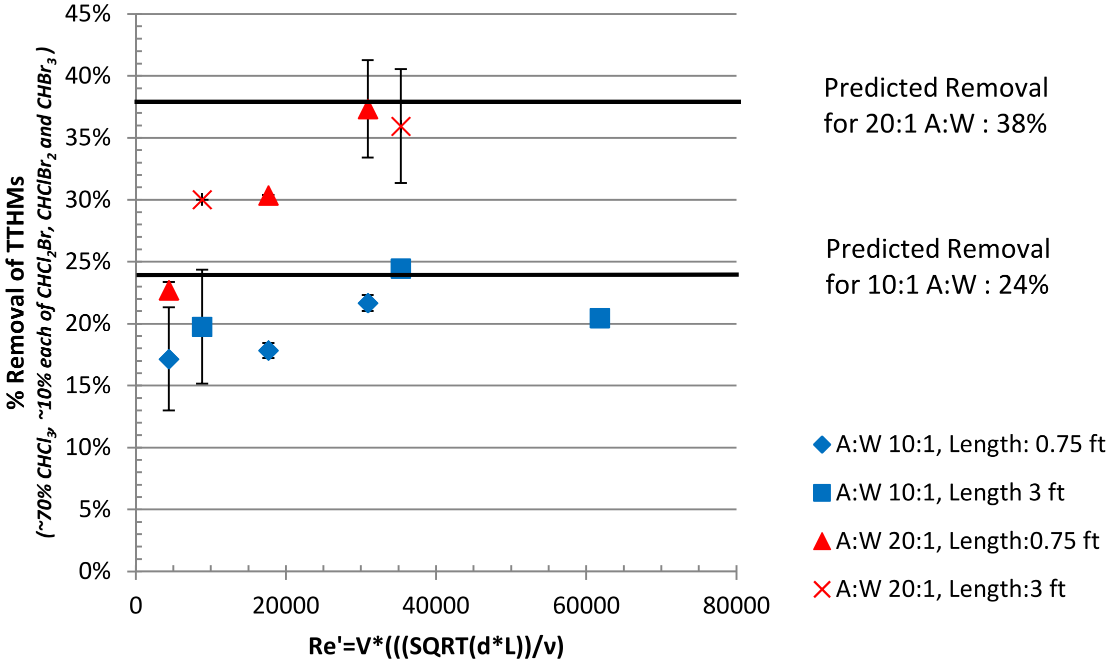


Figure 4.4 % TTHM Removal vs. Re’ for 10:1 A:W ratio using original data points, n=26 (saturation values based on average temperature and influent TTHM concentrations - 10.1.14)

4.2.2 Reynolds Number from Komax: Re_{komax}

- $Re_{Komax} = \frac{\frac{3157QS}{\mu d}}{L_{unit}} \cdot L_{total}$
    - Q = water flow (gpm)
    - S = specific gravity of fluid, in this case, water
    - μ = dynamic viscosity (cp)
    - d = inner diameter of reactor (in)
    - L_{unit} = length of one reactor unit (in)
    - L_{total} = total length of reactor units (in)

Re_{komax} takes the Reynolds number calculation provided by Komax and incorporates length into the unit. Figure 4.5 shows the relationship between Re_{komax} and Re'. It appears that Re_{komax} and Re' are the same method, while one incorporates area and the other does not. This explains the good correlation and the slope of 0.79 that is approximately $\frac{\pi}{4}$.

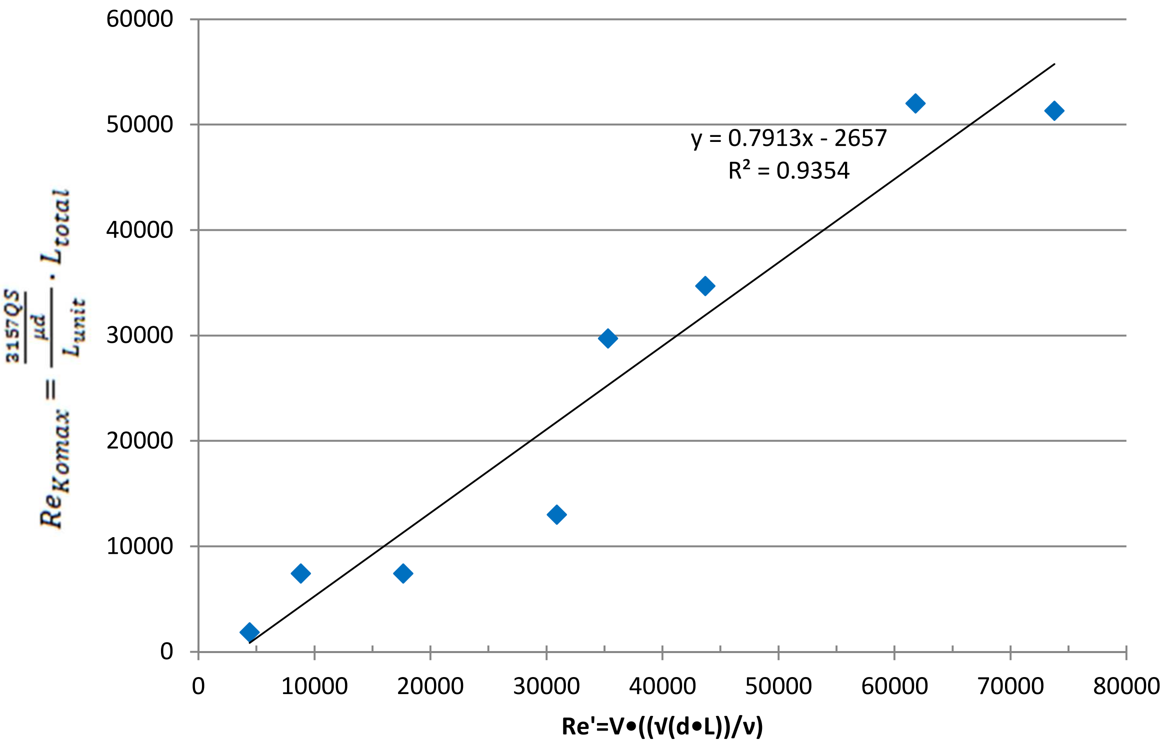


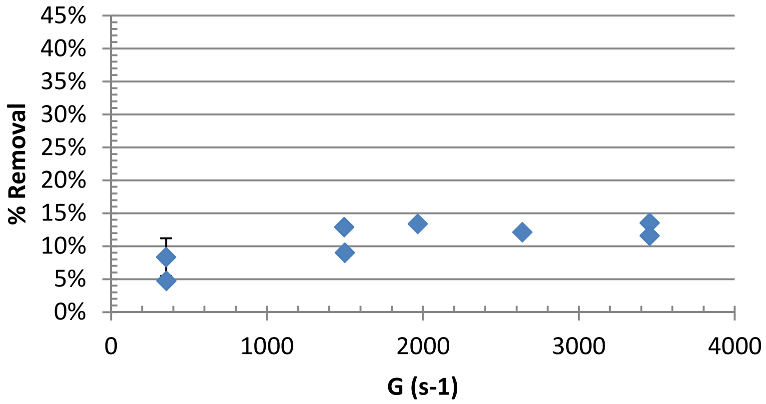
Figure 4.5 Relationship between Rkomax and Re' for 10:1 A:W Ratio Study

4.2.3 Mixing Intensity: G

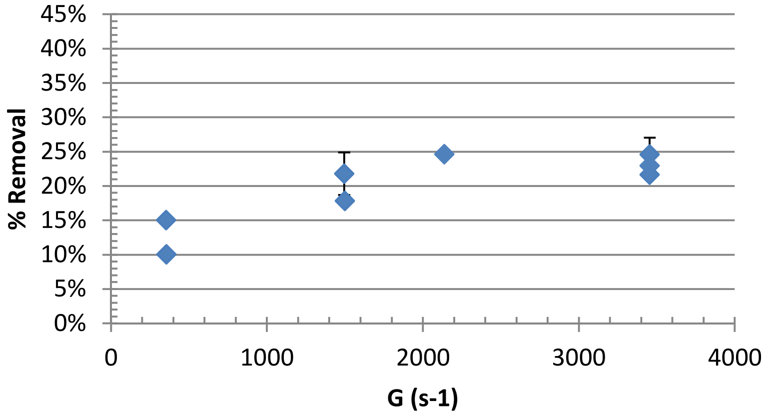
- $G = \sqrt{\frac{g\Delta H}{\nu\theta}}$ where
- G = mean velocity gradient (s^{-1})
- g = acceleration of gravity (ft/s^2)
- ΔH = headloss (ft)
- ν = kinematic viscosity (ft^2/s)
- θ = residence time of total mixer volume (s)

G is a unit of mixing commonly used in water treatment that uses the net power applied including head loss, viscosity and residence time to determine mixing intensity. There is some correlation between G and % removal of TTHMs as seen in figure 4.7, but there seemed to be stratification in % removals due to length. Therefore, Gθ was explored to see if adding the factor of length to G would increase correlation.

a.



b.



c.

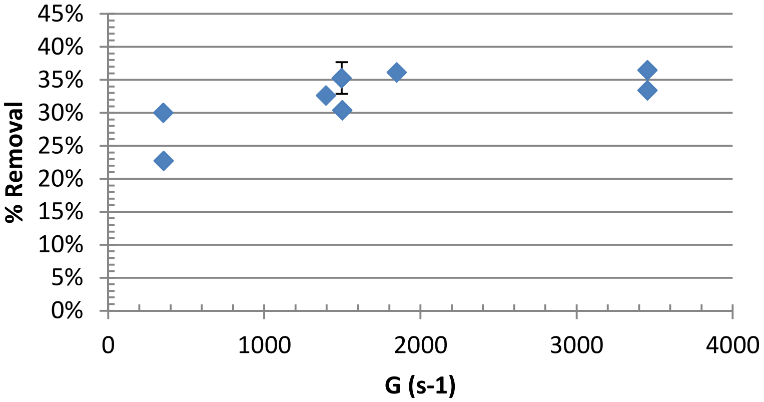


Figure 4.6 a) 5:1 TTHM % removal vs. G, b) 10:1 THM % removal vs. G, and c) 20:1 THM % removal vs. G

4.2.4 Mixing Intensity Times Residence Time: Gθ

Mixing intensity as expressed by G was combined with residence time in the reactor, θ, in order to assure reactor length was incorporated into the mixing expression. There was little correlation (data not shown) between Gθ and % removal, therefore Gθ was not evaluated further.

4.2.5 Relating Mixing Intensity to Head loss

The head loss, or pressure drop, of the system was plotted vs. Re' as shown in Figure 4.8.

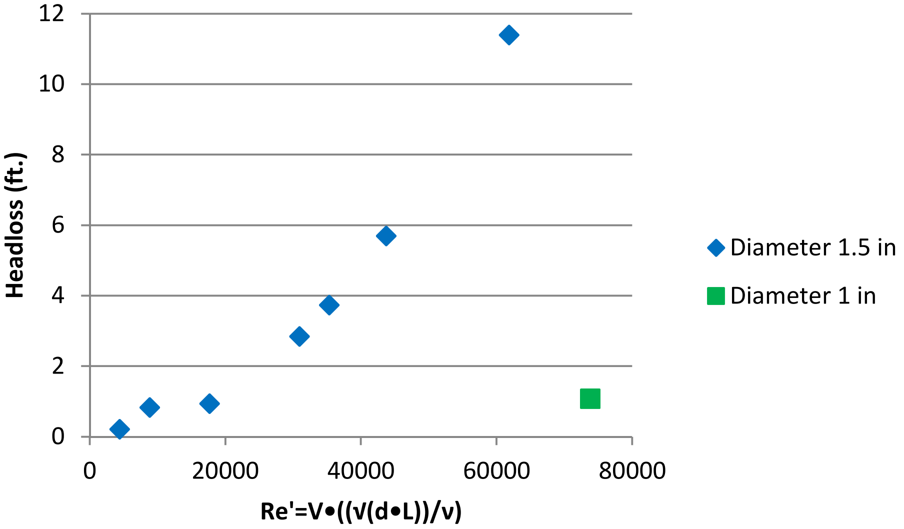


Figure 4.7 Relationship between head loss and Re' for 10:1 A:W ratio study

There is a strong relationship between head loss and Re', but this relationship is highly dependent on the diameter, or length, of the reactor. The head loss is smaller for the 1-inch diameter reactor at a higher Re' and this could be due to the fact that this reactor is 6 inches long, compared to the 1.5-inch diameter reactor which is 9 inches long. The 1-inch data point was a confirmation trial using a smaller diameter for the 10:1 A:W ratio study.

4.2.6 Mixing Intensity Expression Selection

As previously shown in Figure 4.4, Re' is a good measure of mixing intensity and can relate well to TTHM removal mixing conditions. A strong correlation ($R^2 = 0.94$) between R_{komax} and Re' indicates that Re_{komax} can also be an acceptable parameter to define % THM removals. Therefore, Re' will be used for further data analysis but with the acknowledgment that Re_{komax} can be used for similar data analysis.

4.3 Relating Mixing Intensity to Achieving Saturation THM Removal Conditions- A Model Development

Appendix H explains all the data taken and used for 5:1, 10:1, 20:1 A:W Ratios for Komax Static In-line Mixers along with the control experiment and 25 psi experiment.

.

4.3.1 Baseline Control Experiment

A full factorial control experiment was run in order to 1) make sure that mixers are enhancing removals for this system, and 2) to determine what baseline removals can be achieved when no air is added to the system.

When comparing removals with and without mixers at an A:W ratio of 20:1, it can be seen that no mixers is significantly lower with removals at 24.5% and 23.8%, vs. 33.6% and 33.9% with mixers at an A:W ratio of 20:1 at lengths of 0.75 ft. and 3 ft., respectively. This indicated that the mixers are needed to achieve equilibrium removals. Length did not seem to affect % removal in this case which could be due to the fact that the removals were approaching equilibrium for the 20:1 A:W ratio. If mixing intensity is already high, then increasing the length may not have much of an effect than at lower mixing intensities.

Removals of approximately 5% can still be achieved in the pipeline when no air is added either with or without the presence of a mixer as shown in Table 4.6 and Figure 4.9. This slight removal could be due to the fact that the pipe did not flow completely full, so some air and water interaction could still be occurring.

Table 4.6 All data points for full factorial control experiment, n=18 (40 psi, 18 °C, 4 gpm, and influent THM speciation of 69% CHCl3, 10% CHCl2Br, 12% CHClBr2, and 9% CHBr3- 10/27/2014)

Sample	A:W Ratio	Length (ft)	Mixer	Re'	% Removed	% Removed Predicted
1	0	3	Yes	35317	2.1% ± 2.7%	0%
2	20	3	Yes	35317	33.9%	38%
3	0	0.75	Yes	17659	5.12%	0%
4	20	0.75	Yes	17659	33.6%	38%
5	0	0.75	No	17659	5.1%	0%
6	20	0.75	No	17659	24.5%	38%
7	0	3	No	35317	6.1% ± 3.5%	0%
8	20	3	No	35317	23.8%	38%

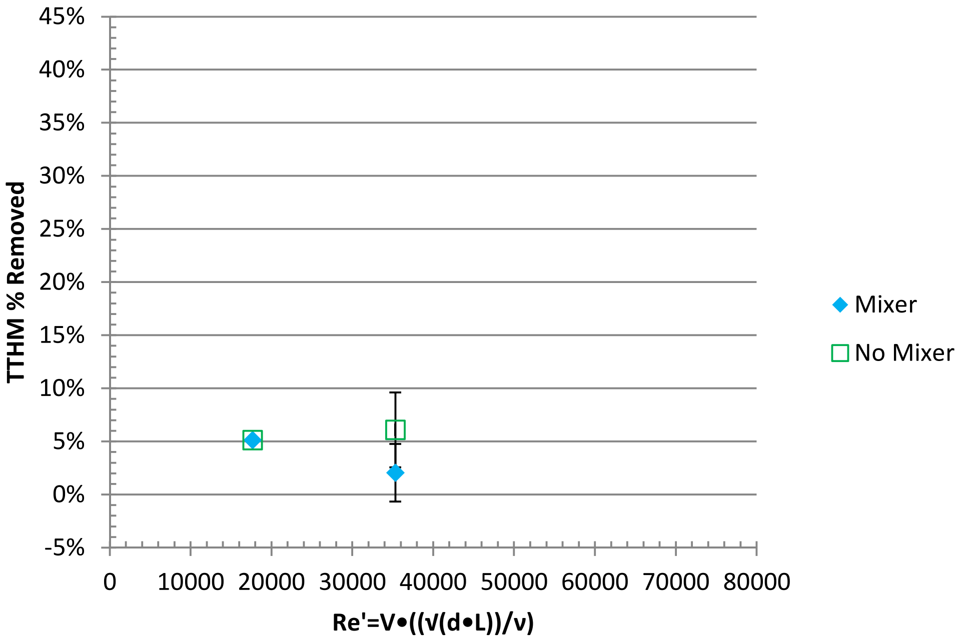


Figure 4.8 Baseline % Removals with No Air Added vs. Re', n=11 (10/27/14)

4.3.2 Relationship of Modified Reynolds Number (Re') to % THM Removals at Various A:W Ratios- Model Development

The TTHM removals for various A:W ratios as a function of Re' are shown in Figure 4.10. All experiments were conducted at approximately 40 psi and had influent values consistently close (±2%) to 70% $CHCl_3$, and 10% each of $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$. The saturation values were calculated using the method used by Zwerneman (2012) as explained in Appendix E. For each A:W ratio, a solid line indicates the predicted saturation % removal, while the shaded area represents the predicted removal within a removal zone of 5%. 5% was chosen because it was achieved in the control study when no air was added and also because this is where removals start to level off and approach saturation.

Overall, % THM removals were able to approach equilibrium or saturation levels after a specific duration and mixing intensity as defined by Re' was reached for each A:W ratio. The desired Re' levels can be reached by different combinations of water flow rate, reactor length, and water temperature. A:W ratio also appeared to be a significant factor in TTHM removals.

Since Re’ and R_{komax} were shown to be a reasonable estimates of mixing intensity and when equilibrium removals could be achieved, several confirmation trials were performed to see if equilibrium removals could also be achieved using different parameter settings that would still be above a minimal Re’ level required to approach steady state or saturation removals. The minimal Re’ level was chosen where data points were above the 5% zone, where saturation was approached or achieved. These new Re’ values were achieved by changing the water flow, mixer length, and mixer diameter. Two confirmation trials were run for each A:W ratio of 5:1, 10:1, and 20:1 and the data can be found in Appendix H.

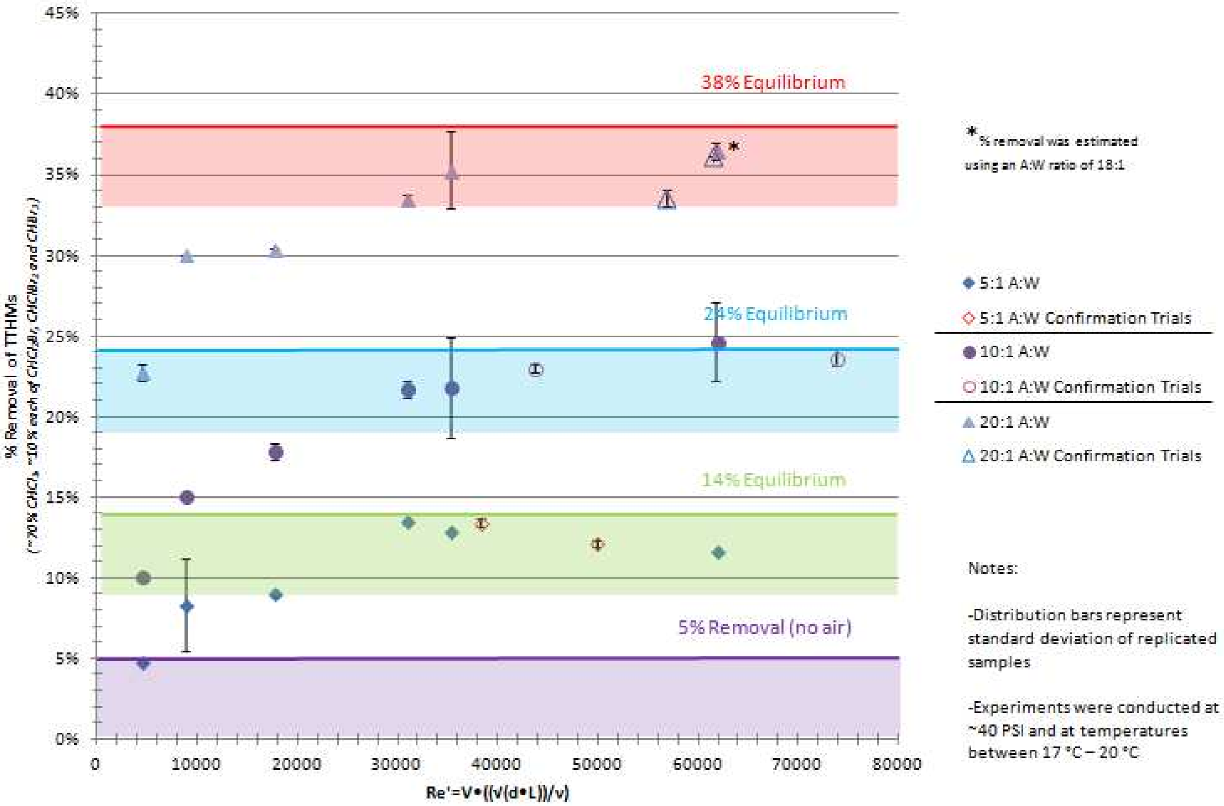


Figure 4.9 TTHM % Removal vs. Re’ including confirmation trials, n=48 (saturation values based on average temperature and influent concentrations of all Komax experimental trials)

Figure 4.10 shows that all confirmation trials for the 5:1 A:W ratio and 10:1 A:W ratios appear to fit well with the other data. Overall, the confirmation trials confirm that using Re’ is a consistent mixing intensity that can reasonably predict TTHM removal.

4.3.3 Development of a TTHM % Removal Model for HILDA System

The % TTHM removals at A:W ratios of 5:1, 10:1, and 20:1 all followed trend lines that resemble exponential curves with asymptotes such as a microbial growth curve or an oxygen sag curve. Therefore, it was desired to create a numerical model that could predict % removal based on Re' for each A:W ratio. JMP® Pro 11 was used to fit a model to the original data points. A 3P exponential model was used in the nonlinear modeling platform of JMP. The 3P model was chosen because the growth increases, and then flattens out into an asymptote using a 3 parameter model. (Jmp® Statistical Discovery™). Original output from JMP can be found in Appendix G, and Figure 4.11 shows the models for each A:W ratio.

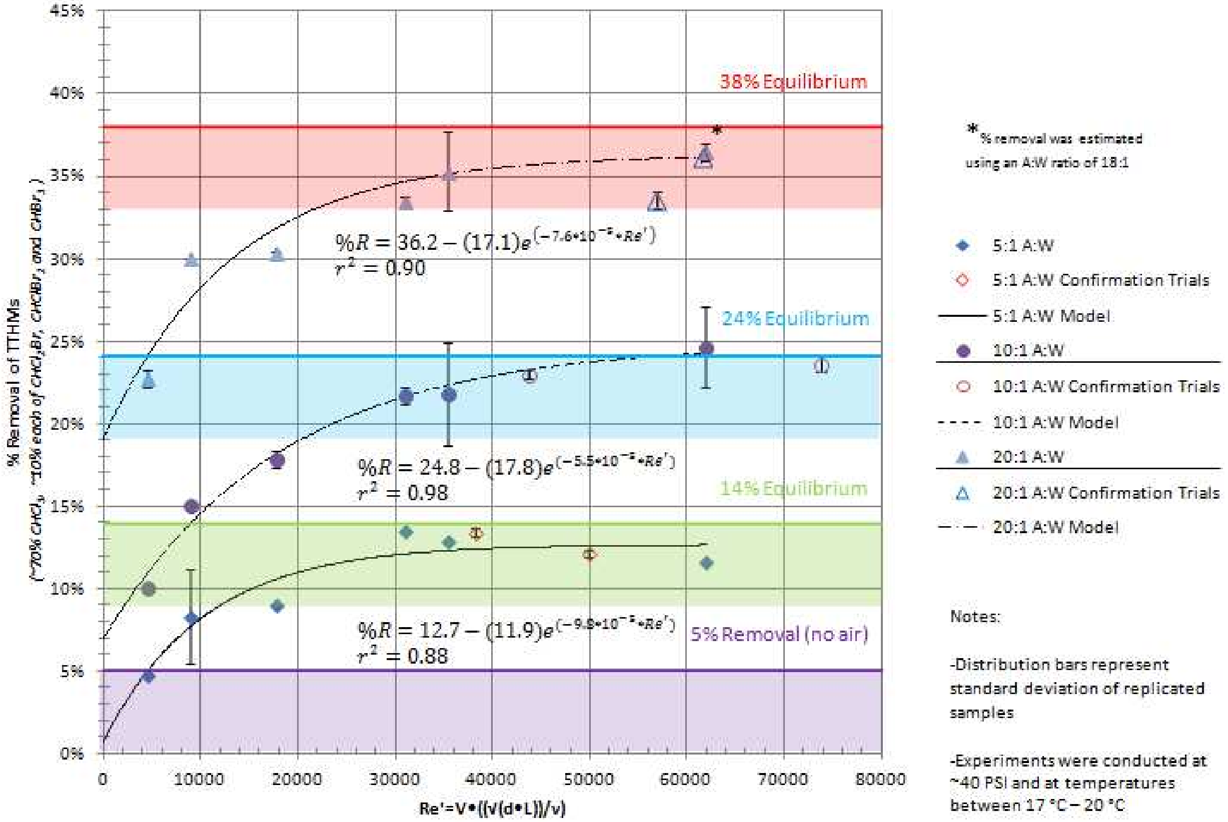


Figure 4.10 Numerical model for final 5:1, 10:1, and 20:1 data sets, excluding confirmation trials n=48 (saturation values based on average temperature and influent concentrations of all Komax experimental trials)

The generic form of the model, as seen in Equation 4.3, consists of three distinct components: asymptote, scale, and growth rate.

$$\%Removal = a + b \cdot e^{(c \cdot Re')} \tag{4.3}$$

where:

- a = asymptote
- b = scale
- c = growth rate

The resulting predictive TTHM removal models based on the Re’ mixing intensity expression for the various A:W ratios at approximately 40 psi can be found below.

$$\%\ Removal\ @\ 5:1 = 12.7 - (11.9)e^{(-9.8 \cdot 10^{-5} \cdot Re')} \tag{4.4}$$

$$\%\ Removal\ @\ 10:1 = 24.8 - (17.8)e^{(-5.5 \cdot 10^{-5} \cdot Re')} \tag{4.5}$$

$$\%\ Removal\ @\ 20:1 = 36.2 - (17.1)e^{(-7.6 \cdot 10^{-5} \cdot Re')} \tag{4.6}$$

Similar predictive models based on R_{Komax} at 40 psi were developed using the same method and are found below.

$$\%\ Removal\ @\ 5:1 = 12.7 - (11.3)e^{(-1.7 \cdot 10^{-4} \cdot R_{komax})} \tag{4.7}$$

$$\%\ Removal\ @\ 10:1 = 24.0 - (17.3)e^{(-1.3 \cdot 10^{-4} \cdot R_{komax})} \tag{4.8}$$

$$\%\ Removal\ @\ 20:1 = 36.3 - (17.7)e^{(-1.4 \cdot 10^{-4} \cdot R_{komax})} \tag{4.9}$$

When adding in the confirmation trials, the equations change slightly, but follow the same pattern. A summary of model components and r-squared values for the Re’ based equations can be found in Table 4.7, while similar values for Re_{komax} based equations can be found in Table 4.8.

Table 4.7 Summary of THM % Removal Model Components Using Re'

	Without Confirmation Trials				With Confirmation Trials			
A:W Ratio	a	b	c	R^2	a	b	c	R^2
5:1	12.7	-11.9	-0.000098	0.88	12.7	-12.2	-0.000099	0.89
10:1	24.8	-17.8	-0.000055	0.98	24.2	-17.7	0.0000614	0.98
20:1	36.2	-17.1	-0.000076	0.9	35.4	-17.7	-0.000095	0.89

Table 4.8 Summary of THM % Removal Model Components Using Re_{Komax}

	Without Confirmation Trials				With Confirmation Trials			
A:W Ratio	a	b	c	R^2	a	b	c	R^2
5:1	12.7	-11.3	-0.00017	0.87	12.8	-11.4	-0.00017	0.88
10:1	23.6	-17.3	-0.00013	0.93	23.6	-17.3	0.00013	0.94
20:1	36.3	-17.7	-0.00014	0.99	35.5	-17.3	-0.00016	0.96

In all cases, the predictive mixing intensity models did a good job of predicting THM removals including in the region where saturation or equilibrium removals were achieved. The model asymptotes were all within 2 % of saturation removals predicted using the Zwerneman (2012) method for each A:W ratio at a pressure of 40 psi. Adding the confirmation results to the model did not significantly change the model parameters therefore providing additional confidence to the validity of the developed models.

The model can be used to predict the minimum needed Re' to reach saturation values within 5% for each A:W ratio, and the relationship is shown in Figure 4.12. It is apparent that lower values of Re' are needed for lower A:W ratios, likely because the saturation value is lower, so saturation can be achieved more quickly. The difference in the required Re' is much smaller between 10:1 and 20:1 A:W ratios vs. 5:1 and 10:1 A:W ratios, and the trend seen in Figure 4.12 indicates that as A:W ratio increases, the Re' needed will level off at one value.

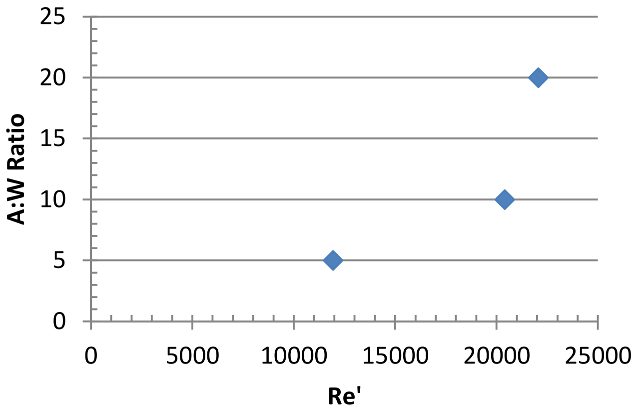
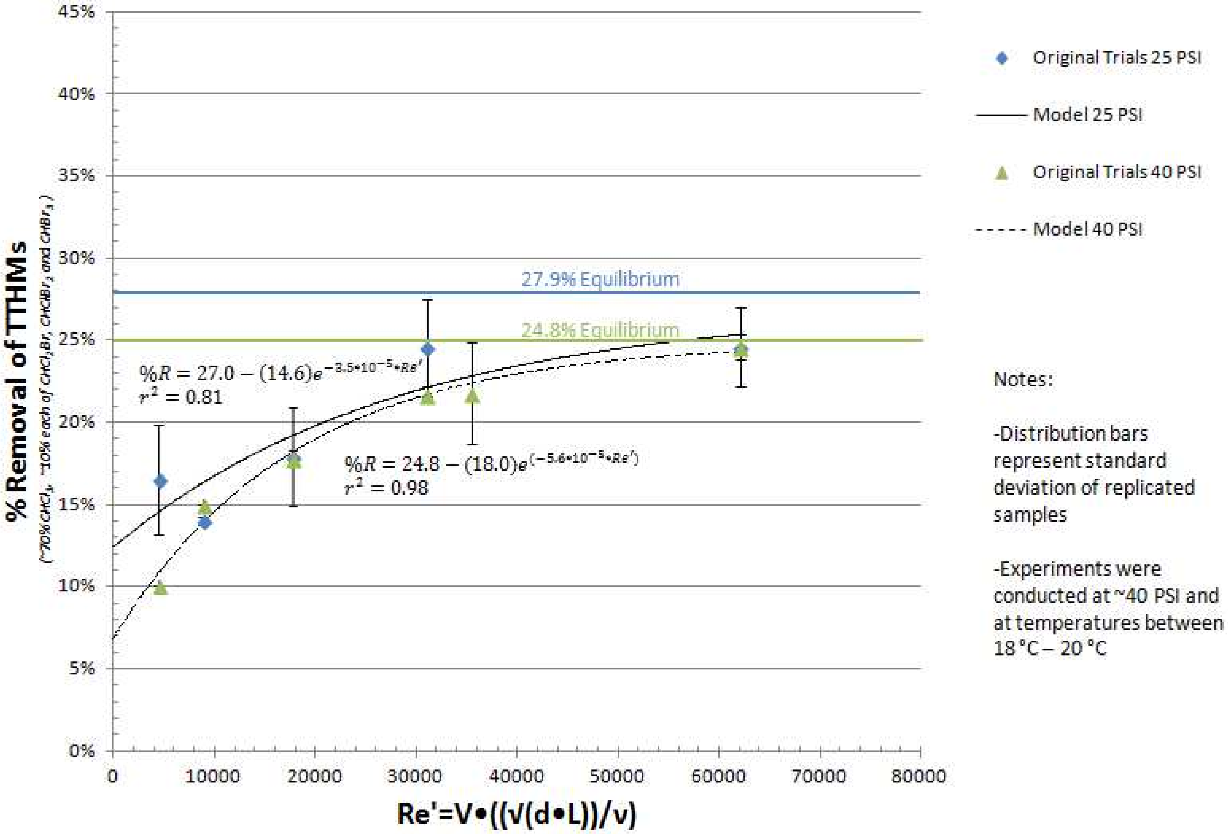


Figure 4.11 A:W ratio vs. minimum needed Re' to achieve saturation values within 5%

4.4 Assessing the Influence of Pressure on Model Predictions

Once the model was created, it was desired to test what impact pressure had on the model and if it would affect any or all of the three model components. Five additional experimental trials were completed but at a pressure of 25 psi instead of 40 psi. The raw data can be found in Appendix H, while the resulting model results at 25 psi plus the previous runs at 40 psi for an A:W ratio of 10:1 are shown in Figure 4.13.

Again, TTHM influent concentration increased for this set of experiments, so either initial or averages between reading influent samples were used to calculate the % removal for each data point.



Notes:

-Distribution bars represent standard deviation of replicated samples

-Experiments were conducted at ~40 PSI and at temperatures between 18 °C – 20 °C

Figure 4.12 Models for 10:1 A:W data at 40 psi and 25 psi n=36 (saturation values calculated from speciation and temperature values associated with each set of data points)

Figure 4.13 shows that, in general, the predictive model at 25 psi increases with the same trend as previously observed at 40 psi with a difference of about 1%-5%. Due to the standard deviation of the lowest Re' 25 PSI point, it is hard to determine if the trend is more or less similar to the 40 PSI trend, however it is assumed that the trend is closer, due to the fact that the high removal replicate for that sample is drastically higher than all other samples taken at that Re'. The asymptote value is slightly higher at 26.3% at 25 psi vs. 24.8% at 40 psi which makes sense because, according to the work of Zwerneman (2012), decreasing pressure would increase the amount of THMs that can be removed at saturation conditions.

4.5 Head Loss Development Using Static In-line Mixers

Head loss is an important consideration when selecting the best mixing configuration. The longer the mixing length, the greater the water flow, and the more air added, the greater the head loss. For Komax static inline mixers, a graph provided by the company as seen in Appendix I can be used to estimate head loss. Some values of head loss for this study were found on the Komax company website (Komax Systems, Inc. Static CPS Mixer) and provided by a company representative (Kshirsagar, 2014) and were used to create calibration curves found in Figure 4.14 for both the 1-inch and 1.5-inch diameter static mixers. For multiple mixing units, the head loss per flow rate found in the figure should be multiplied by the number of units (Kshirsagar, S., 2014).

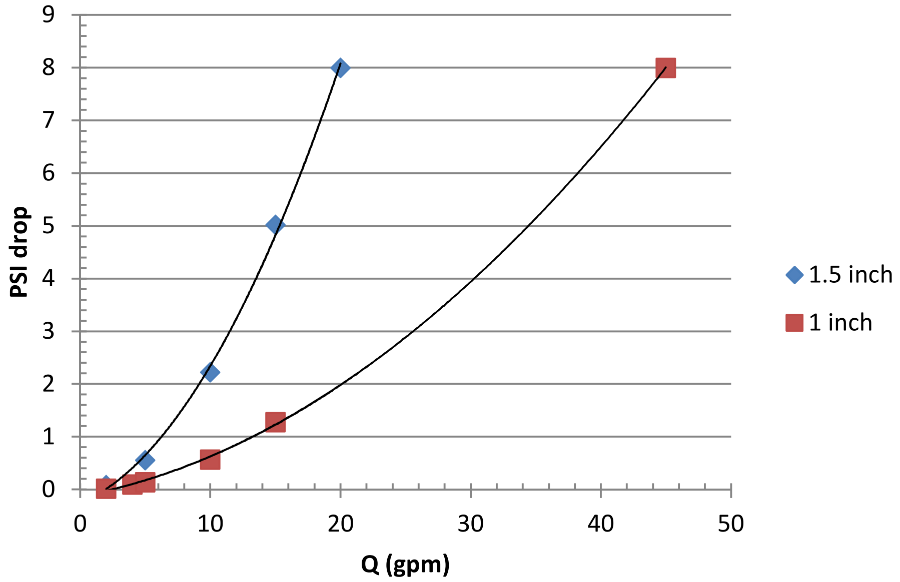


Figure 4.13 Head loss calibration curves for 1.5 inch and 1 inch Komax Static In-line Mixer units as a function of water flow rates

4.6 Statistical Assessment of Mixing and Operational Variables on THM Removal by HILDA

4.6.1 Significant Factors

Statistical analysis was performed using the statistical software JMP® Pro 11. JMP® analysis of the data was performed by plotting the studentized residuals of the points used for final analysis for TTHM removals. These residuals follow a relatively normal distribution as demonstrated in Figure G.2 (Appendix G).

The factor levels as shown in Table 3.1 in the methods and materials were flows of 1, 4, and 7 gpm, A:W ratios of 5:1, 10:1, and 20:1, and lengths of ¾ ft. and 3 ft. Analysis of variance using the fit model platform in JMP® indicated that there are significant factors in this experiment. All data points, excluding confirmation trials, were used to analyze significant variables. Significant variables include flow, A:W, and length. Table 4.9 shows the percent contribution of each variable. A:W ratio had the most influence, with 80.96% contribution, flow had the second most influence with 12.7% contribution, and length had the third most with 3.34% contribution. Error was only 3% for this analysis. Since the % contribution was so small for the interaction variables, they were pooled with the error. The results of this study indicate that all important variables were included, that these variables were controlled well, and that the study has an acceptable amount of analytical error (Ross, 1988). Also, the influence of pressure was investigated for just the 10:1 A:W ratio and the results are shown in Table 4.10.

Table 4.9 ANOVA and percent contribution of experimental factors for final data points at 5:1, 10:1, and 20:1 A:W ratios n=48

Source	Degrees of Freedom	F Ratio	Probability >F	% Contribution
Flow	2	36.96	0.0003	12.7%
A:W	2	230.18	<.0001	81.0%
Length	1	19.88	0.0012	3.3%
Flow x Air	4*	NA	0.1506	
Flow x Length	2*	NA	0.0508	
Air x Length	2*	NA	0.0829	
Pooled Error	12	NA	NA	3.00%

*Degrees of freedom are part of the pooled error

Table 4.10 ANOVA and percent contribution of experimental factors for 25 and 40 psi runs at 10:1 A:W ratio n=36

Source	Degrees of Freedom	F Ratio	Probability >F	% Contribution
Flow	2	497.9	0.0003	87.9%
Length	1	38.467	0.0153	3.3%
Pressure	1*	NA	0.4067	
Flow*Pressure	2*	NA	0.074	
Length*Pressure	1	41.36	0.0138	3.6%
Error	4	NA	NA	5.2%

*Degrees of freedom are part of the pooled error

When including pressure, significant variables were flow, length, and the interaction between length and pressure. Because this interaction is significant, pressure is also significant. However, most of the % contribution comes from flow. This study indicates that for the most part, the difference between 25 psi and 40 psi at a 10:1 A:W ratio does not contribute much to % removals. Therefore, the model could still be viable for small changes in pressure, but more study is needed to look at larger differences and higher pressures which are commonly found in distribution systems.

4.7 Influence of THM Speciation on Overall Removals by HILDA

Since the amount of a THM that can be removed depends on the THM speciation, trends for each THM species were also developed for various A:W ratios vs. mixing intensity. THM species removals for various mixing intensities (Re’) for A:W ratios of 5:1, 10:1, and 20:1, all conducted at approximately 40 psi, are shown in Figures 4.15, 4.16, and 4.17, respectively.

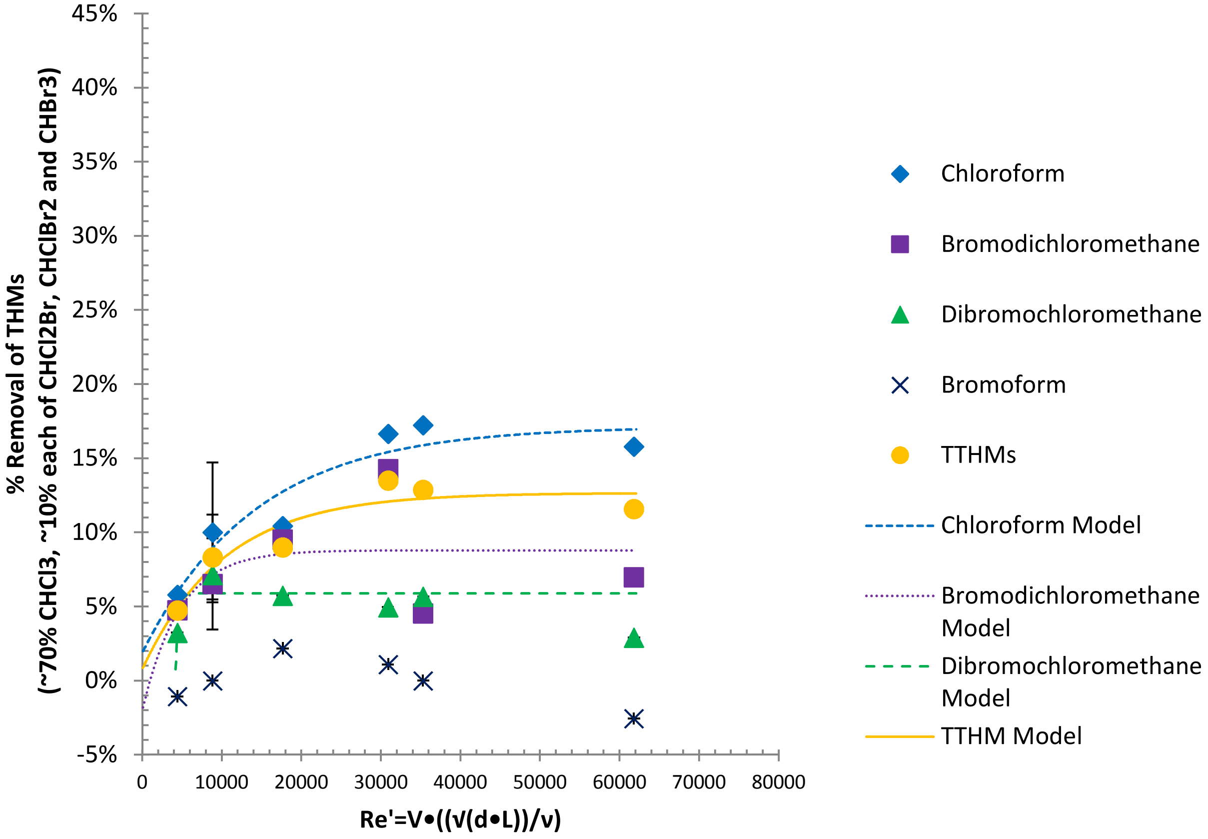


Figure 4.14 Final 5:1 A:W ratio THM removals vs. Re’ for each species and TTHMs, n=15 (final data points used)

For an A:W ratio of 5:1, bromoform and dibromochloromethane appeared to have relatively constant removals at approximately 0% and 5% respectively compared to their predicted removals of 4% and 6% respectively. Apparently, dibromochloromethane is meeting equilibrium removals at each Re’, while bromoform is not being removed at this low A:W ratio. Bromodichloromethane removals varied, while chloroform and TTHM removals appear to increase, and then level off, or decrease slightly, at and Re’ of 35,000. Variation from expected removals from this experiment could be due to the changing influent values, however a trend exists.

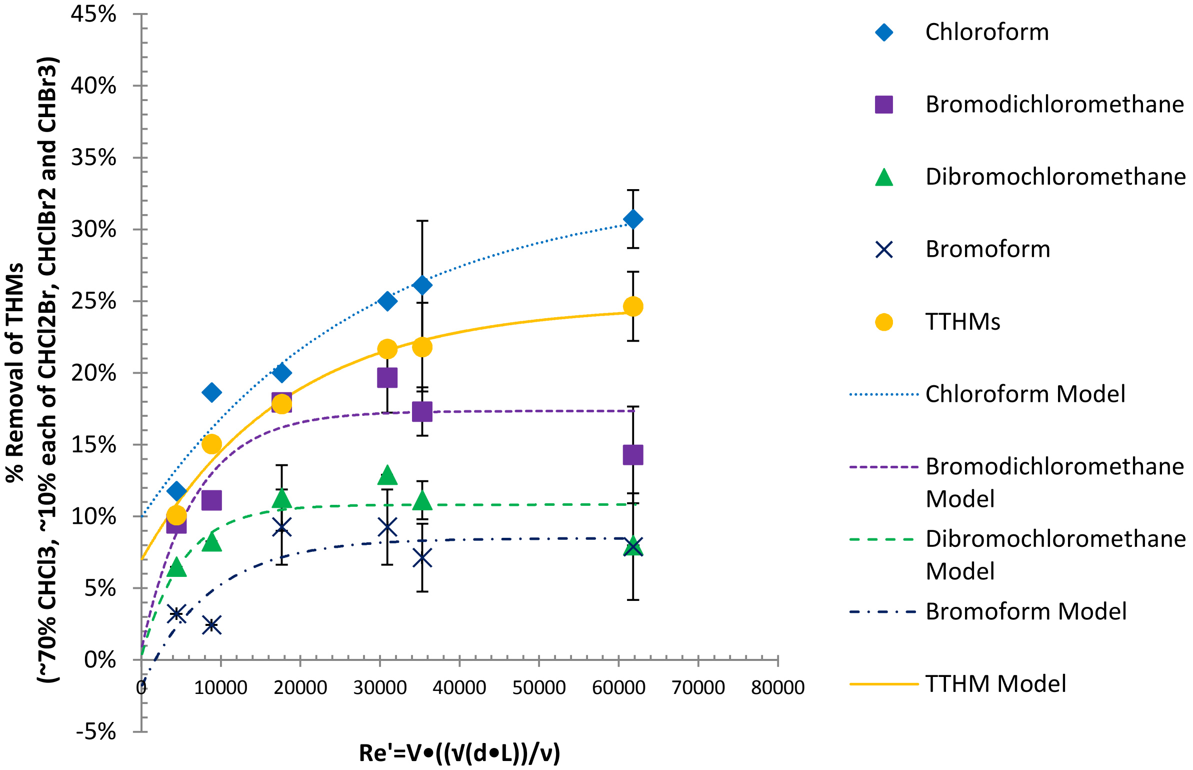


Figure 4.15 Final 10:1 A:W ratio THM removals vs. Re' for each species and TTHMs, n=24 (final data points used)

For an A:W ratio of 10:1, the data shows an increasing trend for total THMs that reach equilibrium removals. This trend visually looks to represent an exponential growth curve that levels off at a saturation value of 25%. Keeping the standard deviation for each data point into account, each THM appears to increase until it reaches its predicted equilibrium value which is 7% for bromoform, 11% for dibromochloromethane, 18% for bromodichloromethane, and 30% for chloroform.

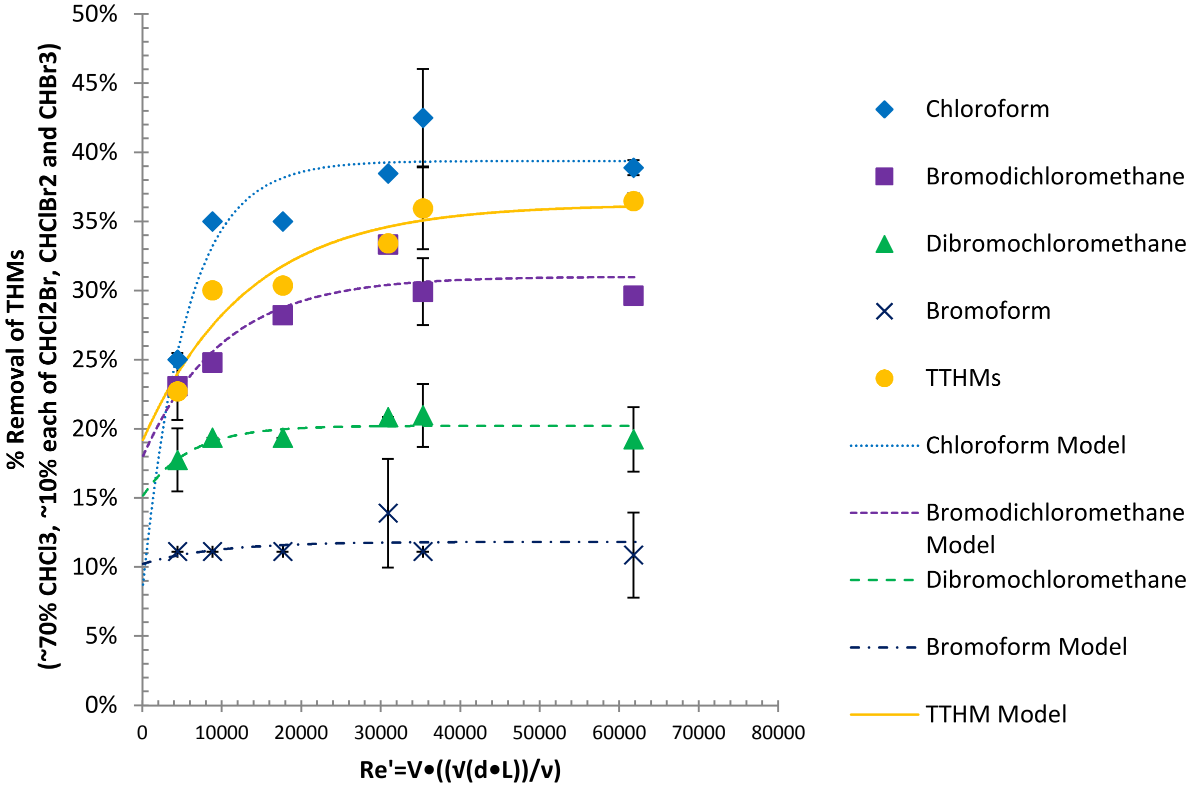


Figure 4.16 Final 20:1 A:W ratio THM removals vs. Re' for each species and TTHMs, n=19 (final data points used)

For an A:W ratio of 20:1, removals followed an exponential type growth for the TTHMs that flatten out at a saturation value at about 37%. Removals for bromoform and dibromochloromethane stay relatively constant at about 11% and 20% respectively, while bromodichloromethane and chloroform follow the same trend as the TTHMs, flattening out at around 30% and 40%, respectively. The predicted removal for bromoform is 13% and dibromochloromethane is 20%. The data indicates that at each Re' number, bromoform and dibromochloromethane removals are saturated across the board, and that it is the bromodichloromethane and chloroform removals that increase as Re' increases.

Since each THM species is removed in different amounts, it makes sense to model the removal of each THM separately. This way, as long as temperature and pressure are relatively similar to that of the current study, then the % removal of TTHMs can still be predicted even if the speciation is different. The model for each THM follows the same pattern as in Equation 4.2. Models were created using the same 3P model in JMP. All six final removal data points were used for each THM except for the case of the 5:1 A:W ratio where the last data point needed to be omitted for dibromochloromethane in order to keep the exponential model from decaying instead of growing. The 5:1 model for Bromoform was not made because removal did not appear to occur. Values for a, b, c, and the R^2 value can be found in Table 4.11.

Table 4.11 Model values for each THM species at each A:W ratio (model created using final % removal values)

A:W Ratio	THM Species	a	b	c	R^2
5:1	Chloroform	17.13755	-0.152514	-0.00007069	0.89
	Bromodichloromethane	8.78696	-0.108183	-0.000214	0.21
	Dibromochloromethane	5.875	-19380.29	-0.003059	0.69
	Bromoform	NA	NA	NA	NA
10:1	Chloroform	32.94139	-0.22999	-0.00003563	0.96
	Bromodichloromethane	17.34657	-0.166339	-0.000152	0.72
	Dibromochloromethane	10.8188	-0.105952	-0.000193	0.55
	Bromoform	8.47658	-0.103522	-0.000117	0.70
20:1	Chloroform	39.36934	-0.311954	-0.000184	0.86
	Bromodichloromethane	31.00443	-0.130864	-0.0001	0.83
	Dibromochloromethane	20.21489	-0.051218	-0.000171	0.66
	Bromoform	11.82396	-0.016018	-0.000108	0.11

4.8 Final Removal Models

Since removal models were found to have similar % removals to those predicted using John Zwerneman's method, it was desired to take all the data, including confirmation trials, and develop final removal models utilizing predictions and all removal data. The final model can be tied back to fundamental factors and principles of Two-Film Theory and Henry's Law. According to Two-Film theory, THMs move from the water into the air (gas phase), which contains no THMs, due to the concentration gradient. Henry's Law describes the extent of the diffusion, and larger ratios of air will result in more THM removal because there will be more opportunities for diffusion to occur.

Factors influencing the asymptote value ("a") in the model include temperature and pressure, which both affect Henry's Law Constant, along with A:W ratio which can be used in a mass balance to predict removals. The scale and growth factors are influenced by the interaction of air and water. The scale factor ("b") is likely influenced by the A:W ratio as this point determines where the model begins. The growth rate factor ("c") determines how fast the model reaches equilibrium. Influences on this parameter could include the mass transfer rate, which is affected by the concentration gradient and mass transfer coefficient. Bubble size would also likely influence this parameter, because smaller bubbles would produce a better surface area to volume ratio, and increase mass transfer (MWH, 2005).

For TTHM removal, this final model can be found in Figure 4.17. Models for THM speciation can be found in Figures 4.18, 4.19, and 4.20. These models were made using the asymptote prediction developed by John Zwerneman for "a", the asymptote, and values determined in JMP® for "b", the scale, and "c", the growth rate. Table 4.12 summarizes a, b, and c for the speciation models.

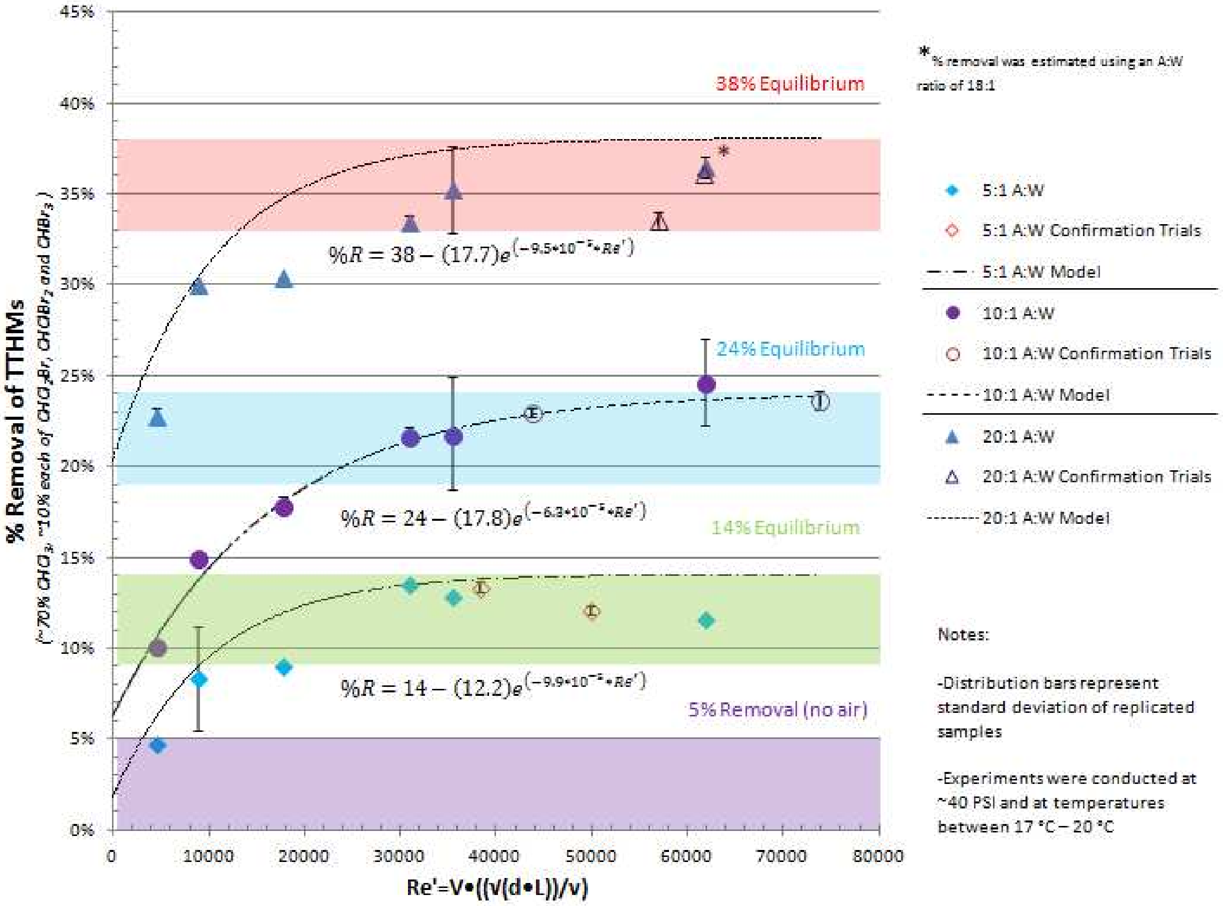


Figure 4.17 Final TTHM removal model for 5:1, 10:1, and 20:1 A:W ratios including all data points and predicted asymptote values

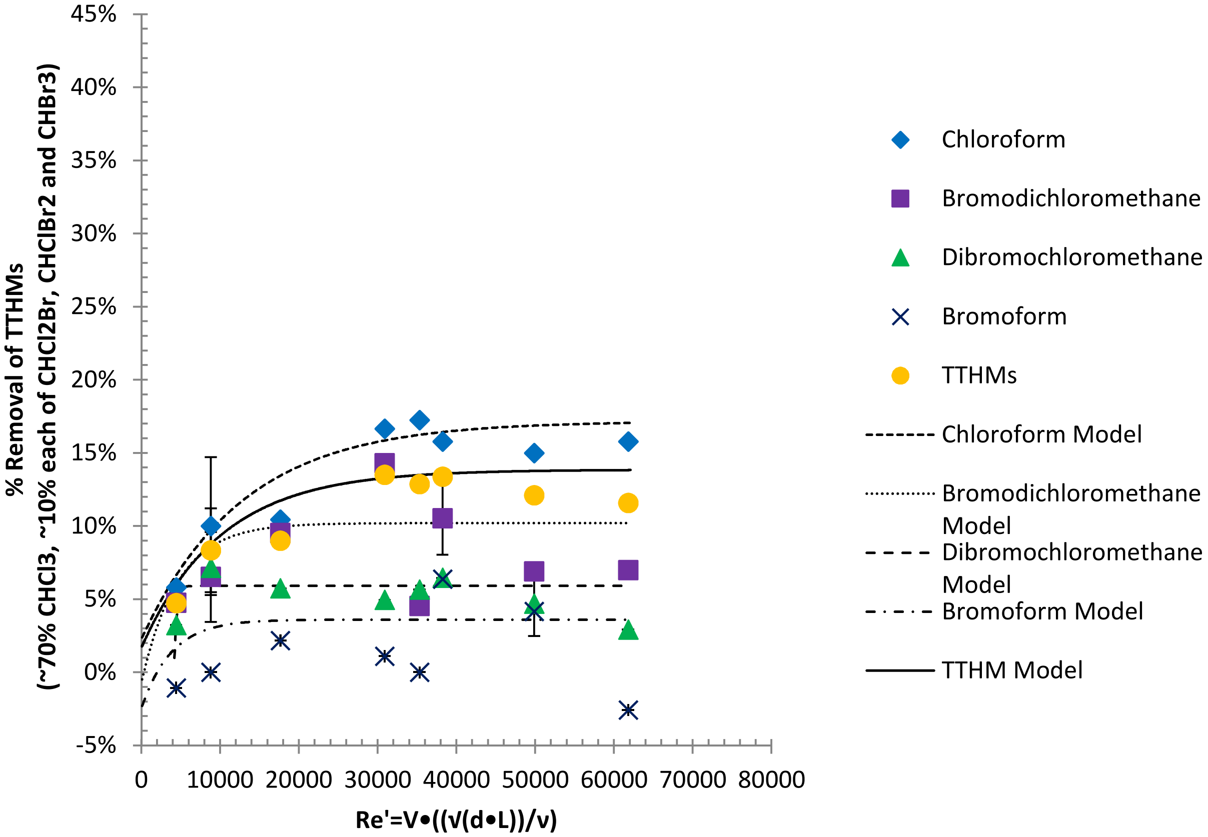


Figure 4.18 Final removal model for 5:1 A:W ratio including all data points and predicted asymptote value

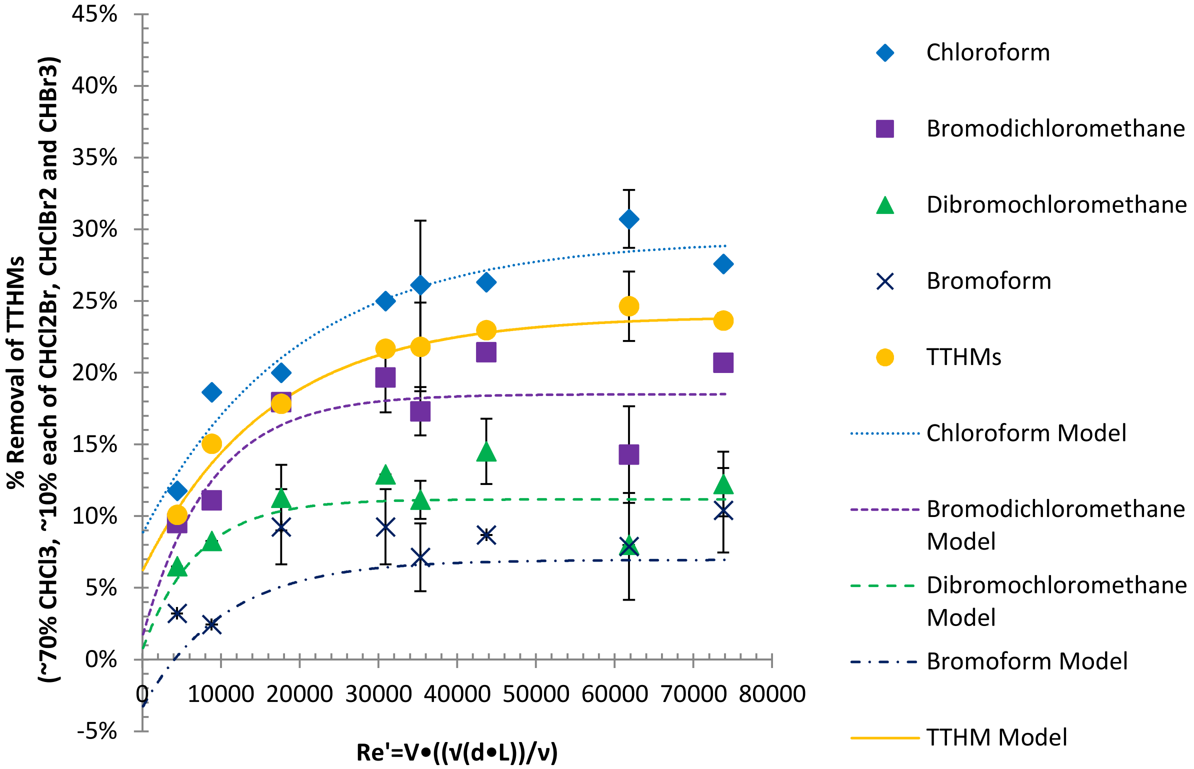


Figure 4.19 Final removal model for 10:1 A:W ratio including all data points and predicted asymptote value

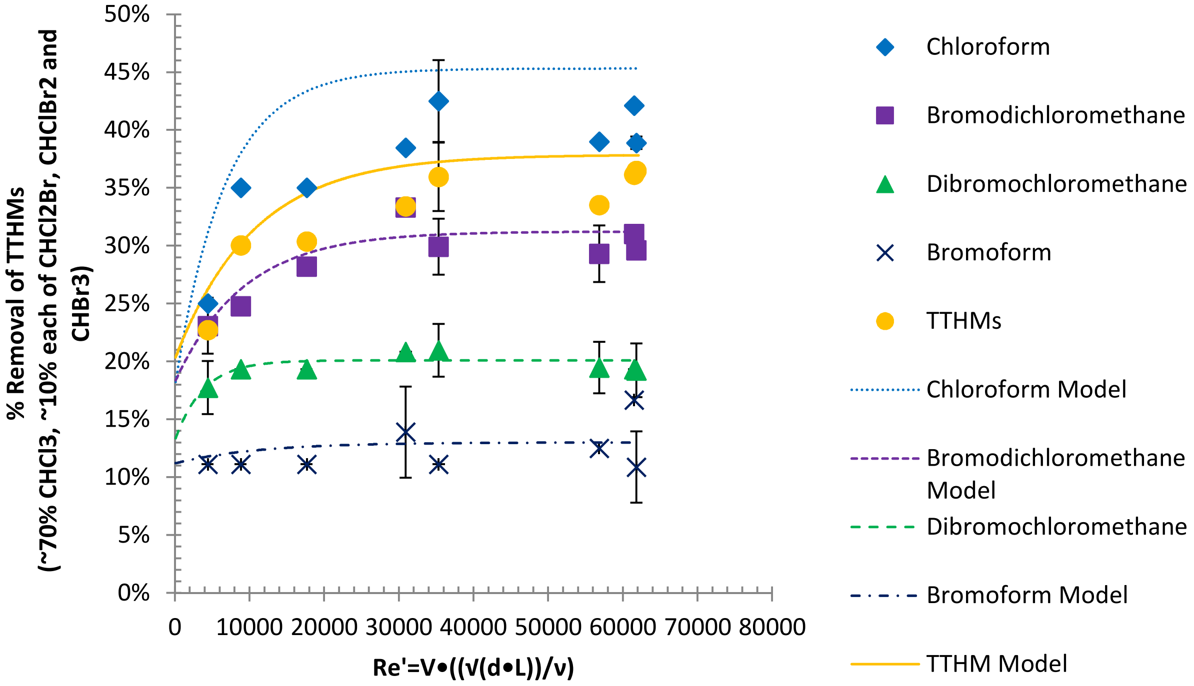


Figure 4.20 Final removal model for 20:1 A:W ratio including all data points and predicted asymptote value

Table 4.12 Values of a, b, and c for final models including the predicted asymptote and all final data points including confirmation trials

A:W Ratio	THM Species	a	b	c
5:1	Chloroform	17.2	-0.148803	-0.00007881
	Bromodichloromethane	10.2	-0.108975	-0.000217
	Dibromochloromethane*	6.0	-19289.43	-0.003067
	Bromoform*	3.6	-0.069046	-0.000264
	TTHM	13.9	-0.121807	-0.00009918
10:1	Chloroform	29.3	-0.205112	-0.00005167
	Bromodichloromethane	18.5	-0.169203	-0.000117
	Dibromochloromethane	11.2	-0.10495	-0.000145
	Bromoform	6.6	-0.102958	-0.000097
	TTHM	24.0	-0.178211	-0.0000624
20:1	Chloroform	45.3	-0.274684	-0.00015
	Bromodichloromethane	31.2	-0.129909	-0.000109
	Dibromochloromethane	20.1	-0.068968	-0.000266
	Bromoform*	13.0	-0.018063	-0.00009069
	TTHM	37.9	-0.176824	-0.00009487

THMs denoted with a * indicates that points needed to be removed. For 5:1, sample 10 was removed from dibromochloromethane, and samples 10, C2, and C6 were removed for bromoform. For 20:1, sample C3 was excluded for bromoform. These samples were excluded because at low % removals, minor changes in % removal caused large changes in the model, causing the models to decrease or become linear.

4.9 HILDA THM Removal Prediction – A Case Study

The town of Durham, NH draws its water from the Oyster and Lamprey rivers to service the town and University of New Hampshire. While Durham is able to meet the regulations for THMs for their LRAA, the water system typically has THM levels that exceed 80 ppb at one location during one sampling period out of the year. The Durham Water Department would like to keep the THM levels below 80 ppb at all locations and at all sampling times throughout the year. Durham is investigating several options, and one such option could be HILDA. The following information provided by the operating personnel from the Durham Drinking Water Treatment Plant and at Durham Water Department (East, 2014 & Richard, 2014) was used to determine what reactor configuration could be used for this situation:

- Pipe size: 8 inch
- Flow in pipe section: 3 gpm (average)
- Temperature: 20 °C
- THM speciation: 110 ug/L chloroform, and 2.3 ug/L bromodichloromethane
- Pressure: 60-70 psi

First, the needed % removal was determined:

$$\frac{112.3\frac{ug}{L} - 80\frac{ug}{L}}{112.3\frac{ug}{L}} * 100\% = 28.8\%$$

Conservatively, 5% was added so that the needed % removal is now 33.8%. In order to assure maximum removal, the 20:1 model was used. Since 98% of the THMs are chloroform, the 20:1 removal model for chloroform was selected:

$$45.3 + (-0.274684) * Exp(-0.00015 * Re') = R$$

By replacing R with 33.8, a value of 5781 for Re’ was calculated. Using Tables J.1 and J.2 located in appendix J, it can be seen that at 3 gpm, Re’ values of 13244 and 21368 for 1.5 inch and 1 inch Komax mixers, respectively, can be achieved with the use of just one mixer. Theoretically, this means more than 33.8% removal could be achieved through the use of just one mixer which would also minimize head loss. The air requirement would be 8.02 standard cubic feet per minute (scfm), and the HILDA system would only need to be run during one quarter out of the year since the elevated THM levels occur seasonally. If the system were implemented it could be fine-tuned to determine the exact amount of air necessary to save on electrical costs. Therefore, using the removal model developed in this study provides a good starting point for the final HILDA system configuration and design requirements.

5 Conclusions and Recommendations

5.1 Conclusions

From the results of this research, the following conclusions can be made concerning the horizontal in-line diffused aeration (HILDA):

1. A HILDA system that could remove THMs from a pressurized piping system was developed with treatment performance modeled from and air-water mixing expression for a static in-line mixer (e.g. Komax). The models created in JMP at air to water ratios of 5:1, 10:1, and 20:1 can be used to predict the needed Re' for required TTHM removals at a speciation of approximately 70% chloroform, and 10% each of the other three regulated THM species, provided that temperature and pressure are reasonably close to 18.4 °C and 40 psi respectively. If the THM speciation varies, then the model can be used for the desired removal for each THM species, and the highest mixing intensity value can be chosen to ensure removals. Once a value of mixing intensity is chosen, an air/water mixer configuration can be determined.
2. Re' and Re_{Komax} are correlated mixing expressions that can be used to describe and model air to water mixing in a horizontal reactor and subsequent TTHM removals.
3. Adding turbulence is required in order to reach saturation TTHM removals especially at lower flow rates. Turbulence can be created by increasing the flow rate, increasing the A:W ratio, increasing the mixing length, decreasing the reactor diameter, or adding a static mixer into the system.
4. For A:W ratios of 5:1, 10:1, and 20:1, significant HILDA factors affecting TTHM removal include A:W ratio, flow, length and their respective % contributions are 81.0%,12.7%, and 3.3%, while error had a 3% contribution. The low experimental error meant that all significant variables were included in the study and were well controlled, and that there is an acceptable amount of analytical error.

5. Changing the pressure of the system from 40 psi to 25 psi at a 10:1 A:W ratio does not appear to have a large contribution to TTHM removals. However, this will likely change for larger differences in the pressure.

5.2 Recommendations for Further Research

One general option for further research is using this system and developing models for other applications such as treatment of groundwater containing VOCs.

A comparison of the data collected in this thesis with data collected by an independent source would help to verify the models produced. The fit curve models were produced at approximately 20 °C, with an influent TTHM value of approximately 250 ug/L, at pressures of 25 and 40 psi. If trying to use any model for applications with parameters that vary greatly from those used in the study, more experimental trials should be conducted that vary the different parameters vs. % removal. If the new data points fall along or close to the model curve, then the original model can be used. For example, five experimental trials were run to compare 25 psi to 40 psi for this study, and the model was found to be similar. Potential changes in the model to test include higher pressures between 60-80 psi, higher or lower influent TTHM concentrations, and temperature.

Considering the work on John Zwerneman and Henry's Law, higher pressures should correspond to lower removals, while higher temperatures should correspond to higher removals. It is hypothesized that lower influent TTHM concentrations may do better at achieving saturation removals than higher concentrations, due to the fact that the added air will be less saturated and THMs would be more likely to come into contact with unsaturated air that they can partition to. This theory should be tested, however.

Another recommendation for further pilot-scale study is to find a more consistent mixing method for THM additions to a source water. While influent values were very close for some studies and could be averaged, they appeared to steadily increase for other studies and needed to be averaged incrementally to produce an influent value for each run that would best represent the influent value for each experimental condition. This influent variation definitely could have contributed to error, however, and should be minimized in the future. It is possible that the use of paddle-mixers to gently stir the source water while minimizing air stripping could also uniformly mix the THM addition.

A small-scale field study would be a good way to test the model and work out operational issues associated with the HILDA post-treatment system. Potential issues that could arise include:

- Head loss due to the addition of static in-line mixers;
- Entrained air in the pipe due to the addition of air into the system and milky (aerated) water at the consumer's tap;
- Placement and design of air release valve for HILDA system;
- The need for variable air flows into the system due to the fact that water flows have peak times and are not constant throughout the day;
- The need to be able to provide adequate fire flows for a community;
- The need to handle potential bidirectional flows in the pipeline;
- Only seasonal use of the HILDA system for part of the year due to seasonal fluctuations in THMs;
- Placement of the air compressor and control equipment for HILDA system;
- Problems with corrosion

Added head loss in the distribution system will occur due to the static in-line mixers used in this study. It is advised to use the model created in this study to choose the smallest number of mixers possible to achieve needed removals while minimizing head loss. If head loss from the mixers is still too great, pumping of the water may be required to increase the pressure to an acceptable level. Depending on the amount of removal needed and the water flow rate, it may also be possible to achieve needed removals without mixer addition, which would limit head loss.

While entrained air is a potential concern, it was not a problem for this study. Air flow was controlled and monitored both entering and leaving the reactor, and the amount of air leaving was found to be the same as entering. To continue to make sure this is not a problem, air flow in and out of the reactor should be monitored in the field design. One potential valve option would be to use an actuator, which would open and release the air once the pressure reaches a certain value.

Since flows can be variable, one potential design consideration for the field study would be to have a computer system that could monitor the water flow rate, and change the air flow rate accordingly. The 1.5 or 1-inch pipes may be too small to provide an adequate fire flow for a community. Also, if THM issues are seasonal, it would not make sense to run the reactor all the time. For these situations, a bypass of the reactor system should be considered so that required fire flows can be achieved and so the water does not have to run though the system and encounter head loss when treatment is not required. Also, since bidirectional flows could occur, the system should also be designed so that THM stripping can take place independent of the flow direction. An interpretation of what this system may look like can be found in Figure 5.1.

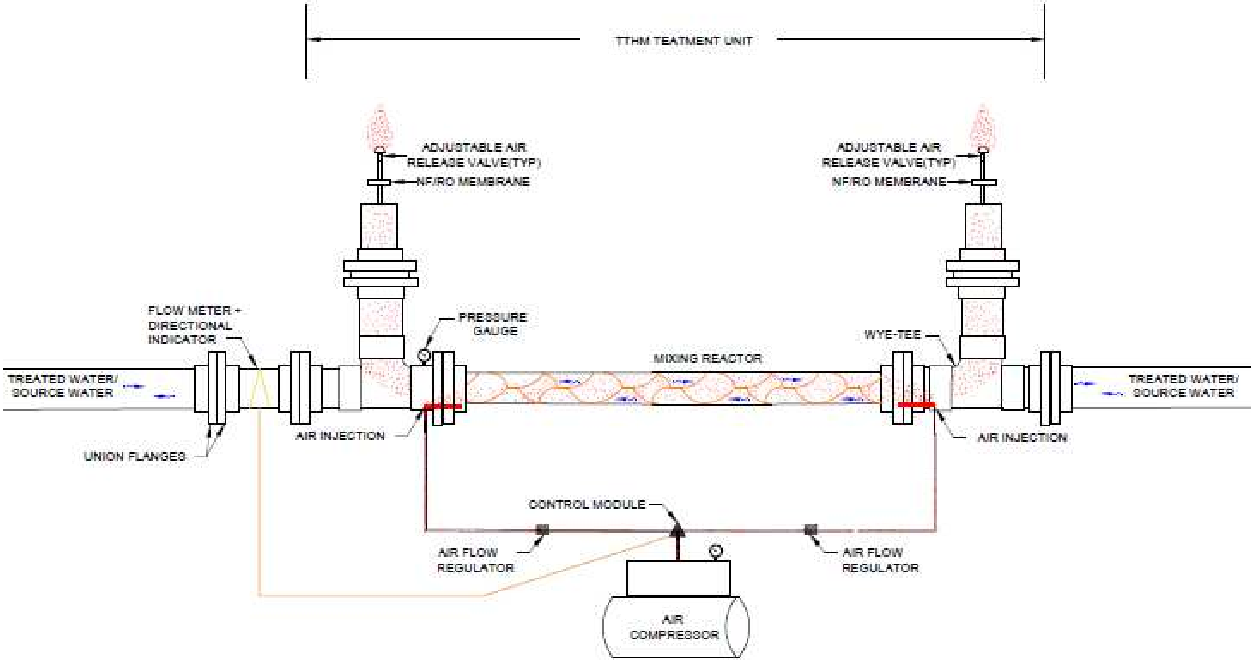


Figure 5.1 Schematic of HILDA system for bi-directional flow (Prepared by WTTAC staff)

The placement of control equipment will also need to be factored into the field design. Any control equipment should be placed inside a housing unit so it is protected. The actual mixing unit should be accessible so that any needed maintenance can be performed. There may need to be an option to temporarily shut of the water flow before the reactor so that any needed cleaning of the static in-line mixer can occur. Heating inside the housing and near the reactor unit may be necessary so that the control equipment does not get too cold and pipe does not freeze.

Corrosion can occur in pipelines due to factors such as flow velocity, temperature, pH, alkalinity, total dissolved solids, hardness, bacteria, and dissolved oxygen. Therefore, the addition of air into the system could cause potential corrosion problems where the air is added into the water before the release valve. This could be remedied by using plastic pipeline, which is resistant to corrosion, between the air inlets and outlets (Mays, 2000). The Komax mixers used in this study came housed in plastic pipes. If plastic pipes are not an option, copper or mild steel pipes may need to be replaced more often since they can corrode in the presence of oxygen (Mays, 2000).

Potential problems that system designers might look into to make sure they will not be a problem include whether or not the chlorine residual will be affected and if biofouling could occur. Research has shown that diffused aeration has little effect on the chlorine residual for A:W ratios between 0 and 100 and at a pH of 6.1. Therefore, decreasing residual and subsequent biofouling due to aeration is not believed to be of concern (Brooke, 2011).

If more THM removals are needed than can be provided with one air injection, it could be possible to have multiple air injectors and mixing reactors which could theoretically remove the same percentage of THMs in each reactor as long as the air from the previous reactor has been released prior to the subsequent reactor. A schematic of what this HILDA series might look like is shown in Figure 5.2.

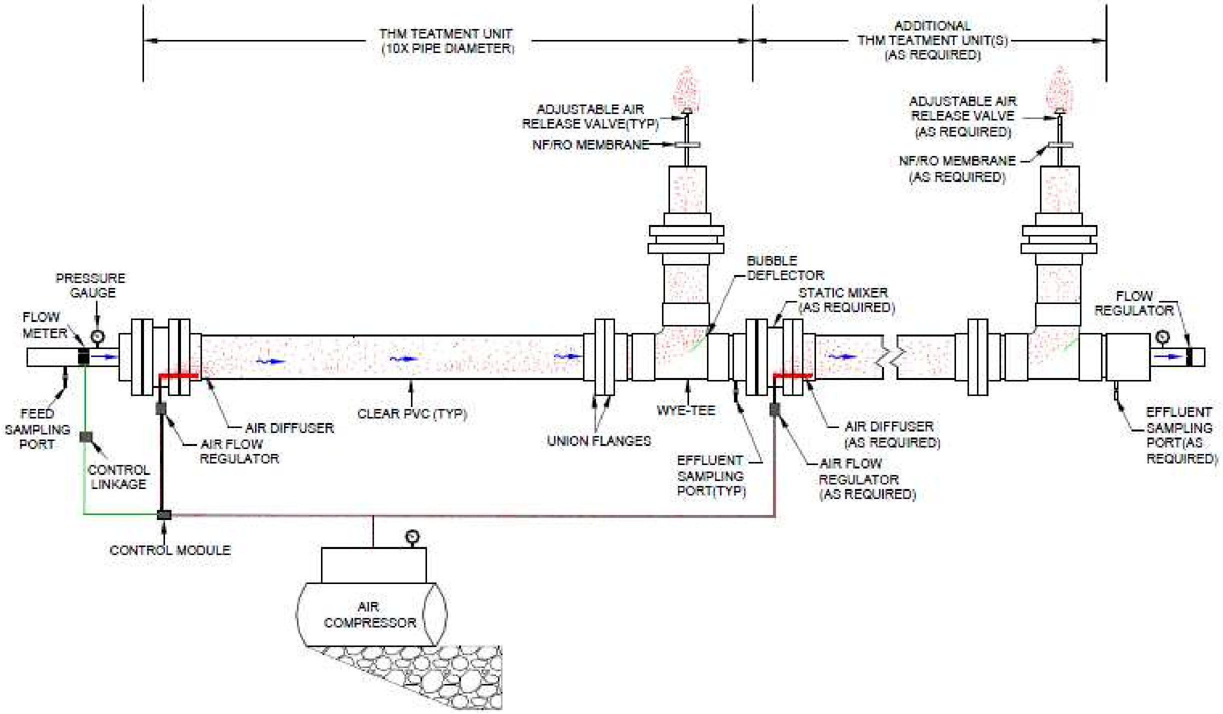


Figure 5.2 Possible configuration of HILDA system using multiple reactors to achieve needed TTHM removals (Prepared by WTTAC Staff).

6 List of References

Ballestero, T., 2014. Personal communication.

Brooke, E. & Collins M.R., 2011. Posttreatment Aeration to Reduce THMs. *Journal AWWA,* 103:10.

Cecchetti, A.; Christmas, E.; Wentworth, B.; Flood, J., Collins, M.R., 2013. Assessment and Design of Post –treatment Aeration Systems to Reduce THMs in Pressurized Distribution Piping. University of New Hampshire.

Çengel, Y.A. & Cimbala, J.M., 2010 (2nd ed.). ***Fluid Mechanics Fundamentals and Applications***. McGraw-Hill, New York, N.Y.

Delta Cooling Towers, Inc., 2015. Delta Pak. www.deltacooling.com/delta-pak/ (accessed March 27, 2015).

East, W., 2014. Personal communication.

González, J.F., 1996. Wastewater Treatment in the Fishery Industry. FAO (Food and Agriculture Organization of the United Nations).

Jones, C.S.; Sotiropoulos, F.; Amirtharajah, A., 2002. Numerical Modeling of Helical Static Mixers for Water Treatment. ***Journal of Environmental Engineering***, 128:5:431.

Jmp® Statistcal Dsicovery.™. The Fit Curve Report. www.jmp.com/support/help/The_Fit_Curve_Report.shtml (accessed March 28, 2015)

Komax Systems, Inc. Static CPS Mixer. http://www.komax.com/static-cps-mixer/ (accessed March 27, 2015).

Komax Systems, Inc. Triple Action Static Mixer. http://www.komax.com/triple-action-static-mixer/ (accessed 3/31/15)

Kshirsagar, S., 2014. Personal Communication.

Mackay, D.; Shiu, W.Y.; Sutherland, R.P.,1981. Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants. ***Environmental Science & Technology***, 13:3:333.

Matter-Müller, C.; Gujer, G.; Giger, G., 1981. Transfer of Volatile Substances from Water to the Atmosphere. ***Water Research***, 15:1271.

Mays, L., 2000. ***Water Distribution Systems Handbook***. McGraw-Hill Companies, Inc., New York, N.Y.

MWH, 2005 (2nd ed.). ***Water Treatment Principles and Design*** (J.C. Crittenden et al., editor). John Wiley & Sons, Inc., Hoboken, N.J.

Nicholson, B.C.; Maguire, B.P.; Bursill, D.B., 1984. Henry's Law Constants for the Trihalomethanes: Effects of Water Composition and Temperature. **Environmental Science & Technology**, 18:7:518.

Richard, D., 2014. Personal communication.
Ross, S., 1988 (3rd ed.). ***A First Course in Probability***. Macmillan USA, New York, N.Y.

Staudinger, J.; Roberts, P., 2000. A Critical Compilation of Henry's Law Constant Temperature Dependence Relations for Organic Compounds in Dilute Aqueous Solutions. ***Chemosphere***, 44:561.

Tchobanoglous, G.; Burton, F.L.; Stensel, H.D., 2002 (4th ed.). ***Wastewater Engineering Treatment and Reuse***. McGraw-Hill, Boston, M.A.

USEPA (United States Environmental Protection Agency), 2014. Aeration and Air Stripping. http://iaspub.epa.gov/tdb/pages/treatment/treatmentOverview (accessed 3/24/15)

USEPA (United States Environmental Protection Agency), 1999.Alternative Disinfectants and Oxidants Guidance Manual. EPA 815-R-99-014.

USEPA (United States Environmental Protection Agency), 2013. Basic Information about Disinfection Byproducts in Drinking Water: Total Trihalomethanes, Haloacetic Acids, Bromate, and Chlorite. http://water.epa.gov/drink/contaminants/basicinformation/disinfectionbyproducts.cfm (Accessed Dec. 5, 2014).

USEPA (United States Environmental Protection Agency), 2006. Initial Distribution System Evaluation Guidance Manual for the Final Stage 2 Disinfectants and Disinfection Byproducts Rule: Appendix A. EPA 815-B-06-002.

USEPA (United States Environmental Protection Agency), 1998. Stage 1 Disinfectant and Disinfection Byproduct Rule. EPA 815-F-98-010.

USEPA (United States Environmental Protection Agency), 2005. Stage 2 Disinfectant and Disinfection Byproduct Rule. EPA 815-F-05-003.

USEPA (United States Environmental Protection Agency), 1981. Treatment Techniques for Controlling Trihalomethanes in Drinking Water. EPA/600/2-81/156, Washington.

Zwerneman, J., 2012. Investigating the Effect of System Pressure on Trihalomethane Post-Treatment Diffused Aeration.

7 Appendices

Appendix A: List of Symbols

{VOCgas}	the activity of the VOC in the air in mole/L of air
{VOCliquid}	the activity of the gas in the water in mole/L of water
ΔH	head loss through basin (m)
°C	degrees Celsius
a	Asymptote
a_i	the interfacial area per unit volume of liquid in (L_d^2/L_d^3)
b	Scale
B	the temperature dependant relationship constant
c	growth rate
C_G	concentration of compound in gas (mg/L or mol/L)
$CHBr_3$	Bromoform
$CHCl_2Br$	bromodichloromethane
$CHCl_3$	Chloroform
$CHClBr_2$	dibromochloromethane
C_L	concentration of compound in liquid (mg/L or mol/L)
Cl_2	Chlorine
cm	Centimeter
C_S	the aqueous solubility of compound (mole/L)
D	pipe diameter of reactor (in or ft)
D_h	the hydraulic diameter of the pipe (m)
F	the mass transfer coefficient of contaminant y out of an aeration system (M_d/t_d)
ft	feet
G	the RMS velocity gradient (s^{-1})
g	Gram
g_a	acceleration due to gravity (9.81 m/s^2)
G_{awi}	the concentration of volatile substance in gas-phase of air-water interface
G_b	the concentration of volatile substance in bulk gas phase
G_e	the concentration of volatile substance in gas phase in equilibrium with bulk water phase
H	the dimensionless equilibrium constant known as Henry's constant
H_{cc}	dimensionless Henry's law constant $=C_G/C_L$

$H_{CC,0}$	the dimensionless Henry's law constant at atmospheric pressure
$H_{CC,20}$	the Henry's law constant at 20 °C
$H_{CC,T}$	the temperature corrected Henry's law constant
H_{PC}	dimensioned Henry's law constant = $(yP_T)/C_L$ ((atm·m^3)/mol)
H_{PX}	dimensioned Henry's law constant = $(yP_T)/x$ (atm)
H_{yx}	dimensionless Henry's law constant =y/x
in	inch
k	the experimentally determined rate constant (psig^{-1})
kg	Kilogram
K_{OL}	the overall mass transfer coefficient (L_d/t_d)
L	Liter
L_{awi}	the concentration of volatile substance in liquid phase in equilibrium with bulk air phase
L_b	the concentration of volatile substance in bulk liquid phase
$L_{b,i}$	the influent concentration of compound (M_d/L_d^3)
L_e	the concentration of volatile substance in liquid phase of air-water interface
L_m	mixer length (ft)
m	Meter
mg	milligrams
ml	milliliter
P	the system pressure (psig)
P	power input (W)
P_T	total atmospheric pressure (atm)
P_V	the vapor pressure of compound (atm)
Q_G	the flow rate of the air (Liters/min) or dimensionless: (L^3/t)
Q_L	the liquid flow rate (gpm) or dimensionless: (L_d^3/t_d)
Re	Reynolds number
Re_{Komax}	Reynolds number equation provided by Komax Systems Inc.
s	Second
S	specific gravity of liquid
t	time (min)
T	temperature °K
ug	microgram
v_{avg}	the average flow velocity (m/s)

V	volume in which mixing occurs (m^3)
V_L	the volume of the liquid (liters)
x	molar of compound in liquid (mol/mol)
y	molar fraction of compound in gas (mol/mol)
θ	detention time (s)
μ	liquid viscosity (cp, (kg/(ms)) or (Ns/(m^3)))
ν	the kinematic viscosity of the liquid (m^2/s) or (ft^2/s)
ρ	the density of the fluid (kg/m^3)
v	water velocity (ft/s)

Appendix B: Surface Area and Reynolds number Calculations for Tubular Mixers and 6 inch Pipe without Mixers

Reynolds number was calculated for the tubular array, DeltaPak® and for the 6 inch pipe without mixers.

First, the surface area of the 6 inch pipe was calculated using the inner radius of the pipe.

$$Area = \pi(0.252706\,ft)^2 = 0.200627$$

Next, the available surface area for each type of mixer was calculated and the results are shown in Table B.1. The percent available for the tubular array was calculated by subtracting the area of the smaller tubes from the area of the 6 inch pipe, and the percent available for the DeltaPak® was calculated by estimating the length of the plastic material and multiplying by the thickness of the plastic.

Table B.1: Surface area of tubular array, DeltaPak® and 6 inch pipe without mixers

Mixer Type	% Blockage	% Available	Area (ft^2)
Tubular	60%	40%	0.08025073
Delta Pak®	8%	92%	0.184576679
None	0%	100%	0.200626825

The following equation was used to calculate Reynolds number:

$$Re = \frac{\mu d_h}{v}$$

Where: $d_h = \frac{4A}{p}$. Each new area found using the % area available was used to calculate a new diameter and perimeter for each mixer type. All calculated values, including area and Reynolds Number can be found in Table B.2.

Table B.2: Calculations for area and Reynolds number for tubular array, DeltaPak® and 6 inch pipe with no mixers.

Mixer Type	Flow gpm	flow (ft^3/s)	Area (ft^2)	v (ft^2/s)	P (ft)	Dh (ft)	u ft/s	Re #
No Mixer	5	0.011	0.201	1.18E-05	1.588	0.505	0.056	2381
	7.5	0.017	0.201	1.18E-05	1.588	0.505	0.083	3572
Tubular Array	2	0.004	0.080	1.18E-05	1.004	0.320	0.056	1506
	4	0.009	0.080	1.18E-05	1.004	0.320	0.111	3012
	7	0.016	0.080	1.18E-05	1.004	0.320	0.194	5272
DeltaPak®	5	0.011	0.185	1.18E-05	1.548	0.477	0.060	2443
	7.5	0.017	0.185	1.18E-05	1.548	0.477	0.091	3665

Appendix C: THM Stock Solution Dilution, Solution Preparation, and Sampling Procedures

THM Stock Solution Dilution Procedure

This procedure creates a 1 g/L total THM solution containing 70% chloroform, 10% dibromochloromethane, 10% bromodichloromethane, and 10% bromoform

Materials

- 1000 mL glass volumetric flask (1)
- 1000 mL Erlenmeyer flask
- 125 mL Erlenmeyer flask (1)
- 40 mL glass vials with Teflon screw caps (25)
- 500 uL glass-barreled, air tight syringe (1)
- 100 uL glass-barreled, air tight syringe (3)
- Glass beakers for methanol and methanol waste (2)
- Glass funnel (1)
- Magnetic stir plate and stir bar
- Autopipettor
- Glass pipette
- Parafilm or tinfoil
- HPLC grade methanol
- HPLC grade reagents- chloroform, dibromochloromethane, bromodichoromethane, bromoform

Cleaning Procedures:

- Clean glassware using reverse osmosis water and Alconox, rinse 7x with RO water
- Flush syringes with methanol before and after use

Dilution Procedure:

1) Measure out 1000 mL of methanol into the 1000 mL volumetric.
2) Place stir bar in 1000 mL volumetric. Pour contents of 1000 mL volumetric into 1000 mL Erlenmeyer.
3) Extract 60 mL of methanol from the flask and place in into the 125 mL Erlenmeyer flask.
4) Cover methanol containing flasks with Parafilm to prevent evaporation.
5) Fill the 500 uL syringe to the 263.5 uL mark with methanol. Then fill the rest of the way to the 500 uL mark with chloroform (this is equal to 236.5 uL of chloroform). Inject syringe contents into the 125 mL flask, making sure that the tip of the syringe is below the methanol surface.
6) Repeat step 5, making sure to rinse syringe with methanol in-between.
7) Gently swirl flask.
8) Fill the first 100 uL syringes to the 49.5 uL mark with methanol. Then fill the rest of the way to the 100 uL mark with bromodichloromehtane (this is equal to 50.5 uL of bromodichloromehtane). Inject syringe contents into the 125 mL flask, making sure that the tip of the syringe is below the methanol surface.
9) Gently swirl flask
10) Fill the second 100 uL syringe to the 58.7 uL mark with methanol. Then fill the rest of the way to the 100 uL mark with dibromochloromethane (this is equal to 41.3 uL of

dibromochloromethane). Inject syringe contents into the 125 mL flask, making sure that the tip of the syringe is below the methanol surface.

11) Gently swirl flask.
12) Fill the third 100 uL syringe to the 65.4 uL mark with methanol. Then fill the rest of the way to the 100 uL mark with bromoform (this is equal to 34.6 uL of bromoform). Inject syringe contents into the 125 mL flask, making sure that the tip of the syringe is below the methanol surface.
13) Gently swirl flask
14) Pour contents of 125 mL flask into 1000 mL Erlenmeyer flask. Cover volumetric with Parafilm.
15) Mix the contents of the flask using the magnetic plate for 35 minutes in the fume hood.
16) Fill 24 40 mL vials with solution in 1000 mL volumetric, making sure 40 mL is added to each vial. Cap al vials.
17) Place the vials in the freezer at -10 °C until ready to use.

Notes:

- Perform all dilution procedures in fume hood.
- Filling each syringe with methanol first was done in order to flush the THMs out of each syringe and into the flask.
- Although zero headspace was desired for the 40 mL vials, this was not possible to achieve. It was assumed that this was not a problem as long as no significant THM losses were observed in the challenge runs.

THM Solution Preparation:

This procedure explains how to prepare the influent THM water for sampling trials.

- Use a previously made solution of 250 ug/L total THM with 70% chloroform and 10% each of dichlorobromomethane, dibromochloromethane, and bromoform.
- Determine the amount of stock solution needed for the desired volume of water was determined.
- Clean 250 gallon tank thoroughly with reverse osmosis water. Fill tank with reverse osmosis water and allowed to sit until a desired temperature of approximately 20 °C is reached.
- Release the stock solution beneath the surface of the reverse osmosis water so as not to introduce any air into the stock solution.
- In order to ensure uniform distribution of the THMs, mix water thoroughly using a submersible pump. Use a small submersible pump attached to the end of a PVC pipe and move it along the bottom of the tank in a slow, systematic manner. Move the pump along the sides of a tank in a square pattern, and then across the middle of the tank diagonally from both corners for a total mixing time of 4 minutes.

THM Sampling Procedure

This procedure explains how to fill, seal, and store THM samples.

- Run sample ports for at least 30 s prior to sampling to make sure they are flushed before sampling
- Samples will be filled so that the nozzle is below the water level in the vial
- Samples will be filled to the top and sealed so that no air is remaining in the vials
- After sampling, let sample sit for at least 30s so that any dissolved air can escape before closing tightly- may tap sides of glass lightly to help bubbles escape
- Samples will be placed in fridge at 0-6 °C until ready to send to Eastern Analytical
- Samples will be transported to Eastern Analytical in a cooler containing ice packs

Appendix D: Raw Data for HILDA

Table D.1: All Raw data taken on each sampling date, including sample ID, flow rate, A:W ratio, length, mixer type, date taken and THM concentration for each species

Sample ID	Flow (gpm)	A:W Ratio	Length (ft)	Mixer	Date	$CHCl_3$ (ug/L)	$CHCl_2Br$ (ug/L)	$CHClBr_2$ (ug/L)	CHB_3 (ug/L)	TTHMs (ug/L)
0.72 Influent	4	10	2	Pipe Array with Static Mixers	5.15.14	160	22	22	21	225
0.72 Effluent	4					140	20	21	21	202
0.72 Port 2	4					130	20	21	21	192
1.82 Influent	2					170	23	23	22	238
1.82 Effluent BV2	2					140	21	22	21	204
1.82 Effluent BV3	2					140	20	21	21	202
1.82 Effluent BV4	2					150	22	22	22	216
1.82 Port 2	2					140	20	21	21	202
3.67 Influent	1					160	22	22	21	225
3.67 Effluent	1					150	21	21	21	213
7.47 Influent	0.5					170	23	23	22	238
7.47 Effluent DUP	0.5					160	22	22	22	226
0.72 Inf 5.30	4	10	2	Pipe Array	5.30.14	190	26	26	25	267
0.72 Eff 5.30	4					140	21	23	24	208
0.72 Eff 5.30 DUP	4					150	22	23	24	219
1.82 Inf 5.30	2					190	26	26	25	267
1.82 Eff 5.30	2					150	22	23	24	219
1.82 Eff 5.30 DUP	2					150	22	24	24	220
3.67 Inf 5.30	1					180	25	25	24	254
3.67 Eff 5.30	1					160	23	24	24	231
3.67 Eff 5.20 DUP	1					160	22	23	23	228
7 gpm Inf 5.30	7					200	28	27	26	281
7 gpm Eff 5.30	7					130	21	22	22	195
7 gpm Eff 5.30 DUP	7					130	21	22	23	196
1-DPf5a10-8.20.14 INF	5	10	2	Delta-Pak®	8.20.14	180	30	37	36	283
1-DPf5a10-8.20.14	5	10				150	26	24	24	224
1-DPf5a10-8.20.14 DUP	5	10				150	26	35	35	246
2-DPf5a20-8.20.14	5	20				110	21	30	32	193
2-DPf5a20-8.20.14 DUP	5	20				110	22	31	32	195

3-DPf5a30-8.20.14 INF	5	30				180	29	36	35	280
3-DPf5a30-8.20.14	5	30				91	19	27	30	167
3-DPf5a30-8.20.14 DUP	5	30				89	19	27	30	165
4-DPf7.5a10-8.20.14	7.5	10				150	26	34	33	243
4-DPf7.5a10-8.20.14 DUP	7.5	10				140	26	33	33	232
5-DPf7.5a20-8.20.14 INF	7.5	20				190	31	37	36	294
5-DPf7.5a20-8.20.14	7.5	20				120	23	30	30	203
5-DPf7.5a20-8.20.14 DUP	7.5	20				120	24	32	31	207
6-NMf5a10-8.20.14	5	10				150	27	33	32	242
6-NMf5a10-8.20.14 DUP	5	10				150	27	34	31	242
7-NMf10a10-8.20.14 INF	10	10				180	32	38	35	285
1-NMf5a20-9.9.14 INF	5	20	N/A	None (6 inch pipe)	9.9.14	150	22	25	25	222
1-NMf5a20-9.9.14	5	20				95	17	22	23	157
1-NMf5a20-9.9.14 DUP	5	20				94	17	21	23	155
2-NMf5a30-9.9.14	5	30				73	14	19	21	127
2-NMf5a30-9.9.14 DUP	5	30				73	14	19	21	127
3-NMf7.5a10-9.9.14 INF	7.5	10				160	23	27	26	236
3-NMf7.5a10-9.9.14	7.5	10				130	20	24	24	198
3-NMf7.5a10-9.9.14 DUP	7.5	10				130	20	24	24	198
1-K1.5f1a10L0.75	1	10	0.75	Komax 1.5 inch Static In-line Mixers	10.1.14	160	23	25	23	231
1-K1.5f1a10L0.75 DUP	1	10				170	24	27	24	245
2-K1.5f1a20L0.75	1	20				150	22	25	24	221
2-K1.5f1a20L0.75 DUP	1	20				150	23	26	24	223
3-K1.5f4a10L0.75	4	10				160	24	27	24	235
3-K1.5f4a10L0.7	4	10				160	24	28	25	237

5 DUP										
4-K1.5f4a20L0.75	4	20				130	21	25	24	200
4-K1.5f4a20L0.75 DUP	4	20				130	21	25	24	200
5-K1.5f7a10L0.75	7	10				150	23	27	24	224
5-K1.5f7a10L0.75 DUP	7	10				150	24	27	25	226
6-K1.5f7a20L0.75 INF	7	20				200	29	31	27	287
6-K1.5f7a20L0.75 INF DUP	7	20				200	29	31	27	287
6-K1.5f7a20L0.75	7	20				110	19	23	23	175
6-K1.5f7a20L0.75 DUP	7	20				120	20	23	22	185
13-K1.5f1a10L3 INF	1	10	3			200	29	31	27	287
13-K1.5f1a10L3	1	10				150	23	26	24	223
13-K1.5f1a10L3 DUP	1	10				160	25	28	25	238
14-K1.5f1a20L3	1	20				130	22	25	24	201
14-K1.5f1a20L3 DUP	1	20				130	22	25	24	201
15-K1.5f4a10L3	4	10				140	24	27	25	216
15-K1.5f4a10L3 DUP	4	10				140	24	28	26	218
16-K1.5f4a20L3 INF	4	20				200	30	31	27	288
16-K1.5f4a20L3	4	20				110	20	24	24	178
16-K1.5f4a20L3 DUP	4	20				120	21	25	24	190
17-K1.5f7a10L3	7	10				150	25	28	25	228
17-K1.5f7a10L3	7	10				150	25	28	26	229

DUP										
18-K1.5f7a20L3	7	20	3	Komax 1.5 inch Static In-line Mixers	10.27.14	110	19	24	20	173
18-K1.5f7a20L3 DUP	7	20	3			110	19	25	21	175
R17-K1.5f7a10L3	7	10	3			120	21	26	21	188
R17-K1.5f7a10L3 DUP	7	10	3			130	23	27	22	202
R15-K1.5f4a10L3	4	10	3			140	22	27	21	210
R15-K1.5f4a10L3 DUP	4	10	3			140	23	27	21	211
1-K1.5CLa0L3My INF	4	0	3			180	27	30	23	260
1-K1.5CLa0L3My	4	0	3			170	27	30	23	250
1-K1.5CLa0L3My DUP	4	0	3			180	27	30	23	260
2-K1.5CLa20L3My	4	20	3			110	19	24	19	172
3-K1.5CLa0L0.75My	4	0	0.75			170	26	29	22	247
3-K1.5CLa0L0.75My DUP	4	0	0.75			170	26	29	22	247
4-K1.5CLa20L0.75My	4	20	0.75			110	19	24	20	173
4-K1.5CLa20L0.75My DUP	4	20	0.75			110	19	24	20	173
5-K1.5CLa0L0.75Mn	4	0	0.75	None (1.5 inch pipe)		170	26	29	22	247
5-K1.5CLa0L0.75Mn DUP	4	0	0.75			170	26	29	22	247
6-K1.5CLa20L0.75Mn INF	4	20	0.75			180	27	31	23	261
6-K1.5CLa20L0.75Mn	4	20	0.75			130	22	25	20	197
6-K1.5CLa20L0.75Mn DUP	4	20	0.75			130	21	25	20	196

7-K1.5CLa0L3Mn INF	4	0	3			180	27	30	23	260
7-K1.5CLa0L3Mn	4	0	3			160	26	29	23	238
7-K1.5CLa0L3Mn DUP	4	0	3			170	27	31	23	251
8-K1.5CLa20L3Mn	4	20	3			130	21	26	21	198
8-K1.5CLa20L3Mn DUP	4	20	3			130	21	26	22	199
R6-K1.5f7a20L0.75 INF	7	20	0.75	Komax 1.5 inch Static In-line Mixers	12.3.14	130	21	24	18	193
R6-K1.5f7a20L0.75	7	20				80	14	19	15	128
R6-K1.5f7a20L0.75 DUP	7	20				80	14	19	16	129
7-K1.5f7a5L0.75	7	5				110	18	23	18	169
7-K1.5f7a5L0.75 DUP	7	5				110	18	23	18	169
8-K1.5f4a5L0.75	4	5				120	19	23	18	180
8-K1.5f4a5L0.75 DUP	4	5				120	19	23	18	180
R1-K1.5f1a10L0.75	1	10				120	19	23	18	180
R1-K1.5f1a10L0.75 DUP	1	10				120	19	23	18	180
9-K1.5f1a5L0.75	1	5				130	20	24	19	193
9-K1.5f1a5L0.75 DUP	1	5				130	20	24	19	193
R17-K1.5f7a10L3 INF	7	10	3			140	21	25	19	205
R17-K1.5f7a10L3	7	10				95	17	22	17	151
R17-K1.5f7a10L3 DUP	7	10				99	18	23	18	158
10-K1.5f7a5L3	7	5				120	20	25	20	185

10-K1.5f7a5L3 DUP	7	5				120	20	25	20	185
11-K1.5f4a5L3	4	5				120	21	25	20	186
11-K1.5f4a5L3 DUP	4	5				120	21	25	20	186
R13-K1.5f1a10L3	1	5				120	20	25	20	185
R13-K1.5f1a10L3 DUP	1	5				120	20	25	20	185
12-K1.5f1a5L3 INF	1	5				150	23	28	21	222
12-K1.5f1a5L3	1	5				130	22	26	21	199
12-K1.5f1a5L3 DUP	1	5				140	21	26	21	208
C1-K1.5f7a10L1.5 INF	7	10	1.5	Komax 1.5 inch Static In-line Mixers	1.12.15	190	28	31	23	272
C1-K1.5f7a10L1.5	7	10	1.5			140	22	26	21	209
C1-K1.5f7a10L1.5 DUP	7	10	1.5			140	22	27	21	210
C2-K1.5f5a5L2.25	5	5	2.25			160	25	29	22	236
C2-K1.5f5a5L2.25 DUP	5	5	2.25			160	26	29	22	237
C3-K1f5a20L1.61 INF	5	20	1.61	Komax 1 inch Static In-line Mixers		190	29	31	24	274
C3-K1f5a20L1.61	5	20	1.61			110	20	25	20	175
C3-K1f5a20L1.61 DUP	5	20	1.61			110	20	25	20	175
C4-K1f4a20L2.15	4	20	2.15			120	20	25	21	186
C4-K1f4a20L2.15 DUP	4	20	2.15			120	21	26	21	188
C5-K1f6a10L1.61	6	10	1.61			140	23	27	21	211
C5-K1f6a10L1.61 DUP	6	10	1.61			140	23	28	22	213
C6-K1f7a5L0.54 INF	7	5	0.54			200	29	32	24	285
C6-K1f7a5L0.54	7	5	0.54			170	27	30	23	250
C6-K1f7a5L0.54 DUP	7	5	0.54			170	27	31	23	251

1-25-k1.5f1a10L0.75 INF	1	10	0.75	Komax 1.5 inch Static In-line Mixers	2.25.15	180	30	32	34	276
1-25-k1.5f1a10L0.75	1					140	25	28	31	224
1-25-k1.5f1a10L0.75 DUP	1					150	26	29	32	237
2-25-k1.5f4a10L0.75	4					150	26	29	33	238
2-25-k1.5f4a10L0.75 DUP	4					140	25	29	32	226
3-25-k1.5f7a10L0.75 INF	7					190	31	33	35	289
3-25-k1.5f7a10L0.75	7					130	24	28	30	212
3-25-k1.5f7a10L0.75 DUP	7					140	25	28	31	224
4-25-k1.5f1a10L3 INF	1		3			170	29	30	32	261
4-25-k1.5f1a10L3	1					140	25	28	31	224
4-25-k1.5f1a10L3 DUP	1					140	25	28	32	225
5-25-k1.5f7a10L3	7					120	23	27	31	201
5-25-k1.5f7a10L3 DUP	7					120	24	28	32	204

Appendix E: Predicting THM Removals

Appendix E illustrates how to predict THM Removals using the 10.1.14 10:1 A:W ratio data and explains predictions for different sets of data.

The following published H_{cc} and B and experimental K values for each THM species in table E.1 are used in predicted removal calculations:

Table E.1: H_{cc}, K and B values for each THM species

Published H_{cc} values (Nicholson et al, 1984)		Experimental K values (Zwerneman, 2012)	Temperature dependant relationship constant (Nicholson et al, 1984)
THM	Ho (20 °C)	K, $psig^{-1}$	B
chloroform	0.121	0.377	2131
bromodichloromethane	0.0642	0.674	2135
dibromochloromethane	0.0352	1.21	2135
bromoform	0.018	1.81	2335

First, temperature corrections to H_{cc} are made using the following equation (Staudinger & Roberts, 2000):

$$H_{cc,T} = \left(H_{cc,20°C}\right)\left[10^{-B\left(\frac{1}{T}-\frac{1}{293}\right)}\right]$$

For the 10.1.14 experiment, the temperature was 18 °C. The corresponding B value was used for each THM, and a value of 291 °K (=18 °C) was used for T. For example, $H_{cc,T}$ was calculated for chloroform. All calculated values can be found in table E.2.

$$H_{cc,T\ chloroform} = (0.121)\left[10^{-2131\left(\frac{1}{291}-\frac{1}{293}\right)}\right] = 0.107844713$$

Table E.2: H_{ccT} calculated for each THM for 18 °C

THM	H_o (20c)	B	T	Hc_{cT}
chloroform	0.121	2131	291	0.107844713
bromodichloromethane	0.0642	2135	291	0.057207726
dibromochloromethane	0.0352	2135	291	0.03136623
bromoform	0.018	2335	291	0.015867218

Next the Henry's law constant was corrected for pressure using the following equation:

$$\frac{1}{H_{cc}} - \frac{1}{H_{cc,0}} = kP$$

The Henry's law constant was corrected to 40 psi for each THM, using its corresponding k value and temperature corrected H_{cc} value, and P of 40 to solve for H_{cc}. For example, H_{cc} was calculated for chloroform. Calculated H_{cc} values for each THM corrected for pressure can be found in table E.3.

$$\frac{1}{H_{cc}} - \frac{1}{0.107844713} = (0.377)(40)$$

$$H_{cc} = \frac{1}{(0.377)(40) + \left(\frac{1}{0.107844713}\right)} = 0.041063391$$

Table E.3: Calculated Hcc values corrected to 40 psi for each THM

Pressure	H_{cc} chloroform	H_{cc} bromodichloromethane	H_{cc} dibromochloromethane	H_{cc} bromoform
40	0.041063391	0.022502171	0.012456182	0.007384269

Next, the percent removed of each THM can be found using the following equation from Matter-Müller et al. (1981):

$$\%\,Removed = 1 - \frac{1}{1 + \frac{Q_G H_{cc}}{Q_L}}$$

The pressure corrected H_{cc} value of 0.041063391 was used, and at a 10:1 A:W ratio, 10 can be used for Q_G, and 1 can be used for Q_L. An example for the % removed of chloroform at 40 psi can be found below. Table E.4 shows the calculated % removals for each THM using this method.

$$\%\,Removed = 1 - \frac{1}{1 + \frac{10 * (0.041063391)}{1}} * 100\% = 29.11\%$$

Table E.4: % removed for each THM at a pressure of 40 psi

Pressure	Chloroform % Removed	Bromodichloromethane % Removed	Dibromochloromethane % Removed	Bromoform % Removed
40	29.11%	18.37%	11.08%	6.88%

The amount of THMs removed depends on the influent concentration. For the 10.1.14 samples, the influent concentration was 200 mg/L chloroform, 29.25 mg/L bromodichloromethane, 31 mg/L dibromochloromethane, and 27 mg/L bromoform for a total of 287.25 mg/L THMs. The amount removed can be found by multiplying the % removed by the influent amount. The amount removed of chloroform can be found below:

$$\frac{mg}{L} removed = 29.11\% * 200 \frac{mg}{L} = 58.22\ mg/L$$

This can be done for each THM, and then summed to find the total mg/L as seen in table E.5.

Table E.5: mg/L removed for each THM at 40 psi

Pressure	Chloroform mg/L removed	Bromodichloromethane mg/L removed	Dibromochloromethane mg/L removed	Bromoform mg/L removed	Total mg/L removed
40	58.2197701	5.372872157	3.433707568	1.85665242	68.883

Finally, the total % removed can be found by dividing the total mg/L removed by the total influent THM concentration:

$$\% \, removed = \frac{68.833 \frac{mg}{L}}{287.25 \frac{mg}{L}} * 100\% = 24\%$$

For each A:W ratio run at a sampling date, the predicted % removal was calculated using the influent THM value for that sample (as found in Appendix F). If graphed, the average influent values for that sampling period were used to calculate the saturation value. For studies that spanned more than one sampling period, weighted average influent values and temperatures depending on the number of samples taken from each sampling period were used to calculate the saturation value. These included averaging all Komax trials, all 10:1 Komax trials at 40 psi, and all 20:1 Komax trials at 40 psi. Influent values and temperatures used can be found in Table E.7.

Table E.7: Influent values and temperatures used to calculate saturation values for all Komax trials, 10:1 Komax trials at 40 psi, and all 20:1 Komax trials at 40 psi

THM	All Komax 18.4 °C	10:1 18.3 °C	20:1 18.9 °C
Chloroform (ug/L)	175.1351	171.4286	190
Bromodichloromethane (ug/L)	26.75	25.82143	28.04167
Dibromochloromethane (ug/L)	29.54955	28.71429	30.16667
Bromoform (ug/L)	24.22523	23	25.66667
Total THMs (ug/L)	255.6599	248.9643	273.875

Appendix F: Influent THM Concentrations

At least two influent samples were taken per sampling event depending on the number of samples being collected. For three sampling events, the influent TTHM values were averaged and used as the influent value for the whole set of samples taken. For samples taken on 10.1.14 and 10.27.14, the influent TTHM values only differed by 1 ug/L. For samples taken on 8.20.14, the influent samples did not steadily increase, so they were averaged. The sampling event date, number of averaged samples, TTHM range, and influent TTHM values can be found for each event in Table F.1.

Table F.1: Averaged influent THM data used for analysis for samples taken on 8.20.14, 10.1.14, and 10.27.14

Sampling Date	# of Samples Averaged	TTHM Range (ug/L)	$CHCl_3$ (ug/L)	$CHCl_2Br$ (ug/L)	$CHClBr_2$ (ug/L)	$CHBr_3$ (ug/L)	TTHM (ug/L)
8.20.14	4	14	182.5	30.5	37	35.5	285.5
10.1.14	4	1	200	29.25	31	27	287.3
10.27.14	3	1	180	27	30.3	23	260.3

For other sampling events, the influent TTHM value increased as sampling progressed. Since influent TTHM values have a large effect on % removals, it was necessary to calculate the most likely influent value for each sample in order to get the best possible estimate of what the TTHM removal would be. For the 5.15.14 and 5.30.14 sampling events, one influent sample was taken for each effluent sample. In this case the influent sample for its corresponding effluent sample was used. For the other sampling events, influent values were used for their corresponding values, and interpolated influent values were used for samples in between. Figure F.1 shows that the increase in influent TTHMs was generally linear, and this assumption was used to calculate the influent TTHM values for 9.9.14, 12.3.14, 1.12.15, and 2.27.15.

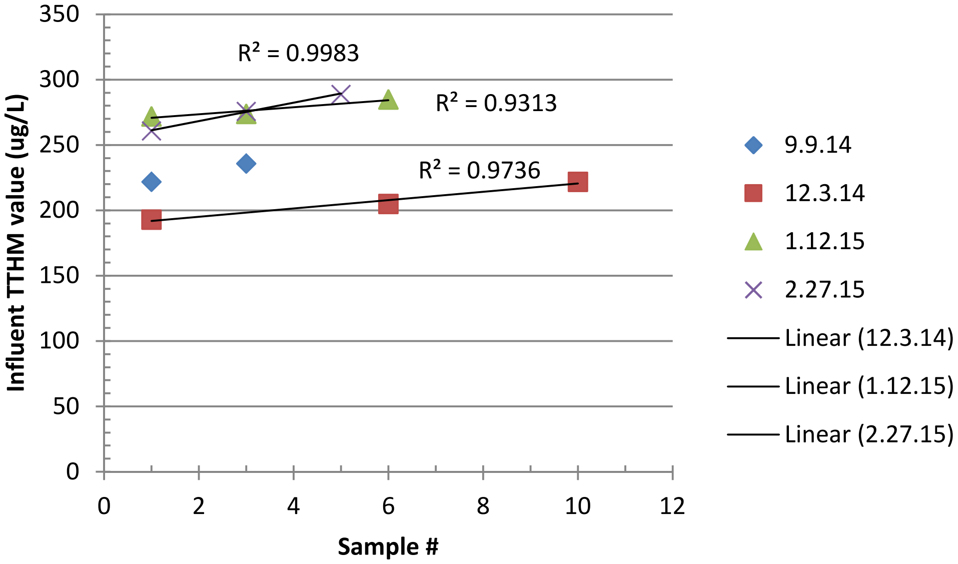


Figure F.1: Influent TTHM value vs. the sample number (in order of sampling) for sampling events on 9.9.14, 12.3.13, 1.12.15, and 2.27.15

Table F.2 shows the sampling date, influent TTHM range, and influent THM value used for each sample. Below are examples for calculating chloroform influent values for sample 7-K1.5f7a5L0.75 on 12.3.14 and sample 5-25-k1.5f7a10L3 on 2.27.15. These methods can be used for each THM species and sample.

Sample 7-K1.5f7a5L0.75 was the first sample taken of four between two influent values, meaning there were five increments between samples. The value of chloroform for this sample is calculated below using data from table F.2:

$$\left(140\frac{ug}{L} - 130\frac{ug}{L}\right)\left(\frac{1}{5}\right) + 130\frac{ug}{L} = 132\frac{ug}{L}$$

Since only one sample was taken between influent samples on 2.27.15, the influent samples taken on either side could be averages. The value of chloroform for sample 5-25-k1.5f7a10L3 is calculated below using data from table F.2:

$$\frac{170\frac{ug}{L} + 180\frac{ug}{L}}{2} = 175\frac{ug}{L}$$

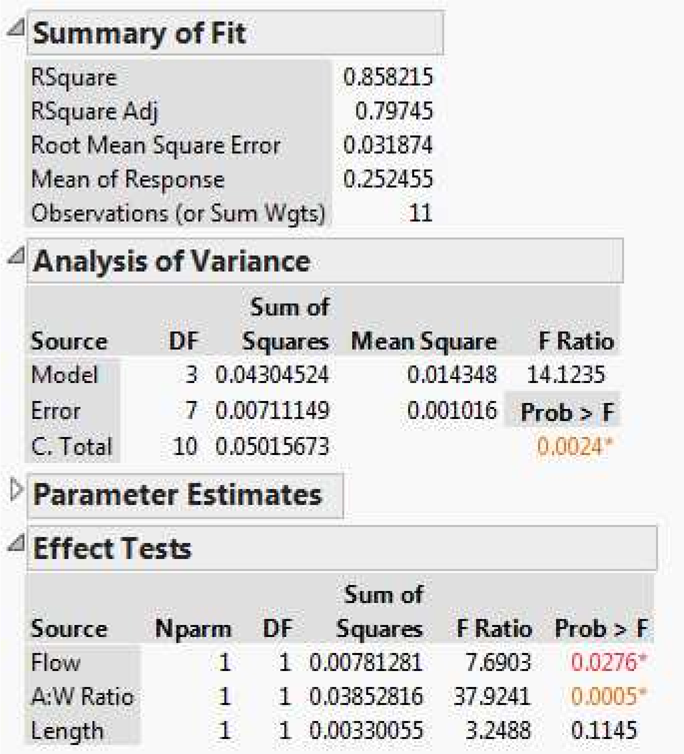
Table F.2: Influent THM values used for each sample on 5.15.14, 5.30.14, 9.9.14, 12.3.14, 1.12.15, and 2.27.25 sampling events

Sampling Date	Sample ID	TTHM Range (ug/L)	$CHCl_3$ (ug/L)	$CHCl_2Br$ (ug/L)	$CHClBr_2$ (ug/L)	$CHBr_3$ (ug/L)	TTHM (ug/L)
5.15.14	0.72	13	160	22	22	21	225
	1.82		170	23	23	22	238
	3.67		160	22	22	21	225
	7.47		170	23	23	22	238
5.30.14	0.72	27	190	26	26	25	267
	1.82		190	26	26	25	267
	3.67		180	25	25	24	254
	7 gpm		200	28	27	26	281
9.9.14	1-NMf5a20-9.9.14 INF	14	150	22	25	25	222

	2-NMf5a30-9.9.14		155	22.5	26	25.5	229
	3-NMf7.5a10-9.9.14 INF		160	23	27	26	236
12.3.14	R6-K1.5f7a20L0.75 INF	29	130	21	24	18	193
	7-K1.5f7a5L0.75		132	21	24.2	18.2	195.4
	8-K1.5f4a5L0.75		134	21	24.4	18.4	197.8
	R1-K1.5f1a10L0.75		136	21	24.6	18.6	200.2
	9-K1.5f1a5L0.75		138	21	24.8	18.8	202.6
	R17-K1.5f7a10L3 INF		140	21	25	19	205
	10-K1.5f7a5L3		142.5	21.5	25.75	19.5	209.25
	11-K1.5f4a5L3		145	22	26.5	20	213.5
	R13-K1.5f1a10L3		147.5	22.5	27.25	20.5	217.75
	12-K1.5f1a5L3 INF		150	23	28	21	222
1.12.15	C1-K1.5f7a10L1.5 INF	13	190	28	31	23	272
	C2-K1.5f5a5L2.25		190	28.5	31	23.5	273
	C3-K1f5a20L1.61 INF		190	29	31	24	274
	C5-K1f6a10L1.61		196.67	29	31.67	24	281.34
	C4-K1f4a20L2.15		193.33	29	31.33	24	277.66
	C6-K1f7a5L0.54 INF		200	29	32	24	285
2.27.15	4-25-k1.5f1a10L3 inf	28	170	29	30	32	261
	5-25-k1.5f7a10L3		175	29.5	31	33	268.5
	1-25-k1.5f1a10L0.75 inf		180	30	32	34	276
	2-25-k1.5f4a10L0.75		185	30.5	32.5	34.5	282.5

	3-25-k1.5f7a10L0.75 inf		190	31	33	35	289

Appendix G: JMP Statistical Output



Summary of Fit

RSquare	0.858215
RSquare Adj	0.79745
Root Mean Square Error	0.031874
Mean of Response	0.252455
Observations (or Sum Wgts)	11

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	0.04304524	0.014348	14.1235
Error	7	0.00711149	0.001016	Prob > F
C. Total	10	0.05015673		0.0024*

Parameter Estimates

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Flow	1	1	0.00781281	7.6903	0.0276*
A:W Ratio	1	1	0.03852816	37.9241	0.0005*
Length	1	1	0.00330055	3.2488	0.1145

Figure G.1: JMP output with ANOVA for initial Komax study on 10.1.14

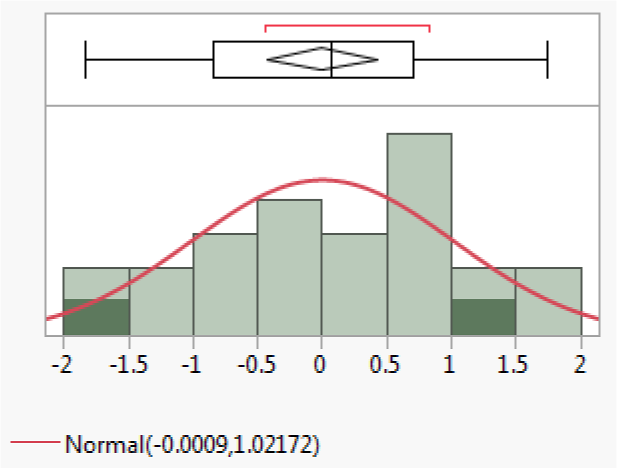
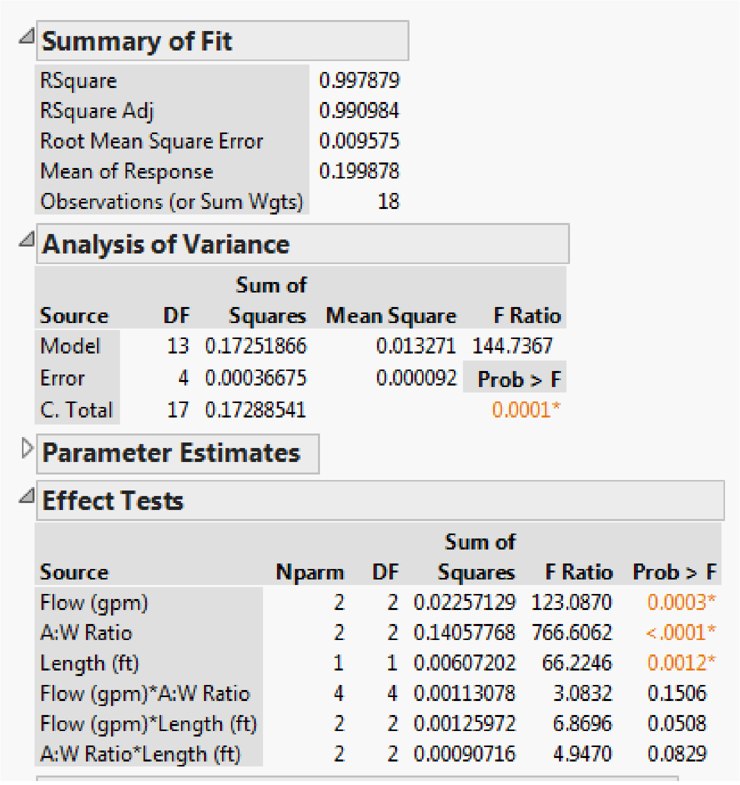
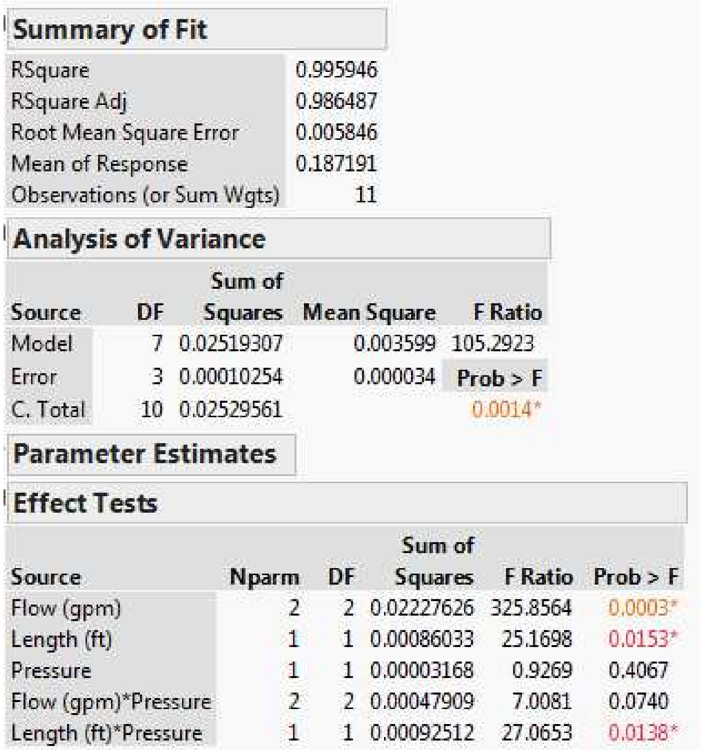


Figure G.2: Studentized residuals of final data for analysis overlaid with normal distribution (Output from JMP Pro 11)



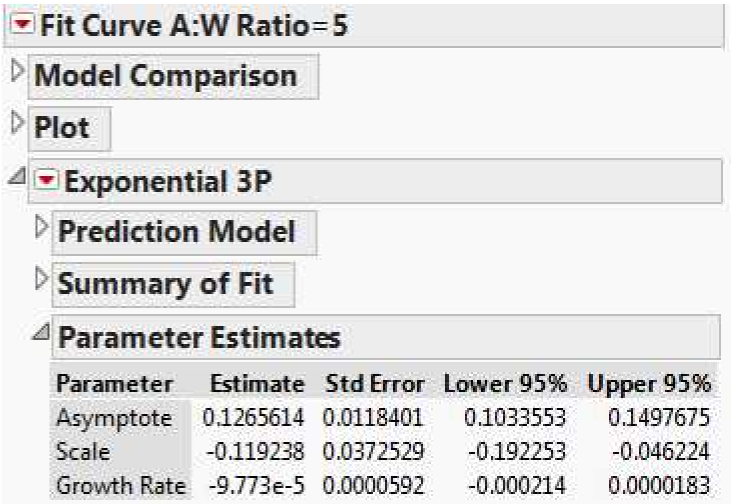
```
Summary of Fit
RSquare                        0.997879
RSquare Adj                    0.990984
Root Mean Square Error         0.009575
Mean of Response               0.199878
Observations (or Sum Wgts)           18

Analysis of Variance
                      Sum of
Source      DF       Squares   Mean Square    F Ratio
Model       13    0.17251866      0.013271   144.7367
Error        4    0.00036675      0.000092   Prob > F
C. Total    17    0.17288541                  0.0001*

Parameter Estimates

Effect Tests
                                               Sum of
Source                     Nparm   DF         Squares    F Ratio   Prob > F
Flow (gpm)                     2    2      0.02257129   123.0870    0.0003*
A:W Ratio                      2    2      0.14057768   766.6062    <.0001*
Length (ft)                    1    1      0.00607202    66.2246    0.0012*
Flow (gpm)*A:W Ratio           4    4      0.00113078     3.0832     0.1506
Flow (gpm)*Length (ft)         2    2      0.00125972     6.8696     0.0508
A:W Ratio*Length (ft)          2    2      0.00090716     4.9470     0.0829
```

Figure G.3: JMP output with ANOVA for final data points for 5:1, 10:1, and 20:1 A:W ratios



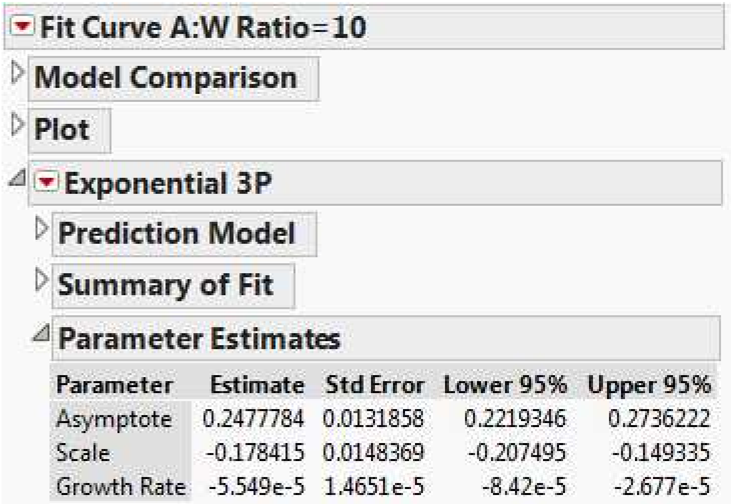
```
Summary of Fit
RSquare                        0.995946
RSquare Adj                    0.986487
Root Mean Square Error         0.005846
Mean of Response               0.187191
Observations (or Sum Wgts)           11

Analysis of Variance
                      Sum of
Source      DF       Squares   Mean Square    F Ratio
Model        7    0.02519307      0.003599   105.2923
Error        3    0.00010254      0.000034   Prob > F
C. Total    10    0.02529561                  0.0014*

Parameter Estimates

Effect Tests
                                           Sum of
Source                   Nparm   DF       Squares    F Ratio   Prob > F
Flow (gpm)                   2    2    0.02227626   325.8564    0.0003*
Length (ft)                  1    1    0.00086033    25.1698    0.0153*
Pressure                     1    1    0.00003168     0.9269     0.4067
Flow (gpm)*Pressure          2    2    0.00047909     7.0081     0.0740
Length (ft)*Pressure         1    1    0.00092512    27.0653    0.0138*
```

Figure G.4: JMP output with ANOVA for final data points for 10:1 A:W ratios at 40 and 25 psi



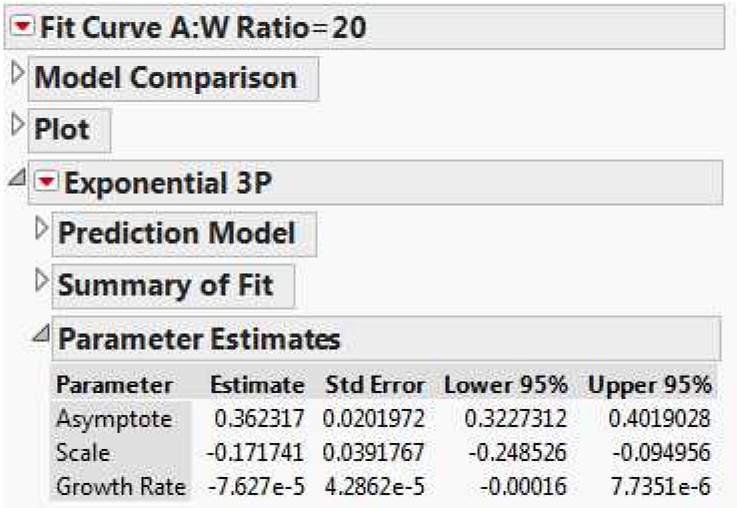
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1265614	0.0118401	0.1033553	0.1497675
Scale	-0.119238	0.0372529	-0.192253	-0.046224
Growth Rate	-9.773e-5	0.0000592	-0.000214	0.0000183

Figure G.5: 5:1 A:W ratio model parameters using 3P Re' TTHM model and final data points excluding confirmation trials (created using JMP® Pro 11)



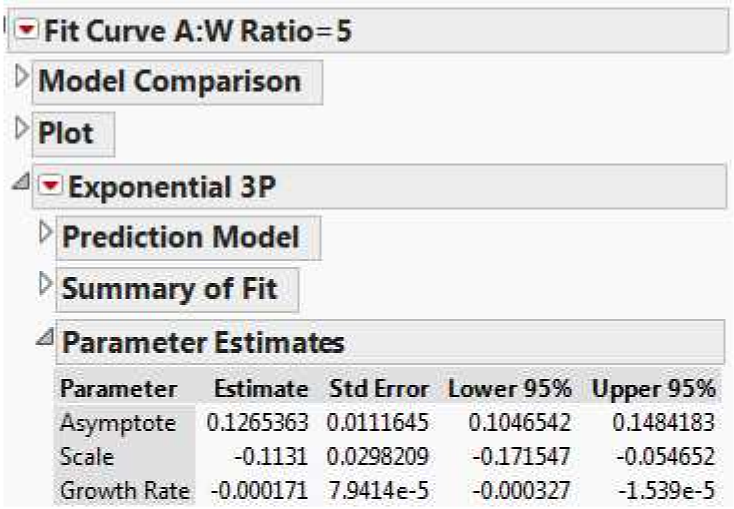
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.2477784	0.0131858	0.2219346	0.2736222
Scale	-0.178415	0.0148369	-0.207495	-0.149335
Growth Rate	-5.549e-5	1.4651e-5	-8.42e-5	-2.677e-5

Figure G.6: 10:1 A:W ratio model parameters using 3P Re' TTHM model and final data points excluding confirmation trials (created using JMP® Pro 11)



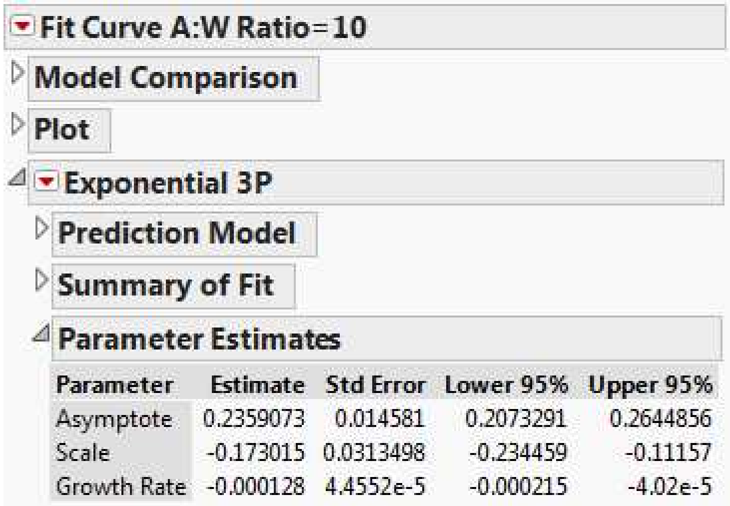
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.362317	0.0201972	0.3227312	0.4019028
Scale	-0.171741	0.0391767	-0.248526	-0.094956
Growth Rate	-7.627e-5	4.2862e-5	-0.00016	7.7351e-6

Figure G.7: 20:1 A:W ratio model parameters using 3P Re' TTHM model and final data points excluding confirmation trials (created using JMP® Pro 11)



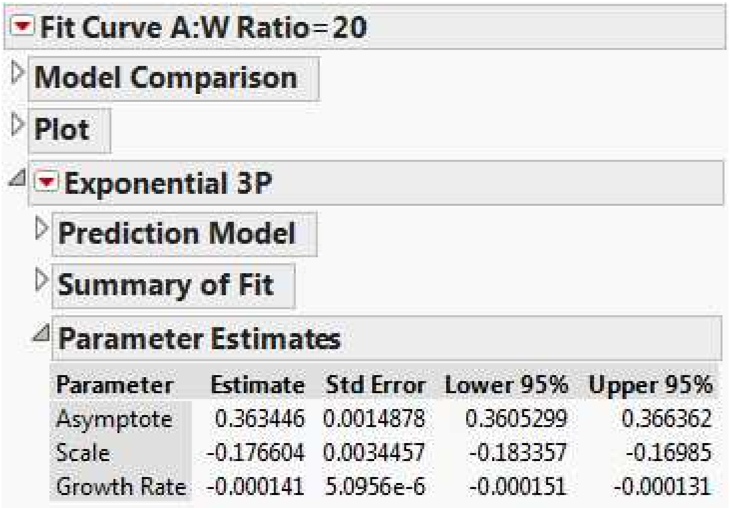
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1265363	0.0111645	0.1046542	0.1484183
Scale	-0.1131	0.0298209	-0.171547	-0.054652
Growth Rate	-0.000171	7.9414e-5	-0.000327	-1.539e-5

Figure G.8: 5:1 A:W ratio model parameters using 3P Re_{Komax} TTHM model and final data points excluding confirmation trials (created using JMP® Pro 11)



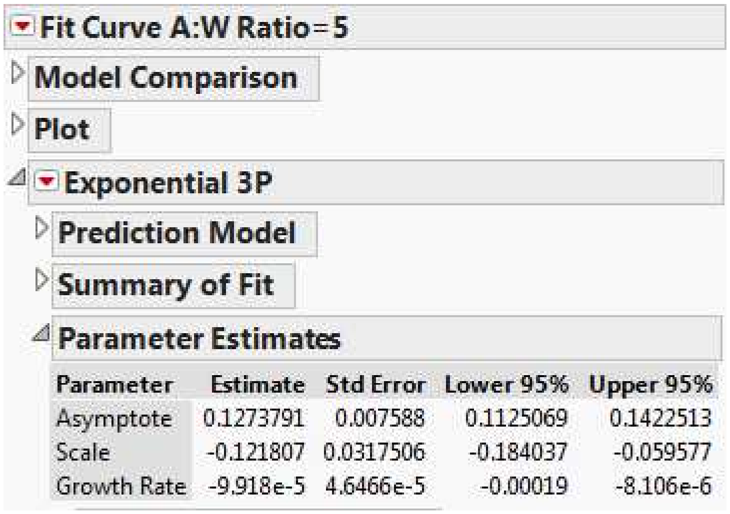
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.2359073	0.014581	0.2073291	0.2644856
Scale	-0.173015	0.0313498	-0.234459	-0.11157
Growth Rate	-0.000128	4.4552e-5	-0.000215	-4.02e-5

Figure G.9: 10:1 A:W ratio model parameters using 3P Re_{Komax} TTHM model and final data points excluding confirmation trials (created using JMP® Pro 11)



Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.363446	0.0014878	0.3605299	0.366362
Scale	-0.176604	0.0034457	-0.183357	-0.16985
Growth Rate	-0.000141	5.0956e-6	-0.000151	-0.000131

Figure G.10: 20:1 A:W ratio model parameters using 3P Re_{Komax} TTHM model and final data points excluding confirmation trials (created using JMP® Pro 11)


Fit Curve A:W Ratio=5

Model Comparison

Plot

Exponential 3P

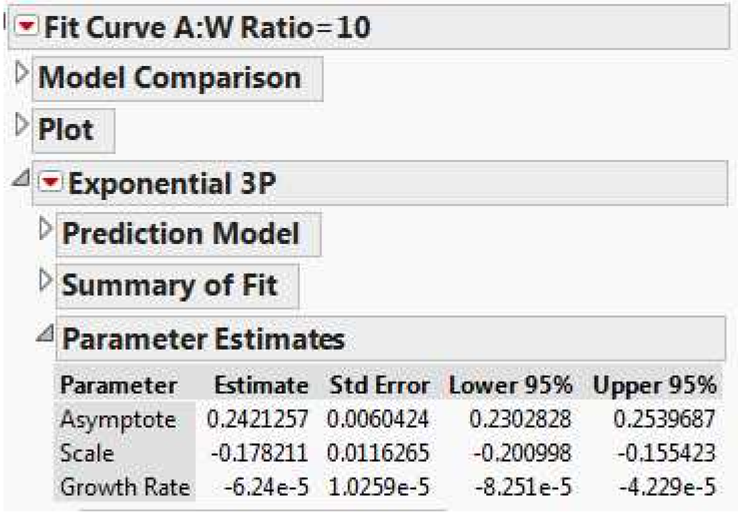
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1273791	0.007588	0.1125069	0.1422513
Scale	-0.121807	0.0317506	-0.184037	-0.059577
Growth Rate	-9.918e-5	4.6466e-5	-0.00019	-8.106e-6

Figure G.11: 5:1 A:W ratio model parameters using 3P Re' TTHM model and final data points including confirmation trials (created using JMP® Pro 11)


Fit Curve A:W Ratio=10

Model Comparison

Plot

Exponential 3P

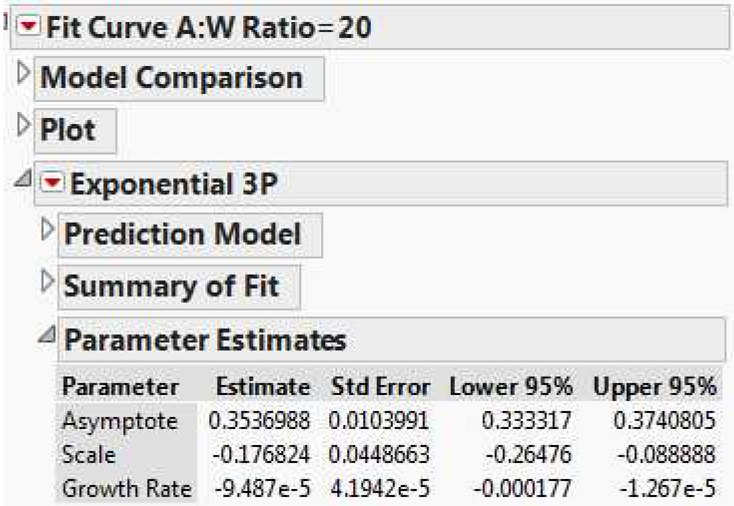
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.2421257	0.0060424	0.2302828	0.2539687
Scale	-0.178211	0.0116265	-0.200998	-0.155423
Growth Rate	-6.24e-5	1.0259e-5	-8.251e-5	-4.229e-5

Figure G.12: 10:1 A:W ratio model parameters using 3P Re' TTHM model and final data points including confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=20

Model Comparison

Plot

Exponential 3P

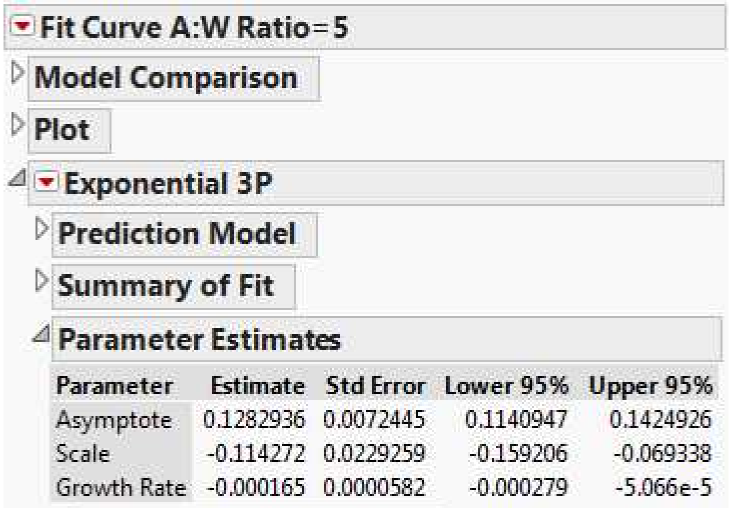
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3536988	0.0103991	0.333317	0.3740805
Scale	-0.176824	0.0448663	-0.26476	-0.088888
Growth Rate	-9.487e-5	4.1942e-5	-0.000177	-1.267e-5

Figure G.13: 20:1 A:W ratio model parameters using 3P Re’ TTHM model and final data points including confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=5

Model Comparison

Plot

Exponential 3P

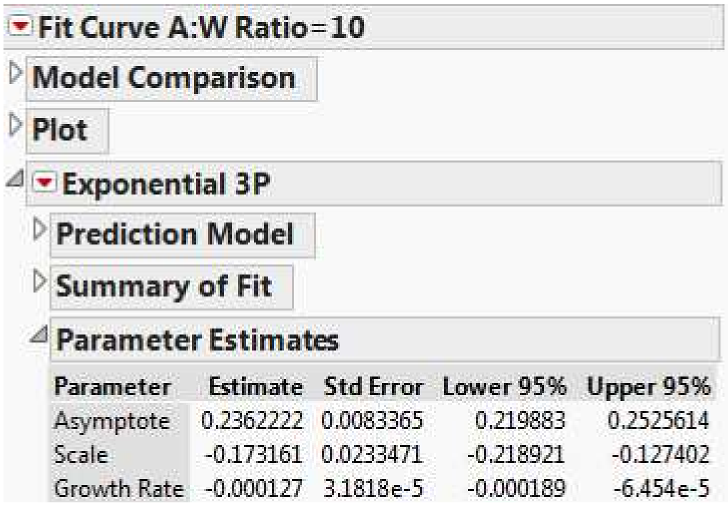
Prediction Model

Summary of Fit

Parameter Estimates

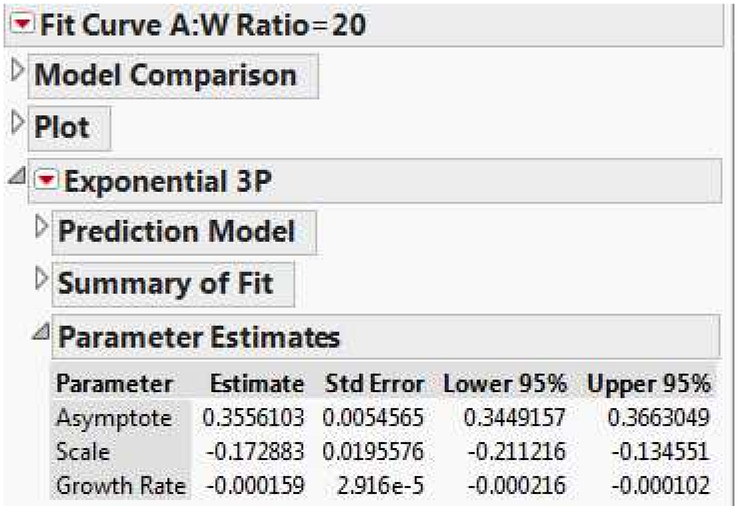
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1282936	0.0072445	0.1140947	0.1424926
Scale	-0.114272	0.0229259	-0.159206	-0.069338
Growth Rate	-0.000165	0.0000582	-0.000279	-5.066e-5

Figure G.14: 5:1 A:W ratio model parameters using 3P Re_{Komax} TTHM model and final data points including confirmation trials (created using JMP® Pro 11)



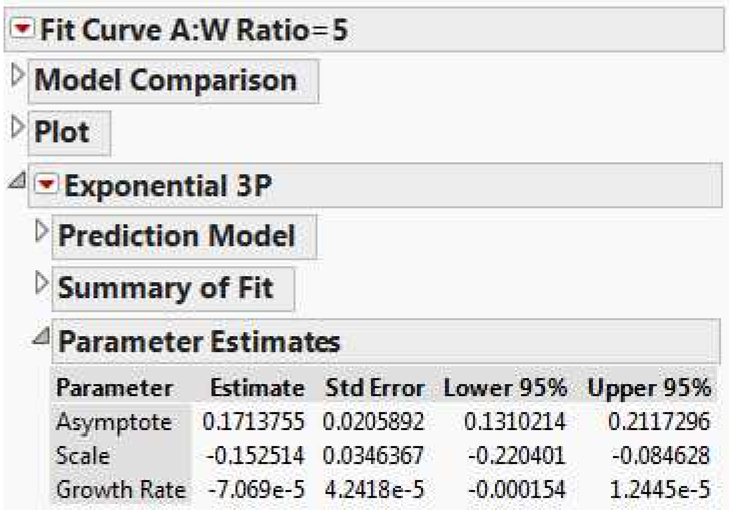
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.2362222	0.0083365	0.219883	0.2525614
Scale	-0.173161	0.0233471	-0.218921	-0.127402
Growth Rate	-0.000127	3.1818e-5	-0.000189	-6.454e-5

Figure G.15: 10:1 A:W ratio model parameters using 3P Re_{Komax} TTHM model and final data points including confirmation trials (created using JMP® Pro 11)



Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3556103	0.0054565	0.3449157	0.3663049
Scale	-0.172883	0.0195576	-0.211216	-0.134551
Growth Rate	-0.000159	2.916e-5	-0.000216	-0.000102

Figure G.16: 20:1 A:W ratio model parameters using 3P Re_{Komax} TTHM model and final data points including confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=5

Model Comparison

Plot

Exponential 3P

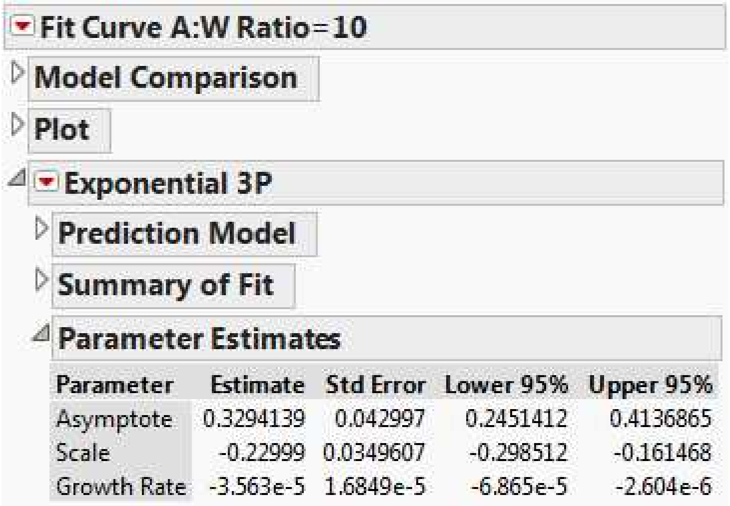
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1713755	0.0205892	0.1310214	0.2117296
Scale	-0.152514	0.0346367	-0.220401	-0.084628
Growth Rate	-7.069e-5	4.2418e-5	-0.000154	1.2445e-5

Figure G.17: 5:1 A:W ratio chloroform model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=10

Model Comparison

Plot

Exponential 3P

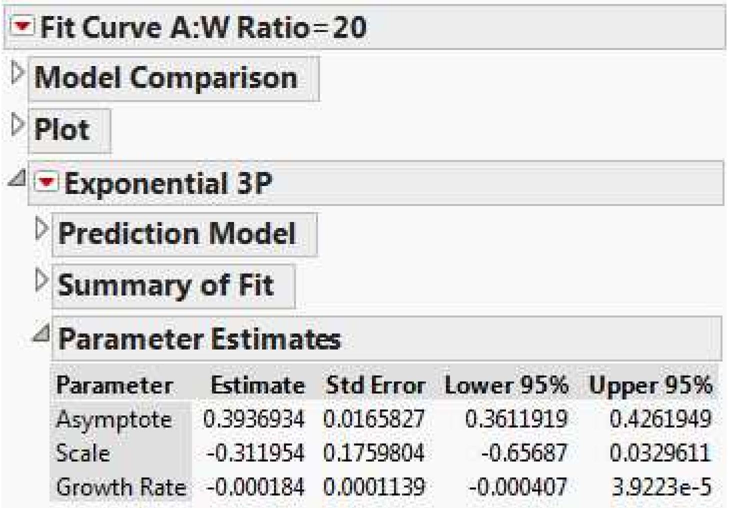
Prediction Model

Summary of Fit

Parameter Estimates

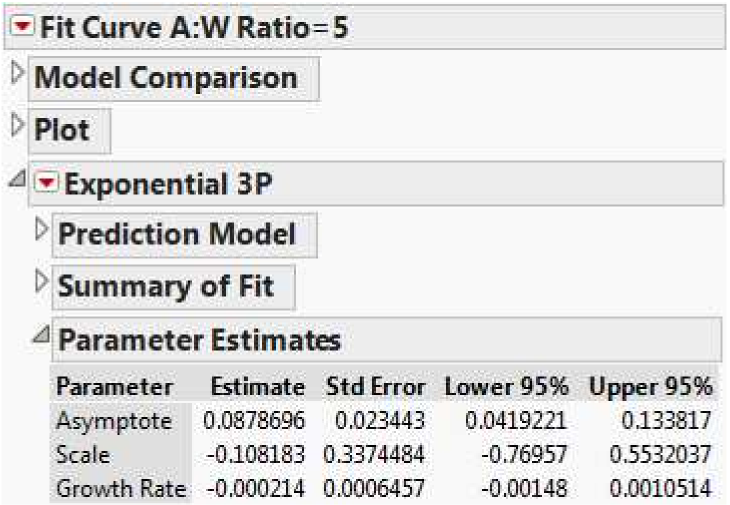
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3294139	0.042997	0.2451412	0.4136865
Scale	-0.22999	0.0349607	-0.298512	-0.161468
Growth Rate	-3.563e-5	1.6849e-5	-6.865e-5	-2.604e-6

Figure G.18: 10:1 A:W ratio chloroform model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



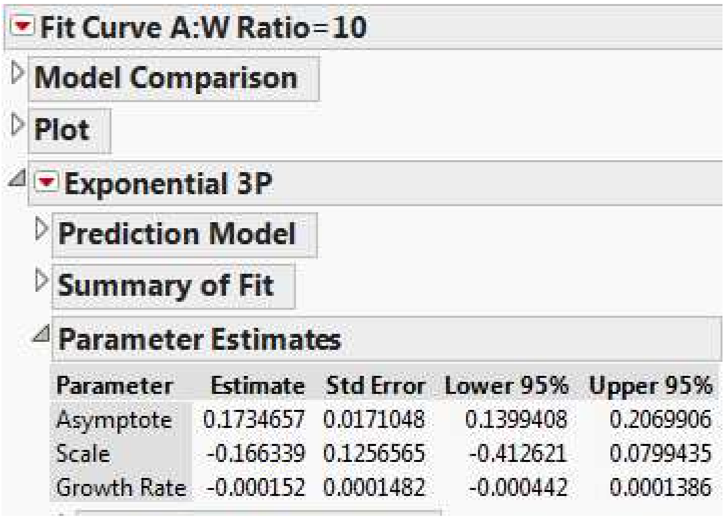
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3936934	0.0165827	0.3611919	0.4261949
Scale	-0.311954	0.1759804	-0.65687	0.0329611
Growth Rate	-0.000184	0.0001139	-0.000407	3.9223e-5

Figure G.19: 20:1 A:W ratio chloroform model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



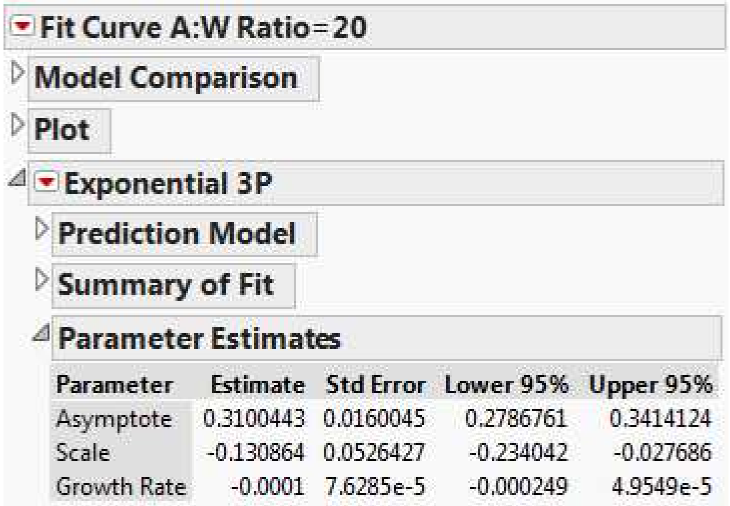
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.0878696	0.023443	0.0419221	0.133817
Scale	-0.108183	0.3374484	-0.76957	0.5532037
Growth Rate	-0.000214	0.0006457	-0.00148	0.0010514

Figure G.20: 5:1 A:W ratio bromodichloromethane model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



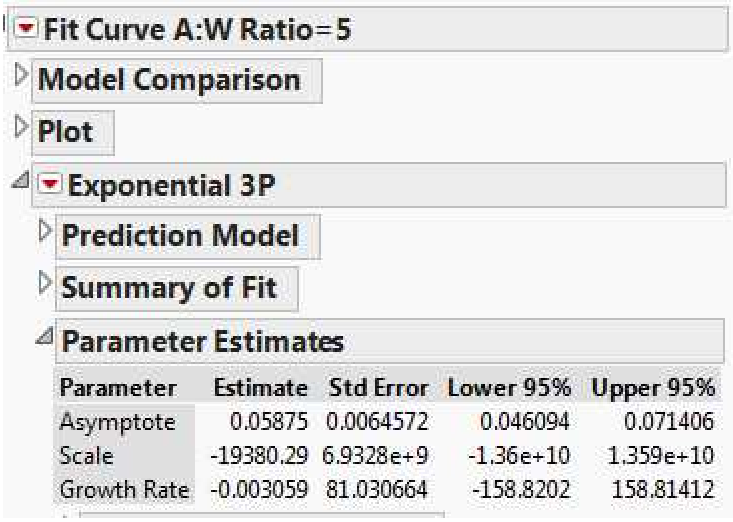
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1734657	0.0171048	0.1399408	0.2069906
Scale	-0.166339	0.1256565	-0.412621	0.0799435
Growth Rate	-0.000152	0.0001482	-0.000442	0.0001386

Figure G.21: 10:1 A:W ratio bromodichloromethane model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



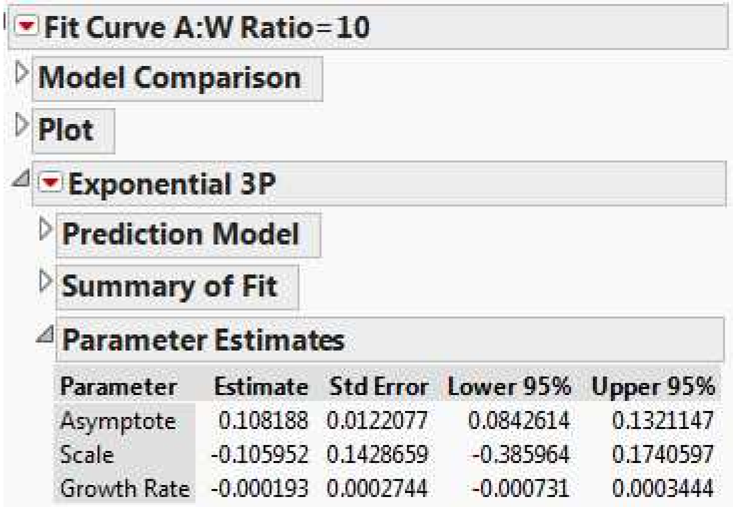
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3100443	0.0160045	0.2786761	0.3414124
Scale	-0.130864	0.0526427	-0.234042	-0.027686
Growth Rate	-0.0001	7.6285e-5	-0.000249	4.9549e-5

Figure G.22: 20:1 A:W ratio bromodichloromethane model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



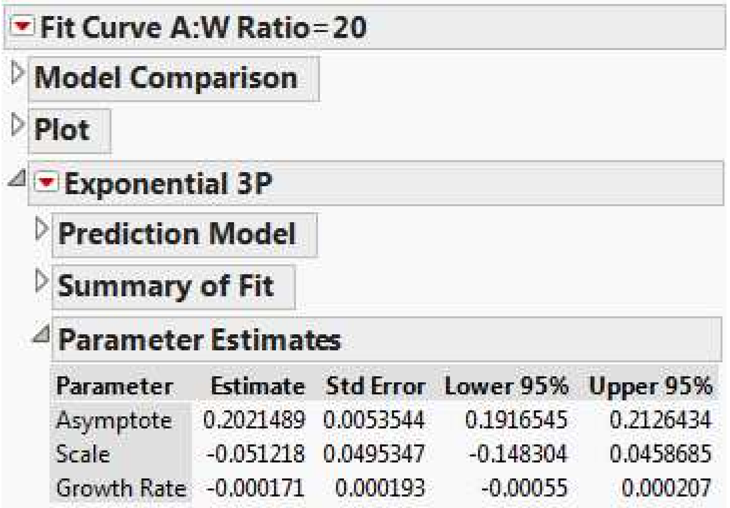
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.05875	0.0064572	0.046094	0.071406
Scale	-19380.29	6.9328e+9	-1.36e+10	1.359e+10
Growth Rate	-0.003059	81.030664	-158.8202	158.81412

Figure G.23: 5:1 A:W ratio dibromochloromethane model parameters using 3P Re' model and final data points excluding confirmation trials and sample 10 (created using JMP® Pro 11)



Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.108188	0.0122077	0.0842614	0.1321147
Scale	-0.105952	0.1428659	-0.385964	0.1740597
Growth Rate	-0.000193	0.0002744	-0.000731	0.0003444

Figure G.24: 10:1 A:W ratio dibromochloromethane model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=20

Model Comparison

Plot

Exponential 3P

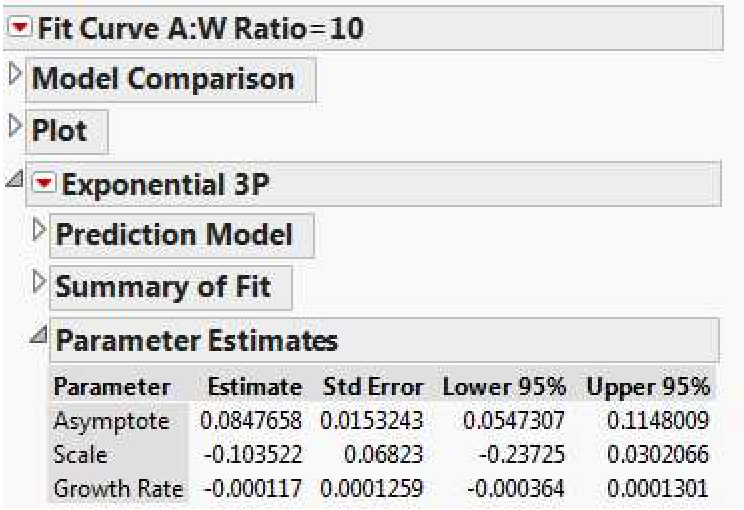
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.2021489	0.0053544	0.1916545	0.2126434
Scale	-0.051218	0.0495347	-0.148304	0.0458685
Growth Rate	-0.000171	0.000193	-0.00055	0.000207

Figure G.25: 20:1 A:W ratio dibromochloromethane model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=10

Model Comparison

Plot

Exponential 3P

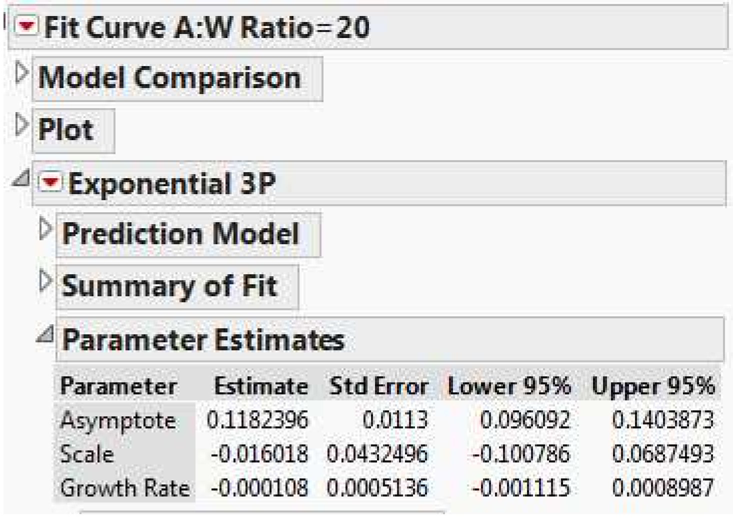
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.0847658	0.0153243	0.0547307	0.1148009
Scale	-0.103522	0.06823	-0.23725	0.0302066
Growth Rate	-0.000117	0.0001259	-0.000364	0.0001301

Figure G.26: 10:1 A:W ratio bromoform model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=20

Model Comparison

Plot

Exponential 3P

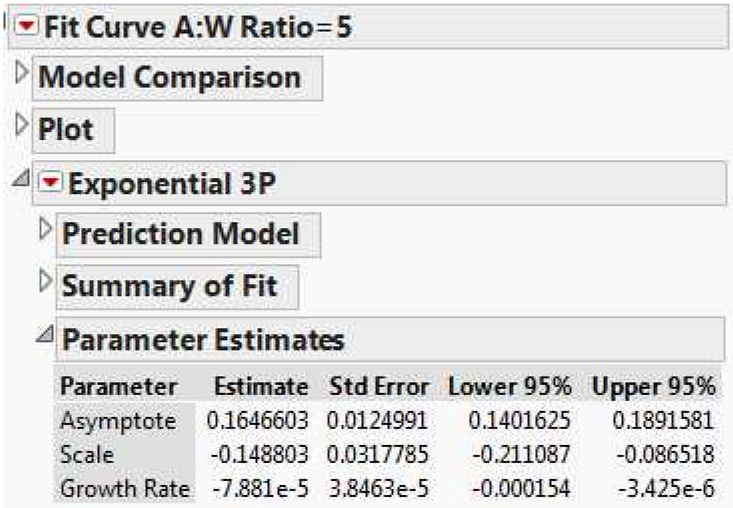
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1182396	0.0113	0.096092	0.1403873
Scale	-0.016018	0.0432496	-0.100786	0.0687493
Growth Rate	-0.000108	0.0005136	-0.001115	0.0008987

Figure G.27: 20:1 A:W ratio bromoform model parameters using 3P Re' model and final data points excluding confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=5

Model Comparison

Plot

Exponential 3P

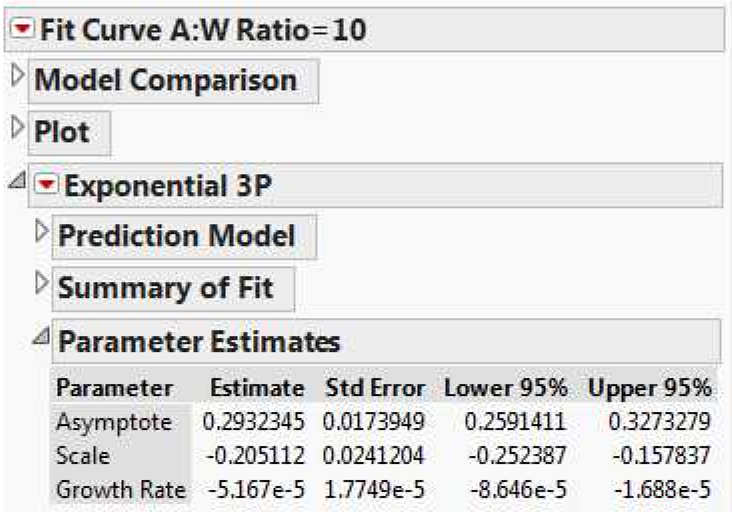
Prediction Model

Summary of Fit

Parameter Estimates

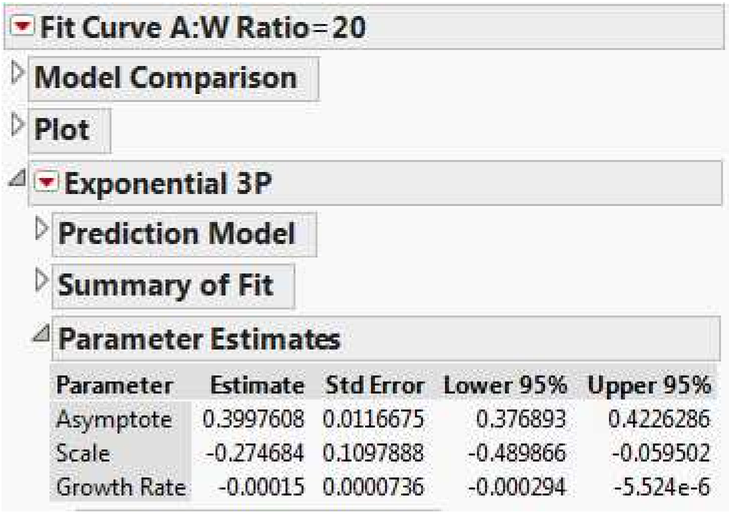
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1646603	0.0124991	0.1401625	0.1891581
Scale	-0.148803	0.0317785	-0.211087	-0.086518
Growth Rate	-7.881e-5	3.8463e-5	-0.000154	-3.425e-6

Figure G.28: 5:1 A:W ratio chloroform model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



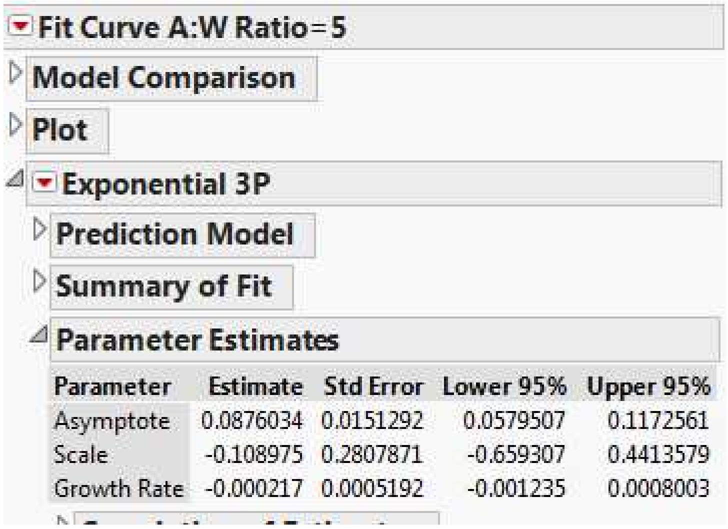
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.2932345	0.0173949	0.2591411	0.3273279
Scale	-0.205112	0.0241204	-0.252387	-0.157837
Growth Rate	-5.167e-5	1.7749e-5	-8.646e-5	-1.688e-5

Figure G.29: 10:1 A:W ratio chloroform model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



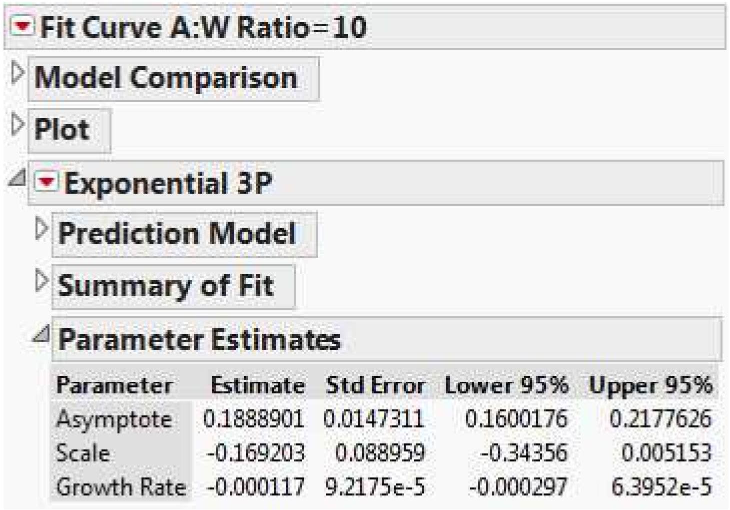
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3997608	0.0116675	0.376893	0.4226286
Scale	-0.274684	0.1097888	-0.489866	-0.059502
Growth Rate	-0.00015	0.0000736	-0.000294	-5.524e-6

Figure G.30: 20:1 A:W ratio chloroform model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



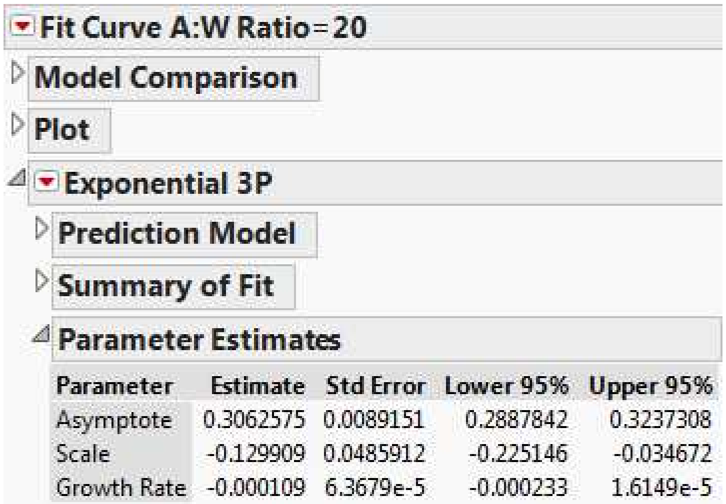
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.0876034	0.0151292	0.0579507	0.1172561
Scale	-0.108975	0.2807871	-0.659307	0.4413579
Growth Rate	-0.000217	0.0005192	-0.001235	0.0008003

Figure G.31: 5:1 A:W ratio bromodichloromethane model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



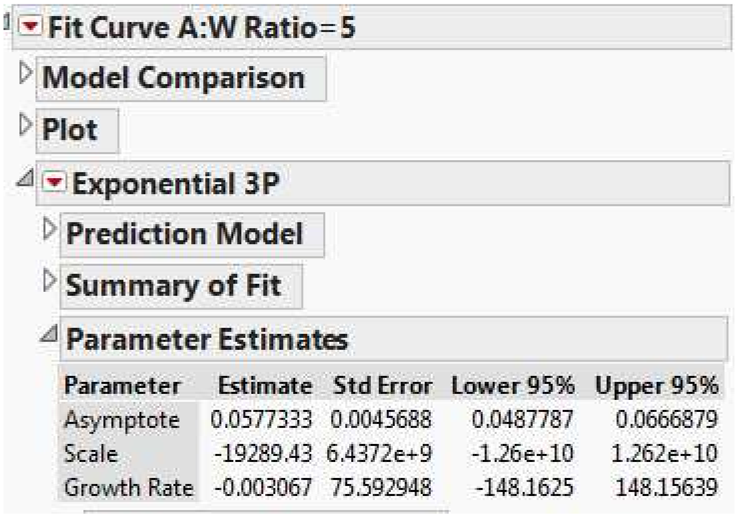
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1888901	0.0147311	0.1600176	0.2177626
Scale	-0.169203	0.088959	-0.34356	0.005153
Growth Rate	-0.000117	9.2175e-5	-0.000297	6.3952e-5

Figure G.32: 10:1 A:W ratio bromodichloromethane model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



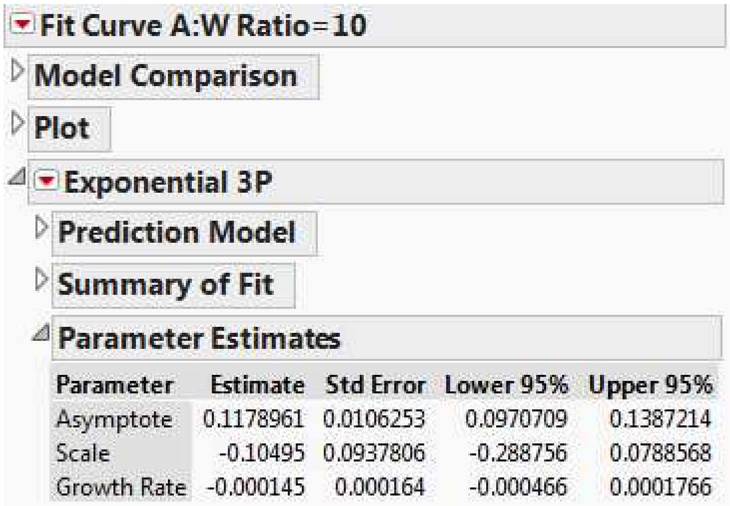
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.3062575	0.0089151	0.2887842	0.3237308
Scale	-0.129909	0.0485912	-0.225146	-0.034672
Growth Rate	-0.000109	6.3679e-5	-0.000233	1.6149e-5

Figure G.33: 20:1 A:W ratio bromodichloromethane model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.0577333	0.0045688	0.0487787	0.0666879
Scale	-19289.43	6.4372e+9	-1.26e+10	1.262e+10
Growth Rate	-0.003067	75.592948	-148.1625	148.15639

Figure G.34: 5:1 A:W ratio dibromochloromethane model parameters using 3P Re' model and final data points including confirmation trials and excluding sample 10 (created using JMP® Pro 11)



Fit Curve A:W Ratio=10

Model Comparison

Plot

Exponential 3P

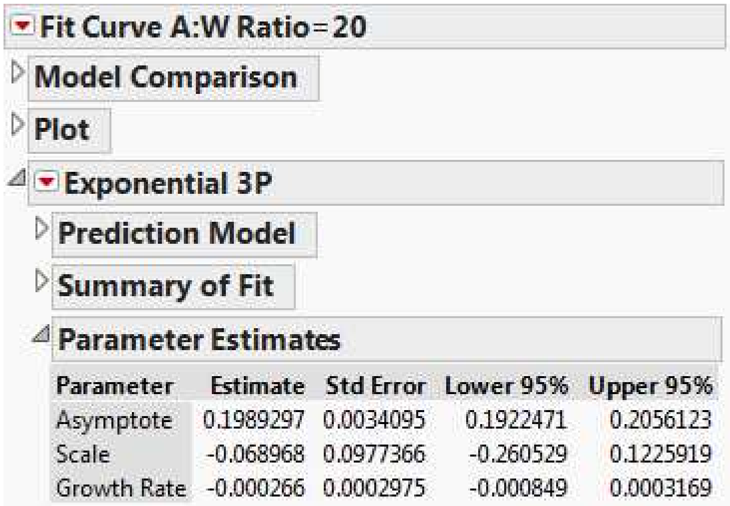
Prediction Model

Summary of Fit

Parameter Estimates

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1178961	0.0106253	0.0970709	0.1387214
Scale	-0.10495	0.0937806	-0.288756	0.0788568
Growth Rate	-0.000145	0.000164	-0.000466	0.0001766

Figure G35: 10:1 A:W ratio dibromochloromethane model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



Fit Curve A:W Ratio=20

Model Comparison

Plot

Exponential 3P

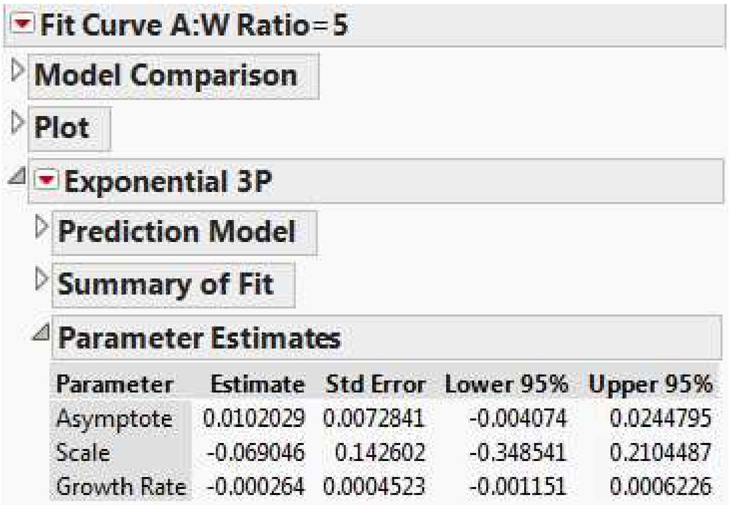
Prediction Model

Summary of Fit

Parameter Estimates

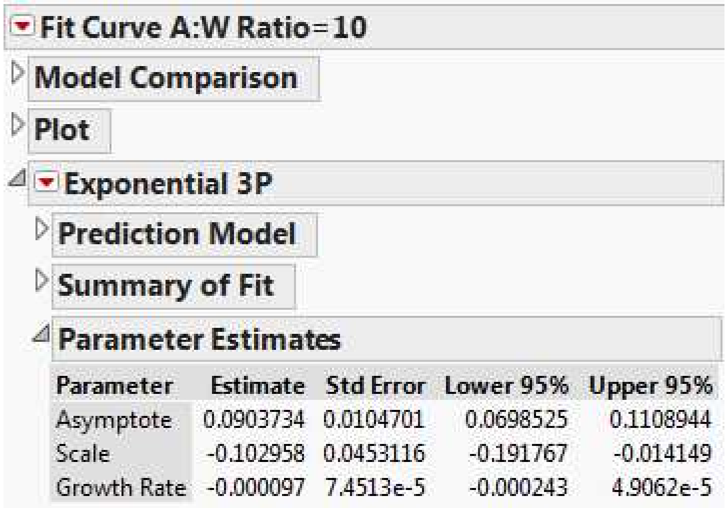
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1989297	0.0034095	0.1922471	0.2056123
Scale	-0.068968	0.0977366	-0.260529	0.1225919
Growth Rate	-0.000266	0.0002975	-0.000849	0.0003169

Figure G.36: 20:1 A:W ratio dibromochloromethane model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



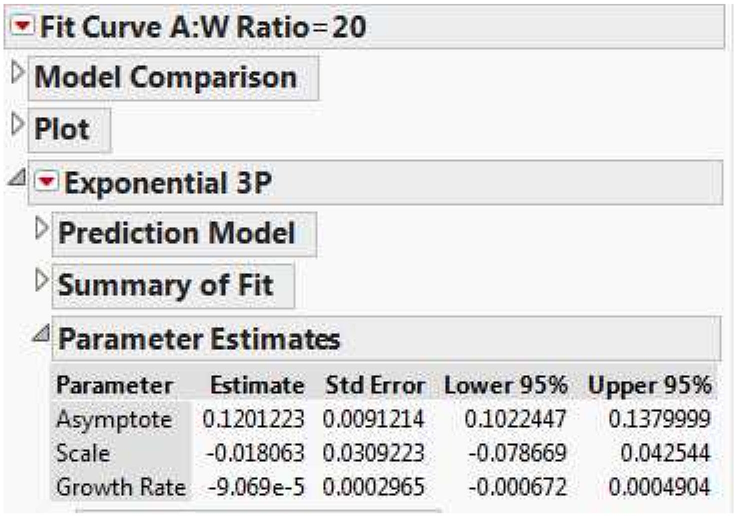
Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.0102029	0.0072841	-0.004074	0.0244795
Scale	-0.069046	0.142602	-0.348541	0.2104487
Growth Rate	-0.000264	0.0004523	-0.001151	0.0006226

Figure G.37: 5:1 A:W ratio bromoform model parameters using 3P Re' model and final data points excluding samples 10, C2, and C6 (created using JMP® Pro 11)



Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.0903734	0.0104701	0.0698525	0.1108944
Scale	-0.102958	0.0453116	-0.191767	-0.014149
Growth Rate	-0.000097	7.4513e-5	-0.000243	4.9062e-5

Figure G.38: 10:1 A:W ratio bromoform model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)



Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Asymptote	0.1201223	0.0091214	0.1022447	0.1379999
Scale	-0.018063	0.0309223	-0.078669	0.042544
Growth Rate	-9.069e-5	0.0002965	-0.000672	0.0004904

Figure G.39: 20:1 A:W ratio bromoform model parameters using 3P Re' model and final data points including confirmation trials (created using JMP® Pro 11)

Appendix H: Explanation of Data Samples and Analysis for 5:1 A:W, 10:1 A:W, 20:1 A:W, Control, Confirmation, and 25 psi Komax Static In-line Mixer Experiments

Table H.1 shows all the data points for the 5:1 A:W ratio experiment. All 5:1 A:W ratio samples were collected on 12/3/2014. No samples were rerun, but influent THM samples increased throughout the sampling period. For this reason influent samples were averaged throughout the sampling period so that each sample had its own influent value. Influent sample value calculations can be found in Appendix F.

Table H.1: All data points for 5:1 A:W experiment (Run on 12/3/2014 at 40 psi, 20 °C, and influent THM speciation of 68% chloroform, 11% bromodichloromethane, 12% dibromochloromethane, and 9% bromoform)

Sample	Flow (gpm)	A:W Ratio	Length (ft)	Diameter (in)	Mixer	Re'	% Removed	STDEV
1	1	5	0.75	1.5	Y	4415	4.74%	0.00%
2	4	5	0.75	1.5	Y	17659	9.00%	0.00%
3	7	5	0.75	1.5	Y	30903	13.51%	0.00%
4	1	5	3	1.5	Y	8829	8.33%	2.87%
5	4	5	3	1.5	Y	35317	12.88%	0.00%
6	7	5	3	1.5	Y	61805	11.59%	0.00%

Table H.2 shows every run that was performed for the 10:1 A:W experiment. Samples 1, 3, 5, 13, 15, and 17 were run on 10/01/2014, sample R15 and R17 were run on 10/27/2014, and samples R1, R13 and R17 were run on 12/3/2014. Samples run on 12/3/2014 used either influent sample values or averaged values between influent samples depending on the run placement due to that the influent THM concentrations increased as the run progressed. Several data points for the 10:1 experiment were run again for a few reasons. Samples 1, 13, and R17 had very large error bars, sample 15 was re-run in order to provide replication data, and sample 17 had removal that was drastically differed from what was expected. Shaded rows in Table H.3 indicate the data that was not used in the final experiment.

Table H.3: All data points for 10:1 A:W experiment including points not used in final analysis (Run on 10/01/2014, 10/27/2014 and 12/3/2014 at 40 psi, average of 18.9 °C, and average influent THM speciation of 69% chloroform, 10% bromodichloromethane, 12% dibromochloromethane, and 9% bromoform)

Sample ID	Flow (gpm)	A:W Ratio	Length (ft)	Diameter (in)	Mixer	Re'	% Removed	STDEV
1-K1.5f1a10L0.75	1	10	0.75	1.5	Y	4415	17.15%	4.16%
R1-K1.5f1a10L0.75	1	10	0.75	1.5	Y	4415	10.09%	0.00%
3-K1.5f4a10L0.75	4	10	0.75	1.5	Y	17659	17.84%	0.49%
5-K1.5f7a10L0.75	7	10	0.75	1.5	Y	30903	21.67%	0.49%
13-K1.5f1a10L3	1	10	3	1.5	Y	8829	19.76%	4.60%
R13-K1.5f1a10L3	1	10	3	1.5	Y	8829	15.04%	0.00%
15-K1.5f4a10L3	4	10	3	1.5	Y	35317	24.46%	0.49%
R15-K1.5f4a10L3	4	10	3	1.5	Y	35317	19.14%	0.27%
17-K1.5f7a10L3	7	10	3	1.5	Y	61805	20.45%	0.31%
R17-K1.5f7a10L3	7	10	3	1.5	Y	61805	25.09%	5.08%
R17-K1.5f7a10L3-2	7	10	3	1.5	Y	61805	24.63%	2.41%

Table H.4 shows all results from experiments run for the 20:1 A:W ratio study. All samples were run on 10/01/2014, except for sample R6 which was run on 12/3/2014. Sample 6 was re-run due to the fact that it had the largest error bars 20:1 study. Upon rerunning the sample, the standard deviation decreased from 3.93% to 0.37%. The shaded row indicates the original sample 6 was not used in the final analysis.

Table H.4: All data points for 20:1 A:W experiment including points not used in final analysis (Run on 10/01/2014 and 12/3/2014 at 40 psi, average of 18.3 °C, and average influent THM speciation of 70% chloroform, 10% bromodichloromethane, 11% dibromochloromethane, and 9% bromoform)

Sample ID	Flow (gpm)	A:W Ratio	Length (ft)	Diameter (in)	Mixer	Re'	% Removed	STDEV
2-K1.5f1a20L0.75	1	20	0.75	1.5	Y	4415	22.72%	0.49%
4-K1.5f4a20L0.75	4	20	0.75	1.5	Y	17659	30.37%	0.00%
6-K1.5f7a20L0.75	7	20	0.75	1.5	Y	30903	37.34%	3.93%
R6-K1.5f7a20L0.75	7	20	0.75	1.5	Y	30903	33.42%	0.37%
14-K1.5f1a20L3	1	20	3	1.5	Y	8829	30.03%	0.00%
16-K1.5f4a20L3	4	20	3	1.5	Y	35317	35.94%	2.95%
18-K1.5f7a20L3	7	20	3	1.5	Y	61805	36.48%	0.54%

*Note: Sample 18 was run at an A:W ratio of 18:1. A proportion was used in order to predict the removal at a 20:1 A:W ratio.

Tables H.5, H.6, and H.7 show the data for the control experiment, confirmation trials, and 25 psi trials, respectively. No samples were re-run for any of these studies.

Table H.5: All data points for full factorial control experiment (Run on 10/27/2014 at 40 psi, 18 °C, and influent THM speciation of 69% chloroform, 10% bromodichloromethane, 12% dibromochloromethane, and 9% bromoform)

Sample ID	Flow (gpm)	A:W Ratio	Length (ft)	Diameter (in)	Mixer	Re'	% Removed	STDEV
1-K1.5CLa0L3My	4	0	3	1.5	Yes	35317	2.05%	2.72%
2-K1.5CLa20L3My	4	20	3	1.5	Yes	35317	33.93%	NA
3-K1.5CLa0L0.75My	4	0	0.75	1.5	Yes	17659	5.12%	0.00%
4-K1.5CLa20L0.75My	4	20	0.75	1.5	Yes	17659	33.55%	0.00%
5-K1.5CLa0L0.75Mn	4	0	0.75	1.5	No	17659	5.12%	0.00%
6-K1.5CLa20L0.75Mn	4	20	0.75	1.5	No	17659	24.52%	0.27%
7-K1.5CLa0L3Mn	4	0	3	1.5	No	35317	6.08%	3.53%
8-K1.5CLa20L3Mn	4	20	3	1.5	No	35317	23.75%	0.27%

No standard deviation is available for sample 2 because only one sample was sent out for analysis. This is because the pressure dropped down to 36 for the second sample meaning it may not have provided an accurate removal value.

Table H.6: All data points for confirmation trials (Run on 1/12/2015 at 40 psi, 18 °C, and influent THM speciation of 70% chloroform, 10% bromodichloromethane, 11% dibromochloromethane, and 9% bromoform)

Sample ID	Flow (gpm)	A:W Ratio	Length (ft)	Diameter (in)	Mixer	Re'	% Removed	STDEV
C1-K1.5f7a10L1.5	7	10	1.5	1.5	Y	43703	22.98%	0.26%
C2-K1.5f5a5L2.25	5	5	2.25	1.5	Y	38232	13.37%	0.26%
C3-K1f5a20L1.61	5	20	1.61	1	Y	61493	36.13%	0.00%
C4-K1f4a20L2.15	4	20	2.15	1	Y	56849	33.53%	0.50%
C5-K1f6a10L1.61	6	10	1.61	1	Y	73792	23.65%	0.51%
C6-K1f7a5L0.54	7	5	0.54	1	Y	49858	12.11%	0.25%

Table H.7: All data points for 25 psi 10:1 A:W ratio study (Run on 2/27/2015 at 40 psi, 18 °C, and influent THM speciation of 65% chloroform, 11% bromodichloromethane, 12% dibromochloromethane, and 12% bromoform)

Sample ID	Flow (gpm)	A:W Ratio	Length (ft)	Diameter (in)	Mixer	Re'	% Removed	STDEV
1-25-k1.5f1a10L0.75	1	10	0.75	1.5	Y	4415	14.13%	0.00%

2-25-k1.5f4a10L0.75	4	10	0.75	1.5	Y	17659	17.88%	3.00%
3-25-k1.5f7a10L0.75	7	10	0.75	1.5	Y	30903	24.57%	2.94%
4-25-k1.5f1a10L3	1	10	3	1.5	Y	8829	13.98%	0.27%
5-25-k1.5f7a10L3	7	10	3	1.5	Y	61805	24.58%	0.79%

Appendix I: Estimating Head Loss for Komax Static In-line Mixers

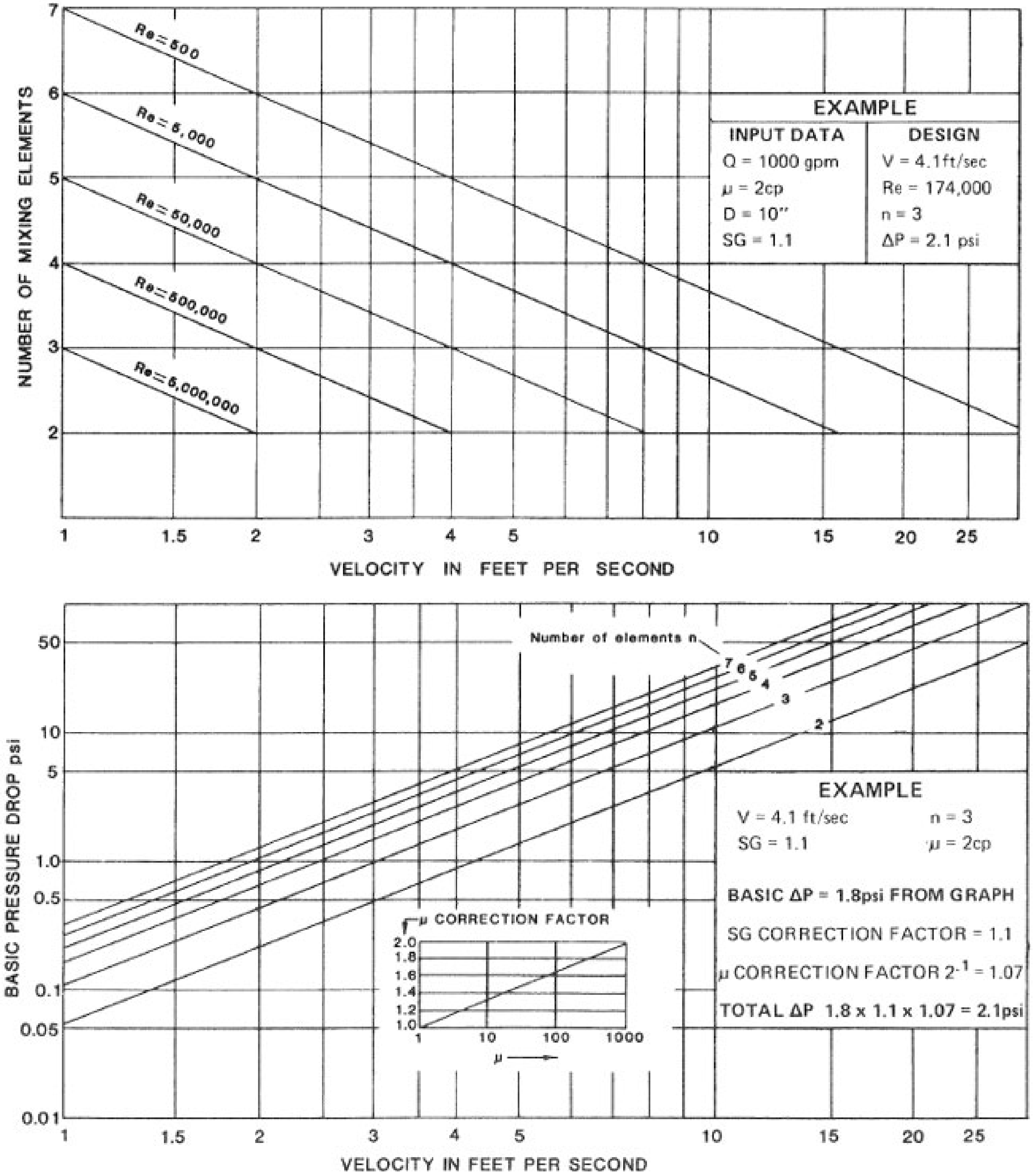


Figure I.1: Graphs used to estimate pressure drop for Komax Static In-line Mixers (Komax Systems, Inc. Triple Action Static Mixer)

Appendix J: Re’, Re$_{\text{Komax}}$, and Air Flow Rates for Various Settings

Tables K.1 and K.2 show values for Re’, Re$_{\text{Komax}}$, and air flow rates for various factor settings for 1.5 inch and 1 inch diameter Komax static in-line mixers, respectively.

Table K.1: Re’, Re$_{\text{Komax}}$, and air flow rates for various factor settings for 1.5 inch Komax static in-line mixer

Q (gal/min)	d (in)	d (ft)	V (ft/s)	# of unit	L (ft)	v (ft^2/s)	Re"= V*(((SQRT(d*L))/v)	Re$_{\text{Komax}}$	Air (10) scfm	Air (20 scfm)
1	1.61	0.13	0.16	1	0.75	0.00001131	4414.68	1857.76	1.34	2.67
2	1.61	0.13	0.31	1	0.75	0.00001131	8829.35	3715.53	2.67	5.35
3	1.61	0.13	0.47	1	0.75	0.00001131	13244.03	5573.29	4.01	8.02
4	1.61	0.13	0.63	1	0.75	0.00001131	17658.70	7431.05	5.35	10.70
5	1.61	0.13	0.79	1	0.75	0.00001131	22073.38	9288.82	6.68	13.37
6	1.61	0.13	0.94	1	0.75	0.00001131	26488.05	11146.58	8.02	16.04
7	1.61	0.13	1.10	1	0.75	0.00001131	30902.73	13004.35	9.36	18.72
8	1.61	0.13	1.26	1	0.75	0.00001131	35317.40	14862.11	10.70	21.39
9	1.61	0.13	1.42	1	0.75	0.00001131	39732.08	16719.87	12.03	24.06
10	1.61	0.13	1.57	1	0.75	0.00001131	44146.75	18577.64	13.37	26.74
1	1.61	0.13	0.16	2	1.5	0.00001131	6243.29	3715.53	1.34	2.67
2	1.61	0.13	0.31	2	1.5	0.00001131	12486.59	7431.05	2.67	5.35
3	1.61	0.13	0.47	2	1.5	0.00001131	18729.88	11146.58	4.01	8.02
4	1.61	0.13	0.63	2	1.5	0.00001131	24973.17	14862.11	5.35	10.70
5	1.61	0.13	0.79	2	1.5	0.00001131	31216.47	18577.64	6.68	13.37
6	1.61	0.13	0.94	2	1.5	0.00001131	37459.76	22293.16	8.02	16.04
7	1.61	0.13	1.10	2	1.5	0.00001131	43703.05	26008.69	9.36	18.72
8	1.61	0.13	1.26	2	1.5	0.00001131	49946.35	29724.22	10.70	21.39
9	1.61	0.13	1.42	2	1.5	0.00001131	56189.64	33439.75	12.03	24.06
10	1.61	0.13	1.57	2	1.5	0.00001131	62432.93	37155.27	13.37	26.74
1	1.61	0.13	0.16	3	2.25	0.00001131	7646.44	5573.29	1.34	2.67
2	1.61	0.13	0.31	3	2.25	0.00001131	15292.88	11146.58	2.67	5.35
3	1.61	0.13	0.47	3	2.25	0.00001131	22939.33	16719.87	4.01	8.02
4	1.61	0.13	0.63	3	2.25	0.00001131	30585.77	22293.16	5.35	10.70
5	1.61	0.13	0.79	3	2.25	0.00001131	38232.21	27866.46	6.68	13.37
6	1.61	0.13	0.94	3	2.25	0.00001131	45878.65	33439.75	8.02	16.04
7	1.61	0.13	1.10	3	2.25	0.00001131	53525.09	39013.04	9.36	18.72
8	1.61	0.13	1.26	3	2.25	0.00001131	61171.53	44586.33	10.70	21.39
9	1.61	0.13	1.42	3	2.25	0.00001131	68817.98	50159.62	12.03	24.06
10	1.61	0.13	1.57	3	2.25	0.00001131	76464.42	55732.91	13.37	26.74
1	1.61	0.13	0.16	4	3	0.00001131	8829.35	7431.05	1.34	2.67
2	1.61	0.13	0.31	4	3	0.00001131	17658.70	14862.11	2.67	5.35
3	1.61	0.13	0.47	4	3	0.00001131	26488.05	22293.16	4.01	8.02

4	1.61	0.13	0.63	4	3	0.00001131	35317.40	29724.22	5.35	10.70
5	1.61	0.13	0.79	4	3	0.00001131	44146.75	37155.27	6.68	13.37
6	1.61	0.13	0.94	4	3	0.00001131	52976.10	44586.33	8.02	16.04
7	1.61	0.13	1.10	4	3	0.00001131	61805.45	52017.38	9.36	18.72
8	1.61	0.13	1.26	4	3	0.00001131	70634.80	59448.44	10.70	21.39
9	1.61	0.13	1.42	4	3	0.00001131	79464.15	66879.49	12.03	24.06
10	1.61	0.13	1.57	4	3	0.00001131	88293.50	74310.55	13.37	26.74
1	1.61	0.13	0.16	5	3.75	0.00001131	9871.51	9288.82	1.34	2.67
2	1.61	0.13	0.31	5	3.75	0.00001131	19743.03	18577.64	2.67	5.35
3	1.61	0.13	0.47	5	3.75	0.00001131	29614.54	27866.46	4.01	8.02
4	1.61	0.13	0.63	5	3.75	0.00001131	39486.06	37155.27	5.35	10.70
5	1.61	0.13	0.79	5	3.75	0.00001131	49357.57	46444.09	6.68	13.37
6	1.61	0.13	0.94	5	3.75	0.00001131	59229.08	55732.91	8.02	16.04
7	1.61	0.13	1.10	5	3.75	0.00001131	69100.60	65021.73	9.36	18.72
8	1.61	0.13	1.26	5	3.75	0.00001131	78972.11	74310.55	10.70	21.39
9	1.61	0.13	1.42	5	3.75	0.00001131	88843.62	83599.37	12.03	24.06
10	1.61	0.13	1.57	5	3.75	0.00001131	98715.14	92888.18	13.37	26.74

Table K.2: Re', Re_{Komax}, and air flow rates for various factor settings for 1 inch Komax static in-line mixer

Q (gal/min)	d (in)	d (ft)	V (ft/s)	# of unit	L (ft)	v (ft^2/s)	Re"= V*(((SQRT(d*L))/v)	Re_{Komax}	Air (10) scfm	Air (20 scfm)
1	1.049	0.09	0.37	1	0.54	0.00001131	7122.63	2851.29	1.34	2.67
2	1.049	0.09	0.74	1	0.54	0.00001131	14245.27	5702.57	2.67	5.35
3	1.049	0.09	1.11	1	0.54	0.00001131	21367.90	8553.86	4.01	8.02
4	1.049	0.09	1.48	1	0.54	0.00001131	28490.53	11405.15	5.35	10.70
5	1.049	0.09	1.85	1	0.54	0.00001131	35613.17	14256.43	6.68	13.37
6	1.049	0.09	2.22	1	0.54	0.00001131	42735.80	17107.72	8.02	16.04
7	1.049	0.09	2.60	1	0.54	0.00001131	49858.43	19959.01	9.36	18.72
8	1.049	0.09	2.97	1	0.54	0.00001131	56981.07	22810.29	10.70	21.39
9	1.049	0.09	3.34	1	0.54	0.00001131	64103.70	25661.58	12.03	24.06
10	1.049	0.09	3.71	1	0.54	0.00001131	71226.33	28512.86	13.37	26.74
1	1.049	0.09	0.37	2	1.07	0.00001131	10026.18	5702.57	1.34	2.67
2	1.049	0.09	0.74	2	1.07	0.00001131	20052.36	11405.15	2.67	5.35
3	1.049	0.09	1.11	2	1.07	0.00001131	30078.55	17107.72	4.01	8.02
4	1.049	0.09	1.48	2	1.07	0.00001131	40104.73	22810.29	5.35	10.70
5	1.049	0.09	1.85	2	1.07	0.00001131	50130.91	28512.86	6.68	13.37
6	1.049	0.09	2.22	2	1.07	0.00001131	60157.09	34215.44	8.02	16.04
7	1.049	0.09	2.60	2	1.07	0.00001131	70183.28	39918.01	9.36	18.72
8	1.049	0.09	2.97	2	1.07	0.00001131	80209.46	45620.58	10.70	21.39
9	1.049	0.09	3.34	2	1.07	0.00001131	90235.64	51323.16	12.03	24.06
10	1.049	0.09	3.71	2	1.07	0.00001131	100261.82	57025.73	13.37	26.74

1	1.049	0.09	0.37	3	1.61	0.00001131	12298.63	8553.86	1.34	2.67
2	1.049	0.09	0.74	3	1.61	0.00001131	24597.25	17107.72	2.67	5.35
3	1.049	0.09	1.11	3	1.61	0.00001131	36895.88	25661.58	4.01	8.02
4	1.049	0.09	1.48	3	1.61	0.00001131	49194.51	34215.44	5.35	10.70
5	1.049	0.09	1.85	3	1.61	0.00001131	61493.14	42769.30	6.68	13.37
6	1.049	0.09	2.22	3	1.61	0.00001131	73791.76	51323.16	8.02	16.04
7	1.049	0.09	2.60	3	1.61	0.00001131	86090.39	59877.02	9.36	18.72
8	1.049	0.09	2.97	3	1.61	0.00001131	98389.02	68430.88	10.70	21.39
9	1.049	0.09	3.34	3	1.61	0.00001131	110687.65	76984.74	12.03	24.06
10	1.049	0.09	3.71	3	1.61	0.00001131	122986.27	85538.59	13.37	26.74
1	1.049	0.09	0.37	4	2.15	0.00001131	14212.25	11405.15	1.34	2.67
2	1.049	0.09	0.74	4	2.15	0.00001131	28424.51	22810.29	2.67	5.35
3	1.049	0.09	1.11	4	2.15	0.00001131	42636.76	34215.44	4.01	8.02
4	1.049	0.09	1.48	4	2.15	0.00001131	56849.01	45620.58	5.35	10.70
5	1.049	0.09	1.85	4	2.15	0.00001131	71061.27	57025.73	6.68	13.37
6	1.049	0.09	2.22	4	2.15	0.00001131	85273.52	68430.88	8.02	16.04
7	1.049	0.09	2.60	4	2.15	0.00001131	99485.77	79836.02	9.36	18.72
8	1.049	0.09	2.97	4	2.15	0.00001131	113698.02	91241.17	10.70	21.39
9	1.049	0.09	3.34	4	2.15	0.00001131	127910.28	102646.31	12.03	24.06
10	1.049	0.09	3.71	4	2.15	0.00001131	142122.53	114051.46	13.37	26.74
1	1.049	0.09	0.37	5	2.68	0.00001131	15867.59	14256.43	1.34	2.67
2	1.049	0.09	0.74	5	2.68	0.00001131	31735.19	28512.86	2.67	5.35
3	1.049	0.09	1.11	5	2.68	0.00001131	47602.78	42769.30	4.01	8.02
4	1.049	0.09	1.48	5	2.68	0.00001131	63470.38	57025.73	5.35	10.70
5	1.049	0.09	1.85	5	2.68	0.00001131	79337.97	71282.16	6.68	13.37
6	1.049	0.09	2.22	5	2.68	0.00001131	95205.57	85538.59	8.02	16.04
7	1.049	0.09	2.60	5	2.68	0.00001131	111073.16	99795.03	9.36	18.72
8	1.049	0.09	2.97	5	2.68	0.00001131	126940.76	114051.46	10.70	21.39
9	1.049	0.09	3.34	5	2.68	0.00001131	142808.35	128307.89	12.03	24.06
10	1.049	0.09	3.71	5	2.68	0.00001131	158675.95	142564.32	13.37	26.74
1	1.049	0.09	0.37	6	3.22	0.00001131	17392.89	17107.72	1.34	2.67
2	1.049	0.09	0.74	6	3.22	0.00001131	34785.77	34215.44	2.67	5.35
3	1.049	0.09	1.11	6	3.22	0.00001131	52178.66	51323.16	4.01	8.02
4	1.049	0.09	1.48	6	3.22	0.00001131	69571.54	68430.88	5.35	10.70
5	1.049	0.09	1.85	6	3.22	0.00001131	86964.43	85538.59	6.68	13.37
6	1.049	0.09	2.22	6	3.22	0.00001131	104357.31	102646.31	8.02	16.04
7	1.049	0.09	2.60	6	3.22	0.00001131	121750.20	119754.03	9.36	18.72
8	1.049	0.09	2.97	6	3.22	0.00001131	139143.08	136861.75	10.70	21.39
9	1.049	0.09	3.34	6	3.22	0.00001131	156535.97	153969.47	12.03	24.06
10	1.049	0.09	3.71	6	3.22	0.00001131	173928.86	171077.19	13.37	26.74