NE-WTTAC

New England Water Treatment Technology Assistance Center

University of New Hampshire ▪ Durham, New Hampshire

A division of the Technology Assistance Center National Network (TACnet)

Assessing Post-Treatment Aeration Variables to Reduce Disinfection Byproducts(THMs) for Small Systems

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What Are Disinfection Byproducts?

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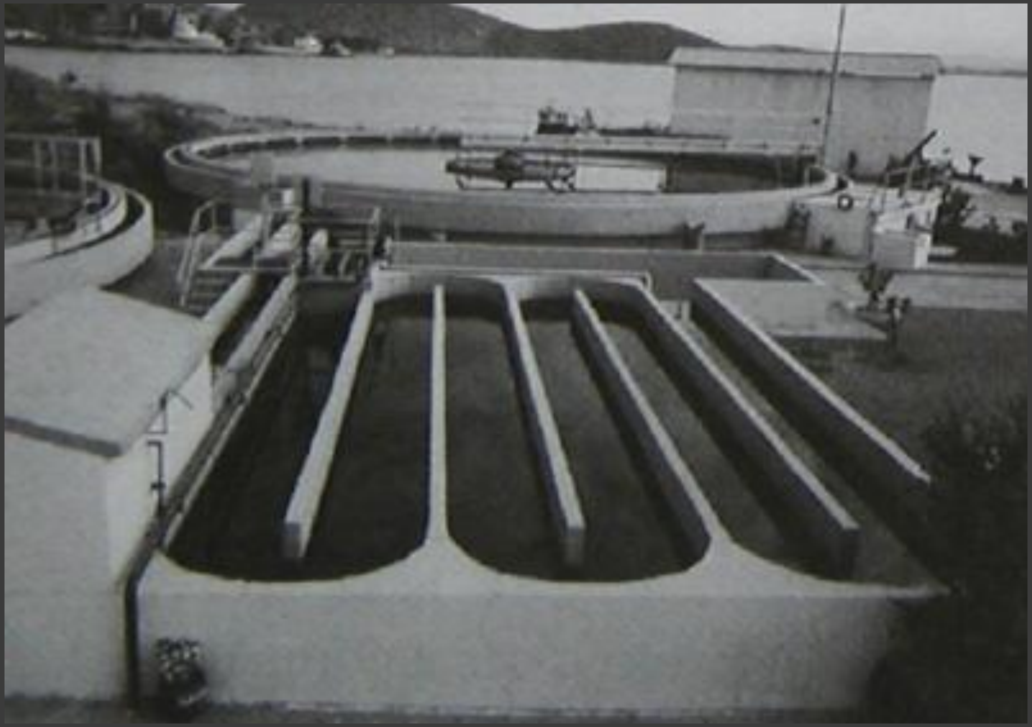
Free Chlorine (CL)

Natural Organic Matter (NOM)

Disinfection Byproducts (DBP)

Stand Pipe Aeration

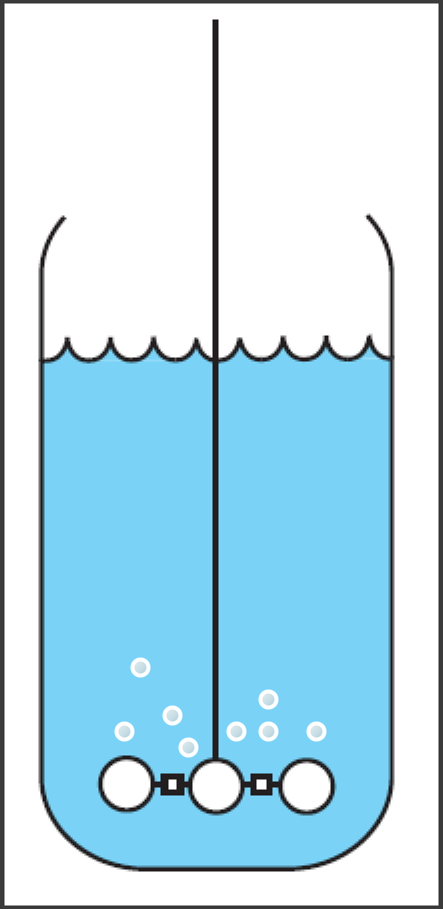
Chlorine Contact Basin Aeration



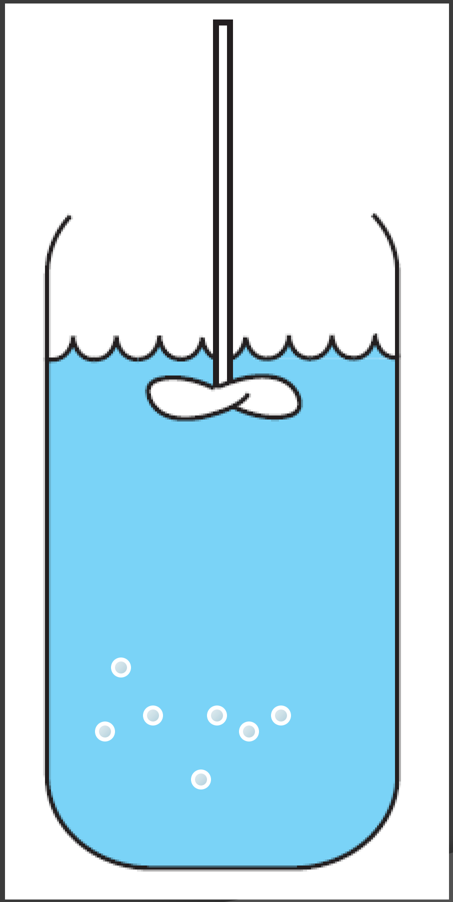
A Potential Solution for Small Systems

- Particularly useful for concurrent systems
- Do not have control over water quality
- Alternative to precursor removal / alternative disinfectant

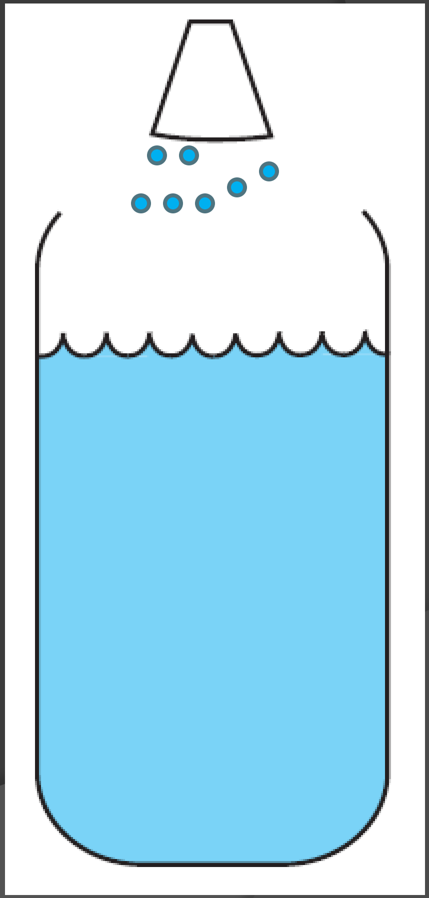
Diffused Aeration



Surface Aeration

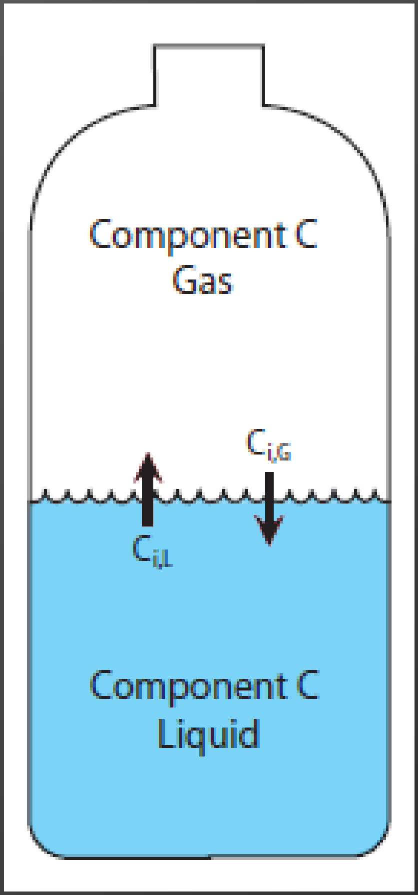


Spray Aeration



Aeration Kinetic Basics

EQUILIBRIUM



Equilibrium is the driving force for all forms of Aeration!

Equilibrium is Expressed by Henry's Constant

$$H_{cc} = \frac{C_G}{C_L} = \left[\frac{\frac{mole_G}{m^3_G}}{\frac{mole_L}{m^3_L}}\right] = \left[\frac{\frac{g_G}{m^3_G}}{\frac{g_L}{m^3_L}}\right] = \text{(Dimensionless)}$$

C_G = compound concentration on a volume basis in gas form

C_L = compound concentration on a volume basis in liquid form

Factors Affecting Henry's Constant

pH
Complex Mixtures: Co-solvents and Co-solutes
Ionic Strength: Dissolved Salts
Suspended Solids
Dissolved Organic Matter
Surfactants
Temperature

Henrys Constant Temperature Correction Equation

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

T = Temperature (Kelvin)
$H_{cc,T}$ = Henrys Constant at Temperature (T)
$H_{cc,20^{\circ}C}$ = Henrys Constant at 20° C
B = Temperature Correction Factor

Henrys Constants and Temperature Correction Factor for TTHMs at 20^0 C and 1^0 C

THM Species	H_{cc} 20^o C	H_{cc} 1^o C	B
Chloroform (CF)	0.127	0.047	183
Bromodichloromethane (BDCM)	0.076	0.024	2130
Chlorodibromomethane (CDBM)	0.035	0.010	2273
Bromoform (BF)	0.018	0.006	2120

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

Henrys Constants for Haloacetic Acids at 20^0 C

Haloacetic Acid Species	**H_{cc} 20^0 C**
Monochloroacetic Acid	0.000000378
Dichloroacetic Acid	0.000000343
Trichloroacetic acid	0.000000553
Monobromoacetic Acid	0.000000267
Dibromoacetic Acid	0.000000181

RECAP of BASICS

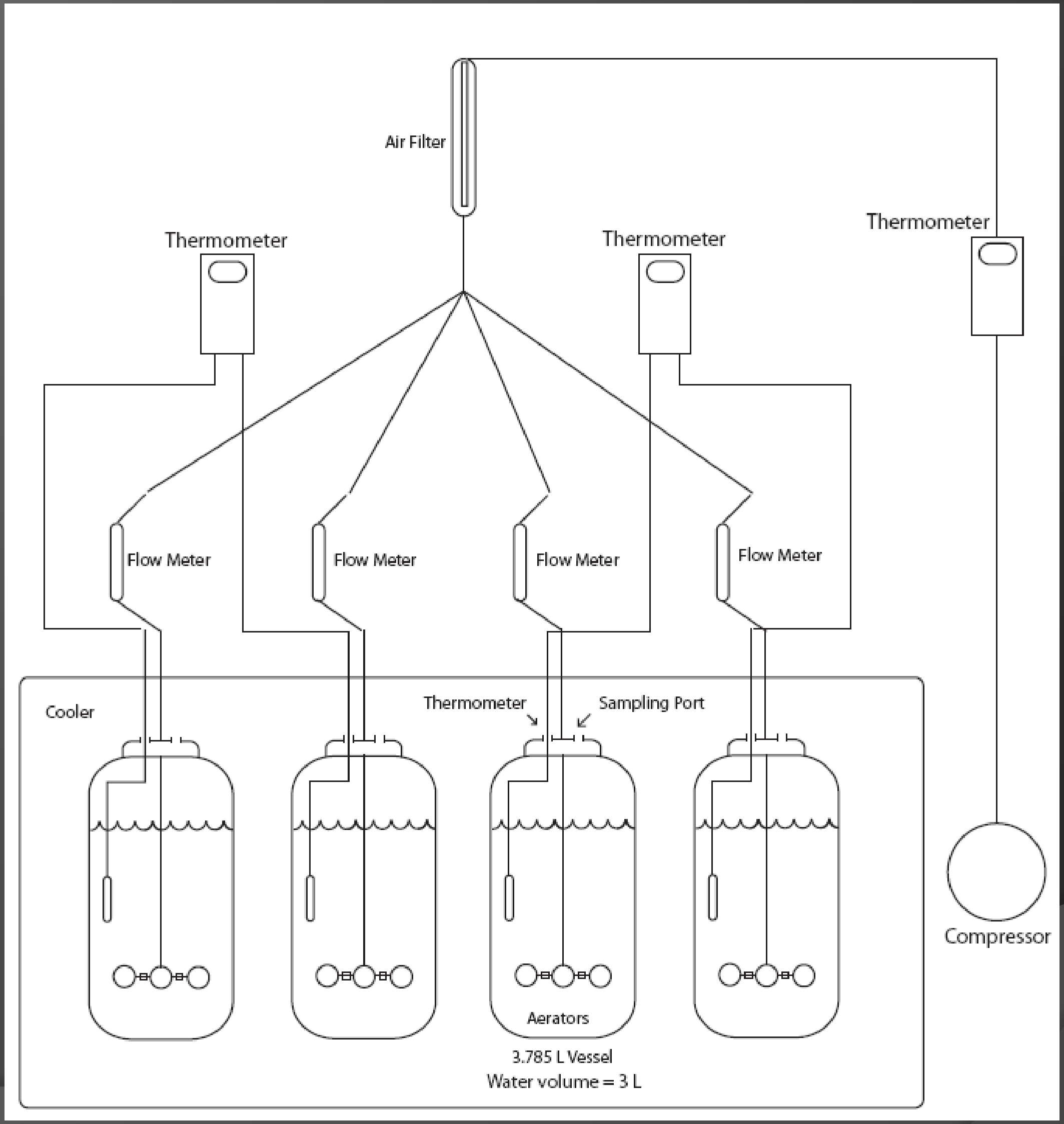
- The tendency of a system to seek equilibrium is the driving force for all forms of aeration.
- Equilibrium is expressed by Henry's constant.
- Temperature has a large effect on Henry's constant.
- Haloacetic acids are not volatile enough to strip effectively; however, THMs are amenable.

Methodology

I. BENCH-SCALE STUDY- Diffused Aeration

- **Assess selected design variables:**
  - Air flow rate, contact time (air/water ratio), diffuser arrangement (bubble size)
- **Assess selected operating conditions:**
  - Air temperature, Water temperature, THM concentration

Bench Scale Experiment



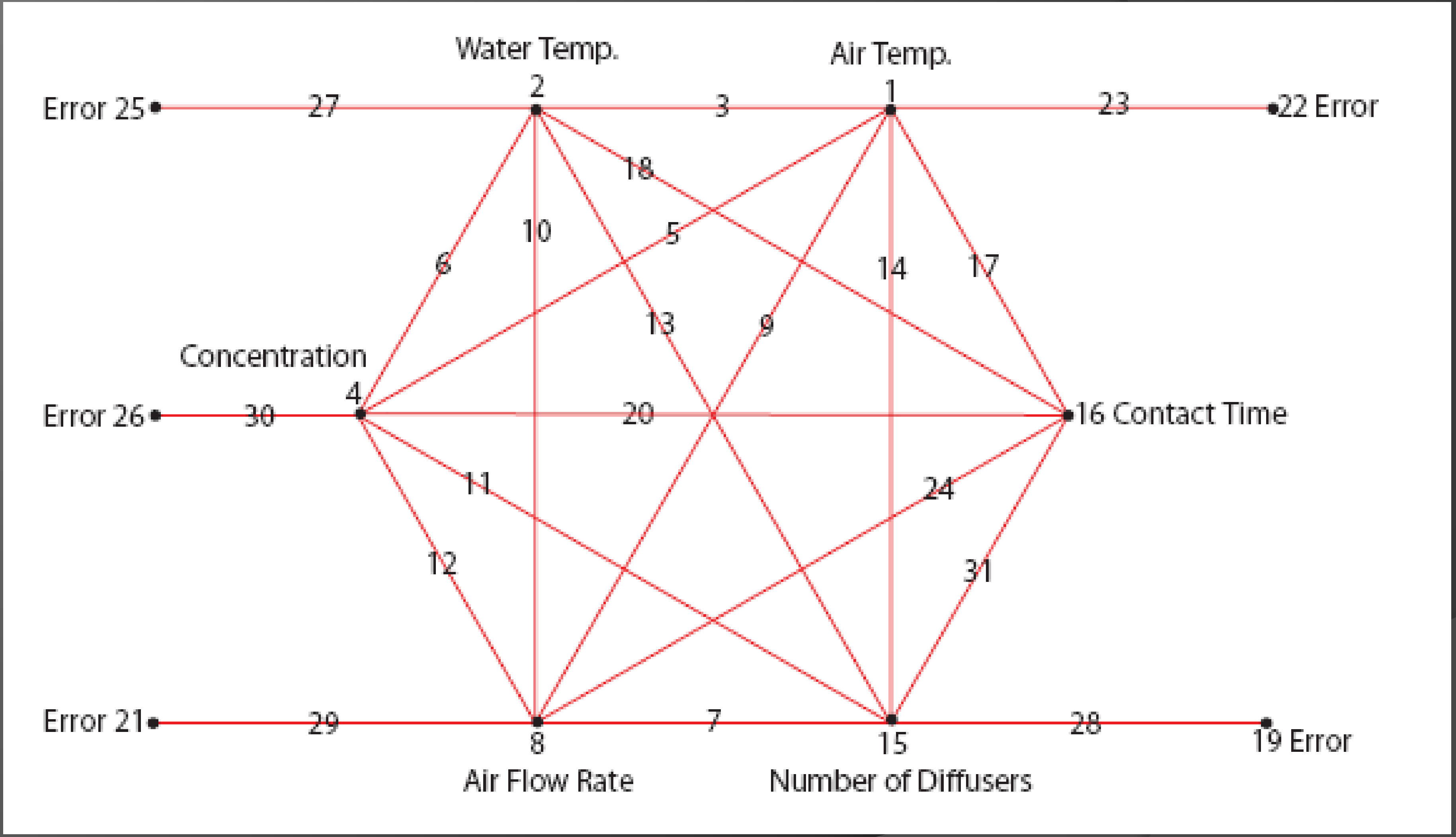
Diffused Aeration Apparatus

Diffused Aeration Apparatus

Bench Scale Variables

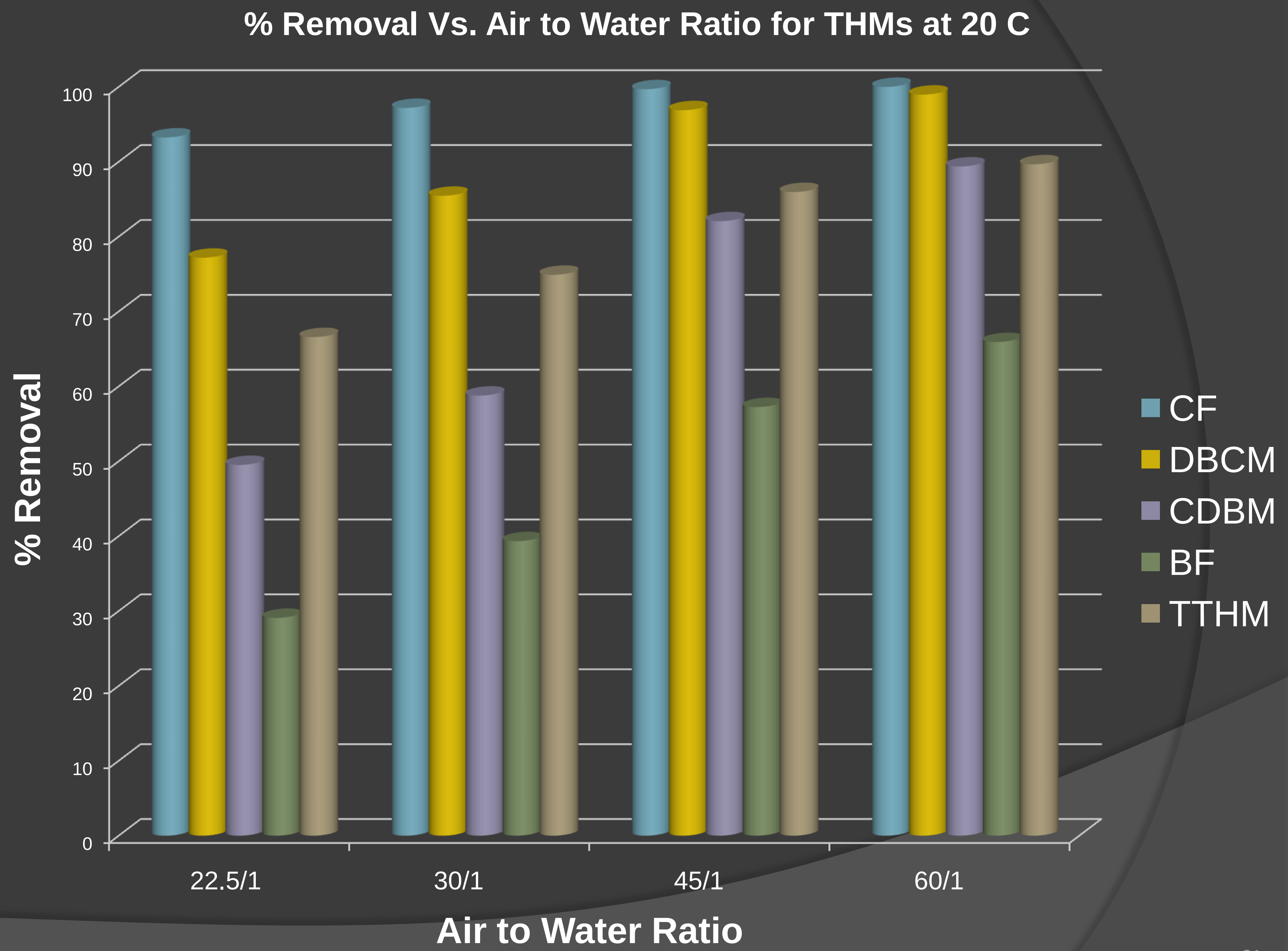
- Air Temperature **4º C and 20º C**
- Water Temperature **4º C and 20º C**
- Air Flow Rate **1L/Min and 3L/Min**
- Number of Diffusers **1 and 4**
- THM Concentration **100 ug/L and 400 Ug/L**
- Contact Time **40 Min and 80 Min**

Experimental Design and Analysis



ANOVA Table and % Contribution of Data Variation for Selected Design Variables and Operating Conditions for Bench Scale Study

Source	DF	Sum of Squares	F Ratio	Prob > F	% Contribution
Water Temperature	1	4976.223	107.1477	< 0.0001	51%
Air Flow Rate	1	2322.669	50.0115	< 0.0001	24%
Aeration Time	1	621.647	13.3853	0.0011	6%
Air Flow Rate*Aeration Time	1	204.455	4.4023	0.0458	2%
Error	26				17%
Total Contribution					100%

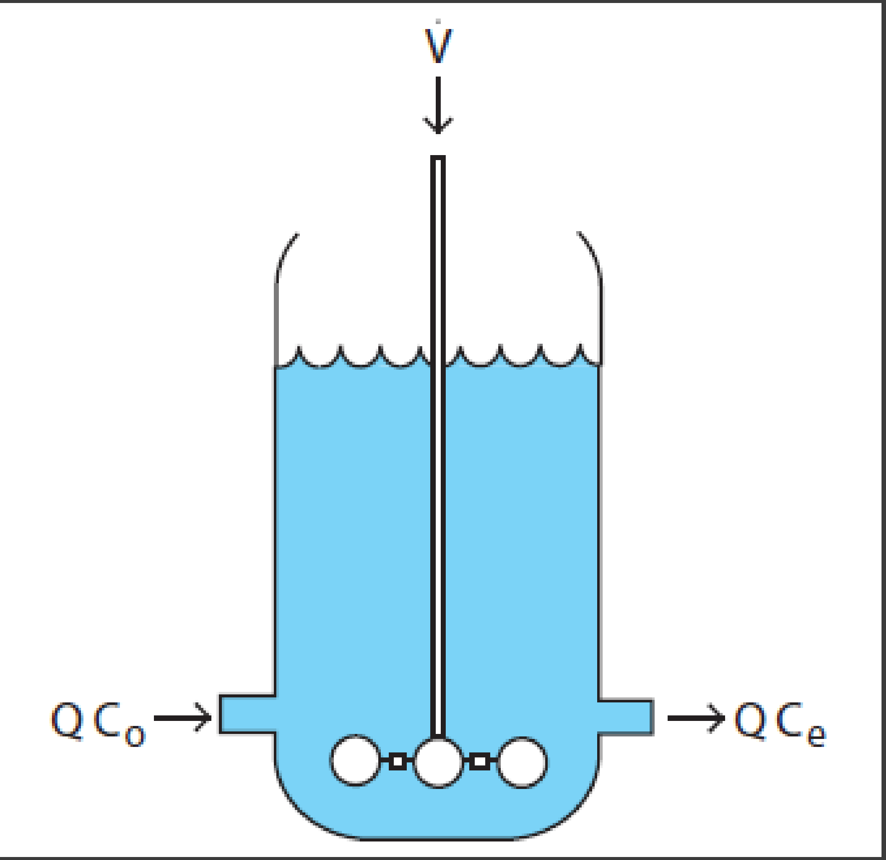

% Removal Vs. Air to Water Ratio for THMs at 20 C
% Removal
0
10
20
30
40
50
60
70
80
90
100
22.5/1
30/1
45/1
60/1
Air to Water Ratio
CF
DBCM
CDBM
BF
TTHM

Bench Scale Experimental Conclusions

- Water temperature and air to water ratio have a significant effect on removals
- Air Temperature and initial concentration did not have a significant effect on removals
- Bubble distribution did not appear to have a significant effect on overall removals

Diffused Aeration

Minimum Air to Water Ratio



$$\left(\frac{\dot{V}}{Q}\right)_{mi} \left(\frac{\dot{V}}{Q}\right) \frac{C_e}{C_e}$$

C_o = Initial Concentration

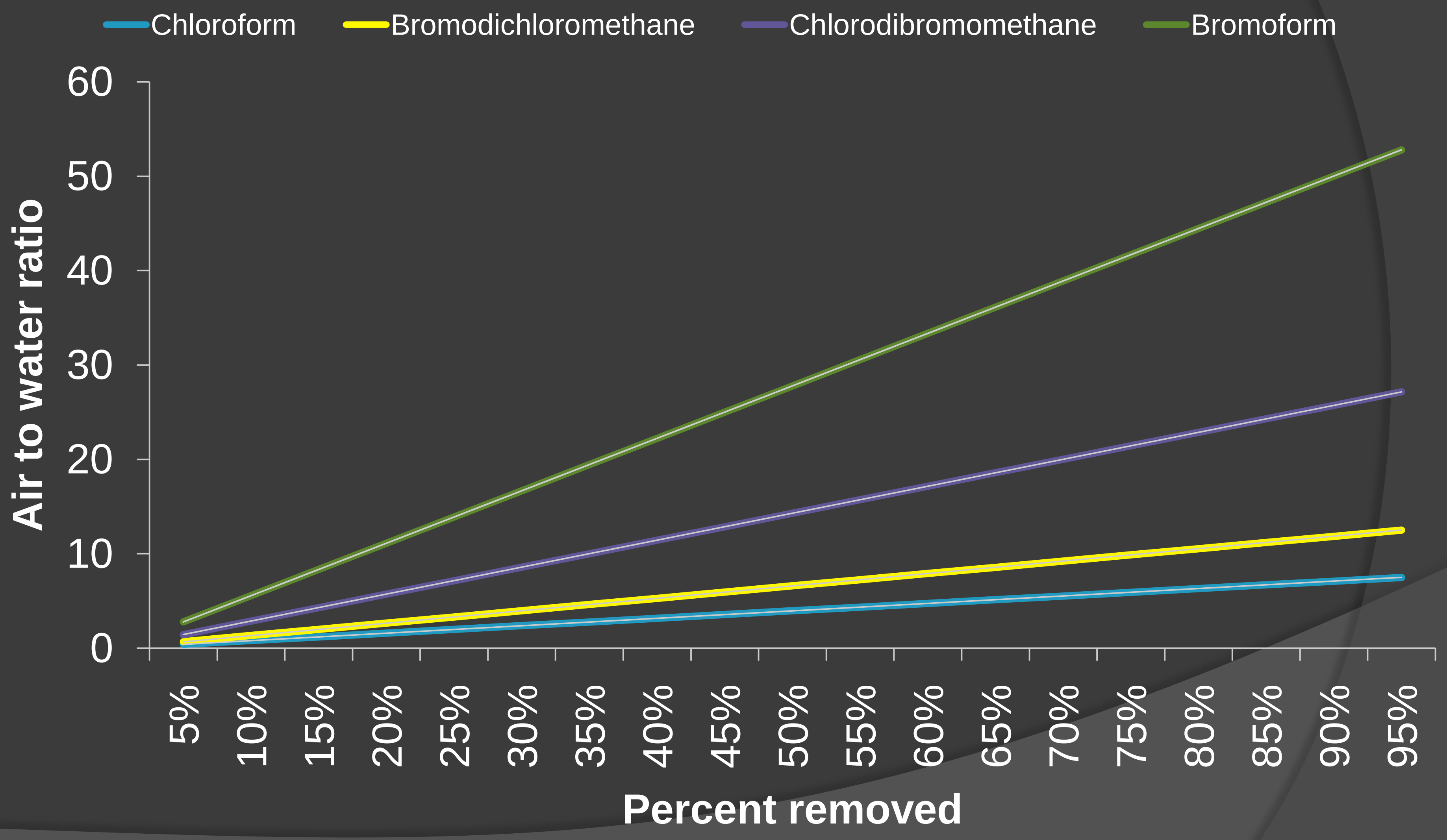
C_e = Effluent Concentration

H_{cc} = Henrys Constant

$\dot{V}$ = Air Flow Rate

Q = Water Flow Rate

Percent removal vs. air to water ratio for THMs at 25º C



Diffused Aeration Assessment Summary

- A simple air diffuser can be placed in a storage tank or chlorine contact basin for THM removal
- Effective for small system THM compliance
- No removal of HAAs
- Most effective for Chloroform
  - Dominant species in most chlorinated water
- Most effective during warm weather months

Methodology

I. BENCH-SCALE STUDY- Diffused Aeration

- **Assess selected design variables:**
  - Air flow rate, contact time (air/water ratio), diffuser arrangement (bubble size)
- **Assess selected operating conditions:**
  - Air temperature, Water temperature, THM concentration

II. PILOT –SCALE STUDY- Spray Aeration

- Evaluate the role of temperature on spray aeration removal rates
- Develop a relationship between percent removals and physical characteristics of aeration equipment with respect to Henry's constants of THM species
- Assess the role of operating parameters (e.g. operating pressure / head loss and flow rate) in determining mass transfer coefficients and interfacial surface area (K_La)

Assessing Mass Transfer Coefficients and Interfacial Surface Area With Respect to Spray Aeration Equipment

$$-\ln \frac{C_e}{C_o} = K_L at$$

C_e = Concentration of Effluent (mg/L)

C_o = Initial Concentrataion (mg/L)

a = Specific Interfacial Area (m^3 / m^2)

K_L = Overall Mass Transfer Coefficent (m/s)

t = Time (min)

Mass Transfer Coefficient (K_La) and Two Film Theory

$$N_A = k_L(C_b - C_s) = k_g(y_s - y_b) = K_L(C_b - C_s^*)$$

K_L = overall mass transfer coefficent, m/s

N_A = Flux of A across air-water interface, mg/m^3S

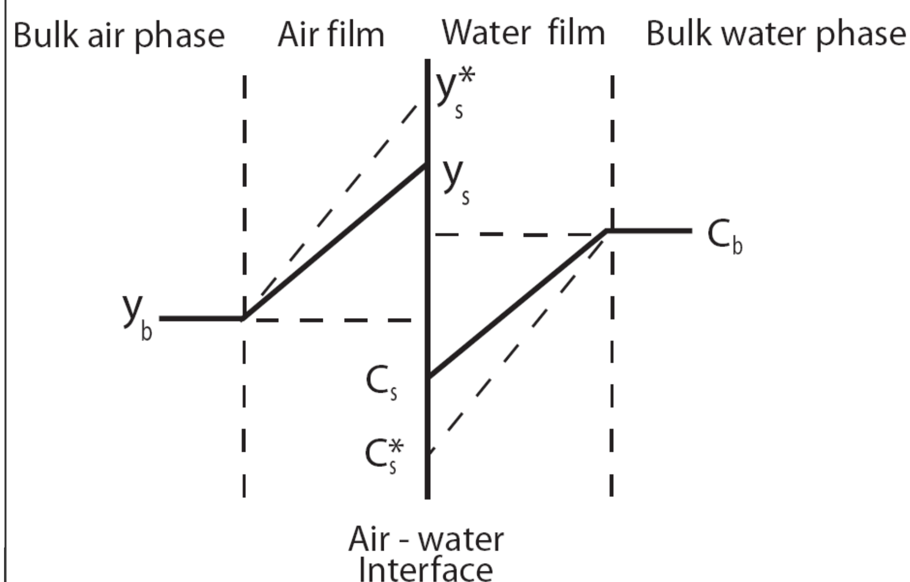
k_L = liquid-phase mass transfer coefficent for rate at wich contaminent A is transfered from bulk aquious phase to air-water interface, m/s

k_g = gas-phase mass transfer coefficent for rate at wich contaminent A is transfered from air- water interface to bulk gas phase, m/s

C_s^* = Liquid phase concentration of A that is in equlibrium with bulk air concentration, mg/L

y_s^* = Gas phase concentration of A that is in equlibrium with bulk water concentration mg/L

Air Stripping



Droplet Size and Interfacial Surface Area (a)

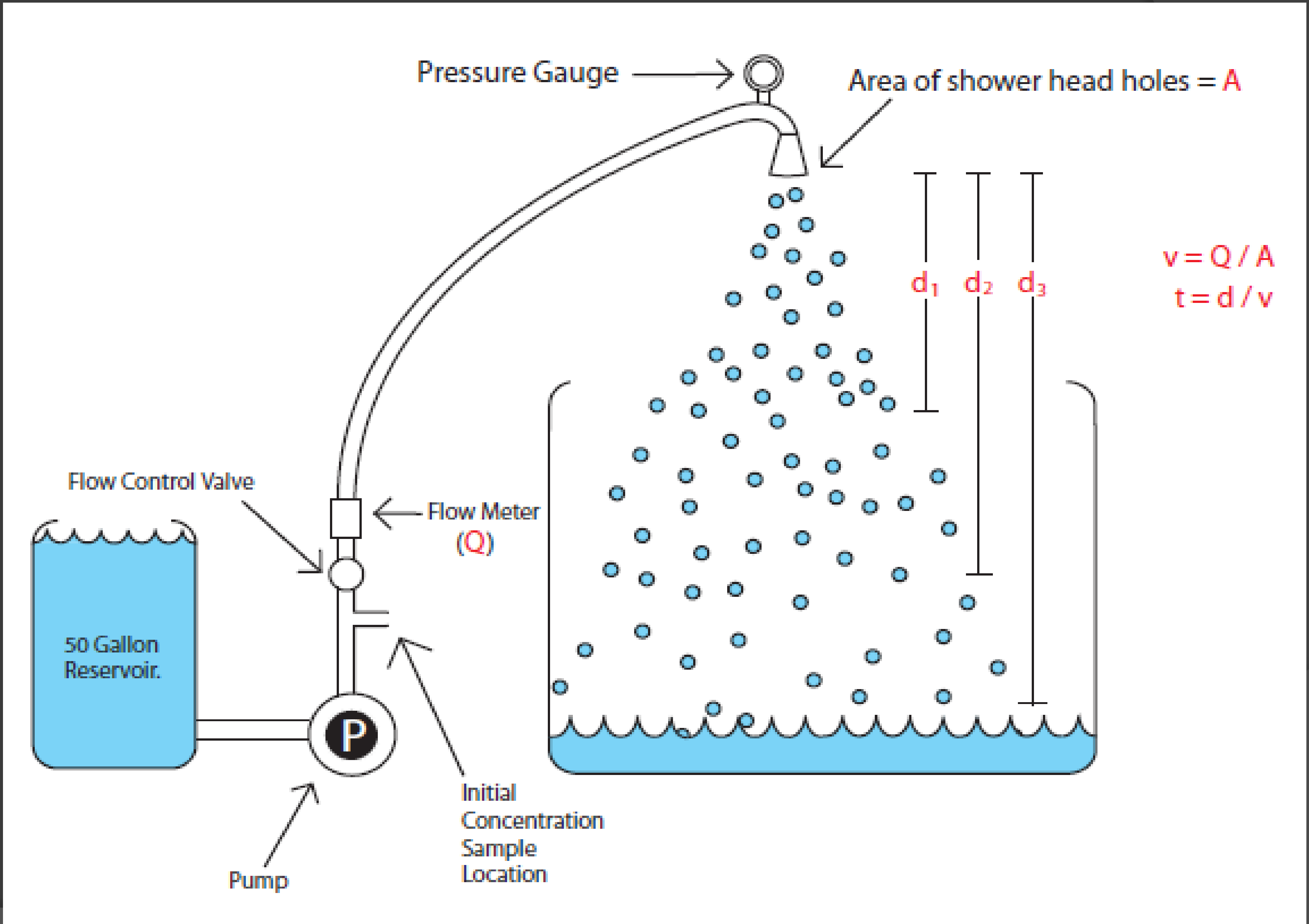
$$a = M^2 / M^3 = (M^{-1})$$

$$a = 6 / d_p$$

- d_p = Sauter Mean Diameter (SMD) (average droplet diameter determined by photographic analysis, provided by nozzle manufacturer)

➡ d_p is a function of flow rate and nozzle characteristics

Spray Aeration Pilot Schematic




PHIPPS&BIRD

Initial Pilot Scale Study: Assessing Selected Shower Heads

Temperature (C)	Shower Head	Flow Rate (m^3/min)	Height (m)	% TTHM Removal
22	1	0.00379	.74	31
22	1	1.135	.74	35
22	2	0.00379	.74	38
22	2	1.135	.74	38
22	3	0.00758	.74	55
22	3	1.135	.74	77

Pilot Scale Assessment of Selected Spray Aeration Variables

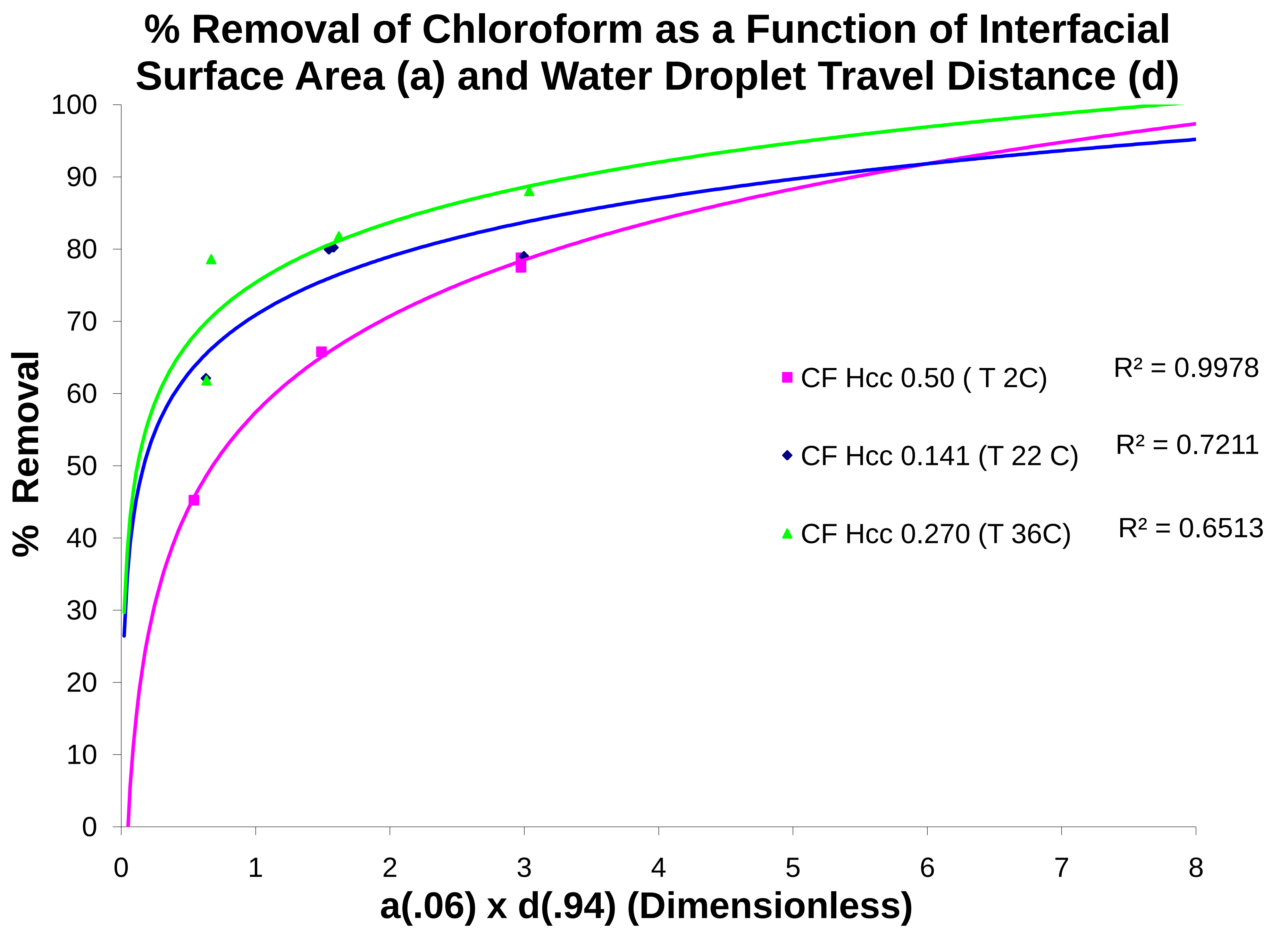
- Nozzle Height
  0.74 m, 2.13 m, 4.27 m

- Water Temperature
  2º C, 22º C, 36º C

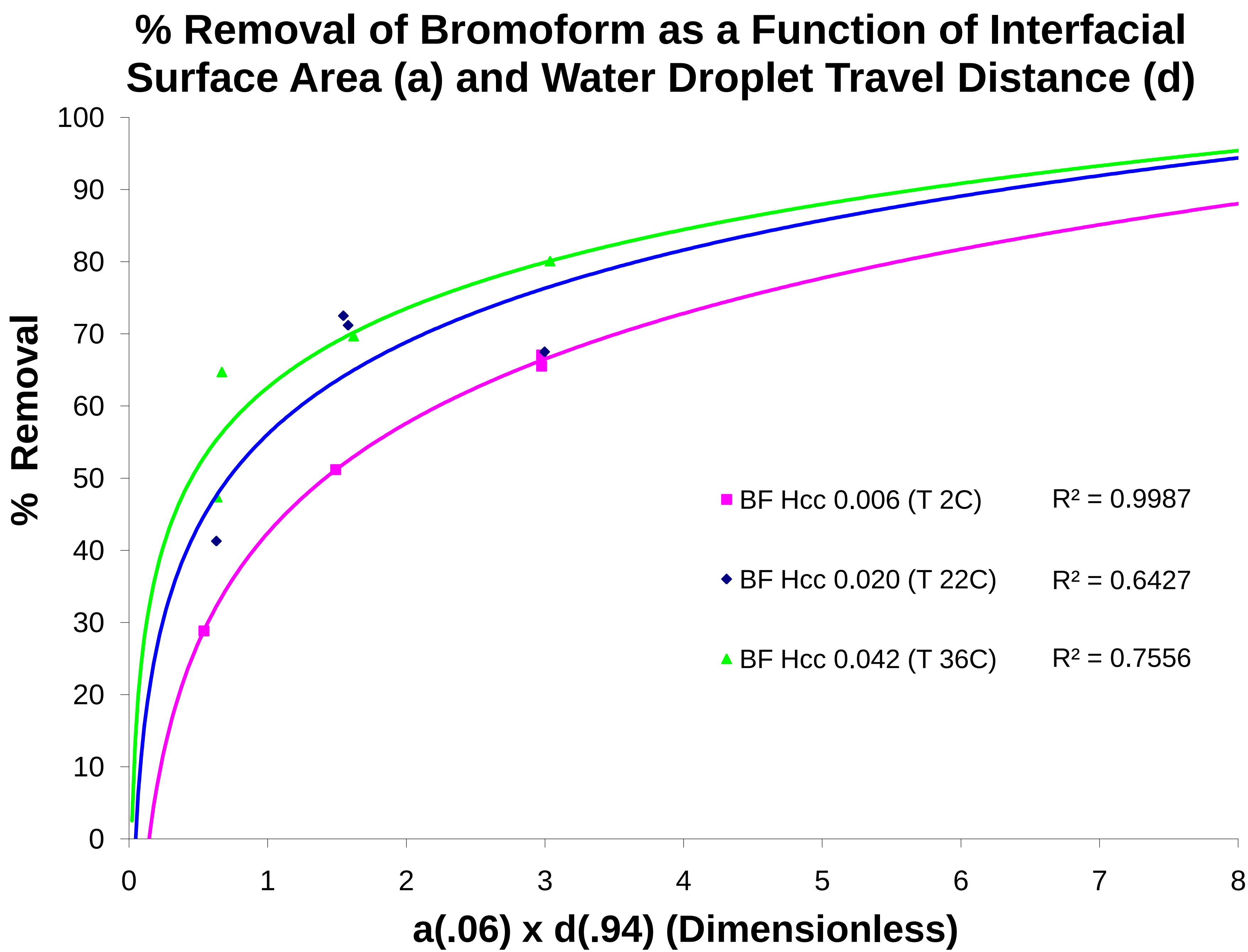
- Water flow rate
  - **0.00758 m^3/min (a= 0.8571 m^{-1})**
  - **1.135 m^3/min (a = 1.7142 m^{-1})**

ANOVA Table and % Contribution of Data Variation for Selected Design Variables and Operating Conditions for Pilot Scale Study

Source	DF	Sum of Squares	F Ratio	Prob > F	% Contribution
Height	2	1334	22	0.0017	67%
Temp	2	587	10	0.0130	28%
Flow	1	112	4	0.1016	4%
Error	6	180			1%
Total Contribution					100%

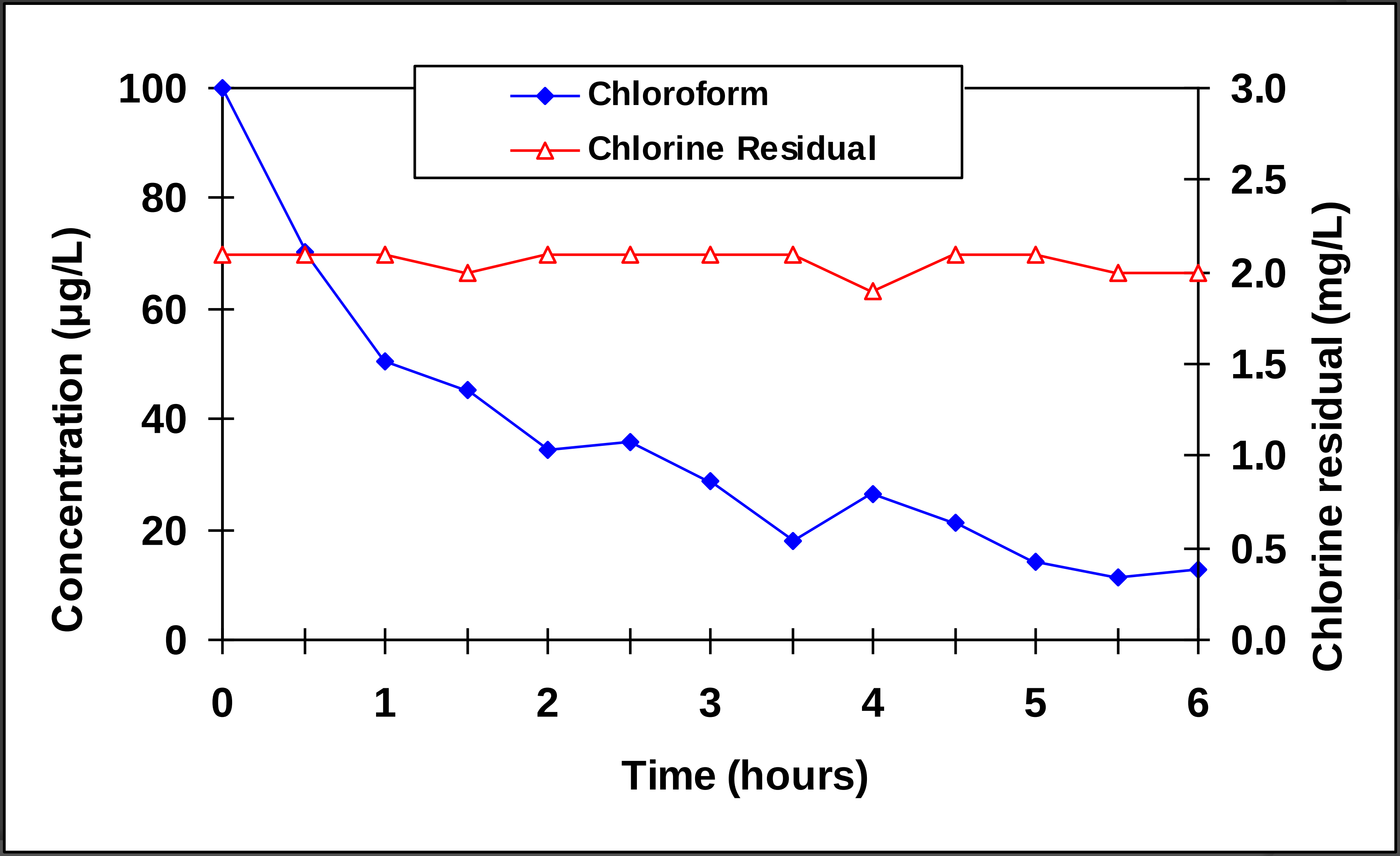


% Removal of Chloroform as a Function of Interfacial Surface Area (a) and Water Droplet Travel Distance (d)
100
90
80
70
60
50
40
30
20
10
0
% Removal
0
1
2
3
4
5
6
7
8
a(.06) x d(.94) (Dimensionless)
CF Hcc 0.50 (T 2C)
CF Hcc 0.141 (T 22 C)
CF Hcc 0.270 (T 36C)
R² = 0.9978
R² = 0.7211
R² = 0.6513


% Removal of Bromoform as a Function of Interfacial Surface Area (a) and Water Droplet Travel Distance (d)
% Removal
a(.06) x d(.94) (Dimensionless)
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
BF Hcc 0.006 (T 2C)
R² = 0.9987
BF Hcc 0.020 (T 22C)
R² = 0.6427
BF Hcc 0.042 (T 36C)
R² = 0.7556

Chlorine Residual Results
Penn State-Harrisburg

(Xie et al, June 2008)



Chlorine Chemistry

$$Cl_2(g) \rightleftharpoons Cl_2(aq) + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

$$\upharpoonleft\downharpoonright$$

Assume pH = 8

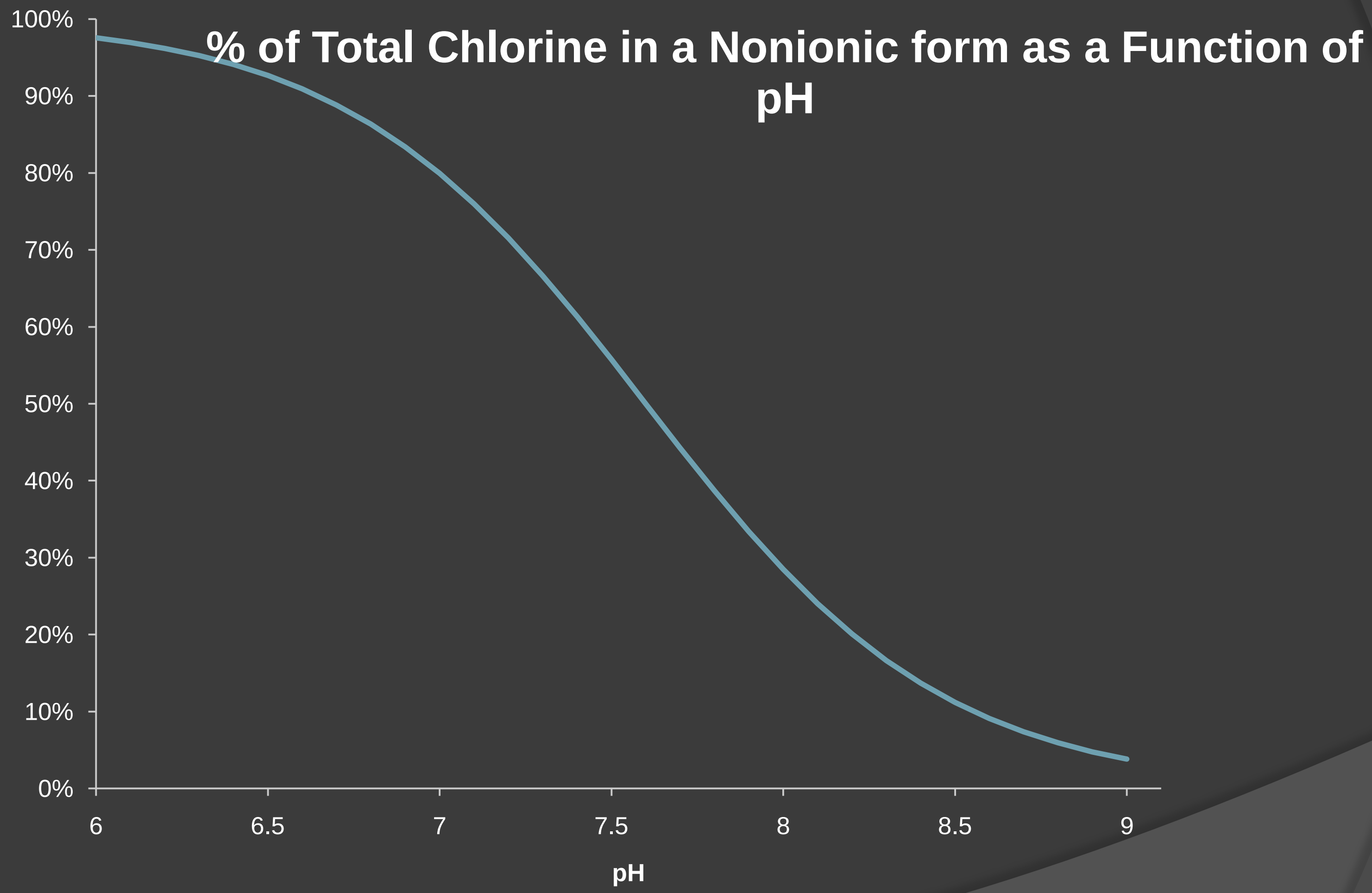
$pK_a = 7.60$

$$Cl_t = (HOCl) + (OCl^-)$$

$$\alpha_0 = \frac{(HOCl)}{(Cl_t)} = \frac{(H^+)}{(H^+) + K_a} = \frac{10^{-8}}{10^{-8} + 10^{-7.60}} = 0.284\ HOCl$$

$$\alpha_1 = \frac{(OCl^-)}{Cl_t} = \frac{K_a}{(H^+) + K_a} = 0.715\ OCl^-$$

% of Total Chlorine in a Nonionic Form (HOCl) as a Function of pH



Conclusion

- Aeration provides a way to remove THMs after they have formed with a minimal capital investment
- Temperature has a significant effect on removal efficiencies
- Diffused aeration can achieve significant removals based on air to water ratio
- Spray aeration can achieve significant removals of THMs dependent primarily on shower head type and droplet travel distance