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Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #18

Chloramines with Surface Reactions: Pipe walls & degradation in Distribution Systems

Primary Literature

David A. Reckhow

Introduction

Breakpoint Reactions

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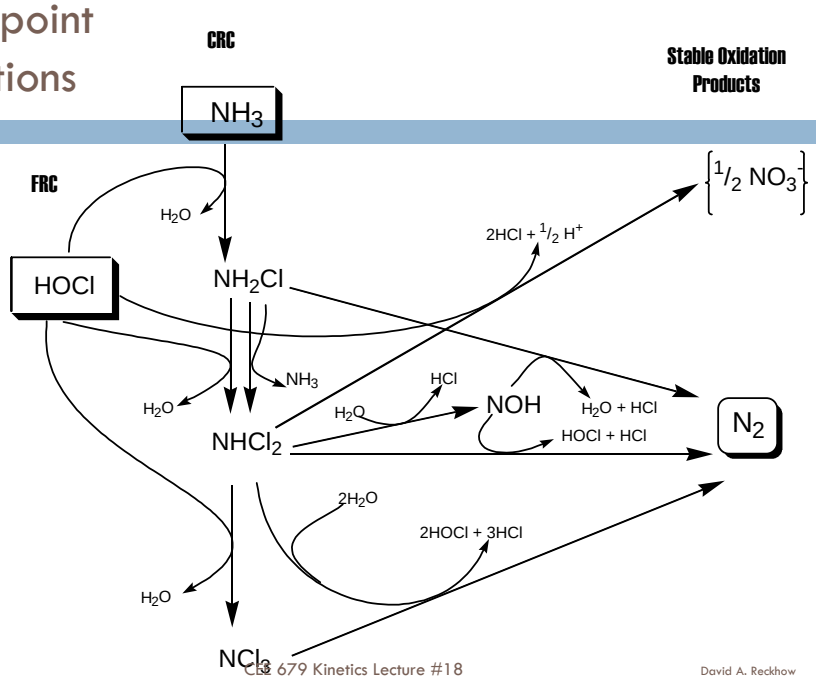

Statistics

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- Error types
  - Analytical measurements
    - Constant vs. proportional vs in-between
  - Experimental conditions
    - e.g., pH, temperature
  - Model error
- Need for homoskedasticity
  - Use best transformation (or none at all)
    - Use log for data with errors directly proportional to concentration
    - No transform for data with constant error
    - Use data weighting for other error distributions
  - Plot residuals to determine heteroskedasticity

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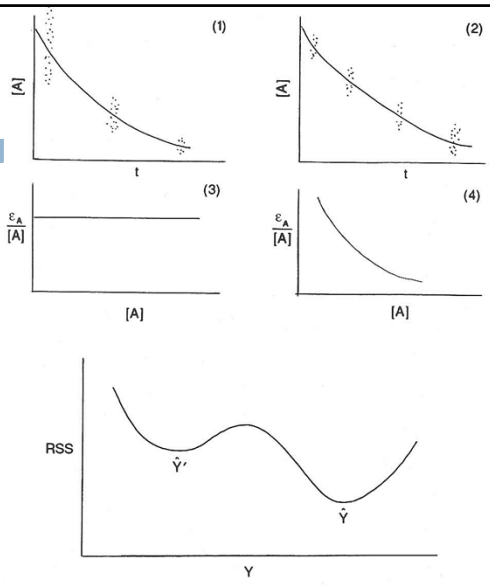

Figure 2-10. (a) Sketches showing effects of (1) proportional and (2) constant error on hypothetical reactant vs. time curves; (3) relative error is constant fraction of [A] for proportional error, but (4) constant error leads to increasing relative error as [A] decreases. (b) Locally optimal solution ($\hat{Y}'$) and true optimum ($\hat{Y}$) in regression analysis; RSS = root mean sum of squares.

Kinetic Spectrum Analysis

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- For mixtures of many closely related compounds
  - A new continuum of rate constants
    - E.g., NOM ⟶
      - Kinetic: Shuman model
      - Equilibria: Perdue model

$$[C]_t = \sum_{i=1}^{n} [C_i]_0 e^{-k_i t}$$

  - Very general, but highly subject to errors

Seasonal Variability & Biodegradation

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- Chen & Weisel study
- JAWWA, April 1998
- Intensive study of Elizabethtown, NJ system
  - 125 MGD conventional plant
  - 4.9 mg/L DOC (raw water average)
  - pH 7.2

Elizabethtown, NJ: THMs

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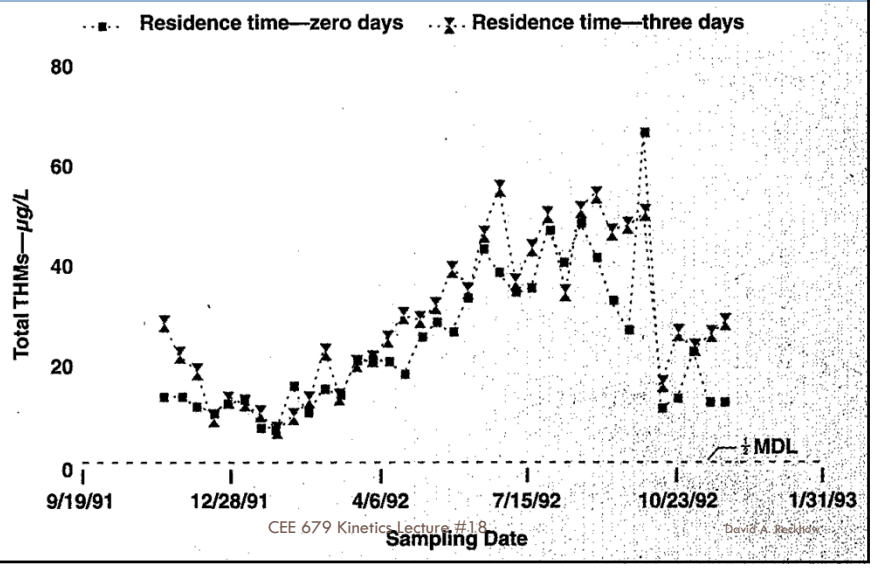

Elizabethtown, NJ: TCAA

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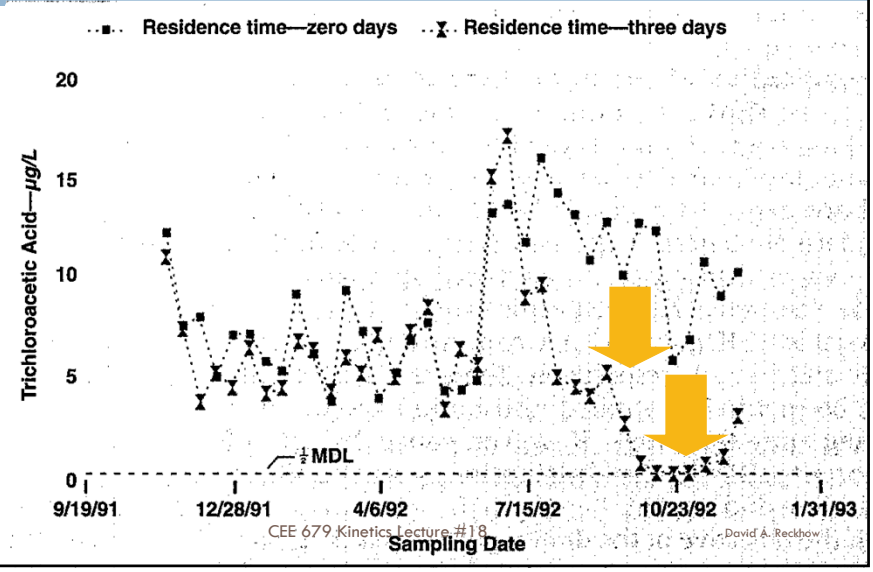

HAA Degradation

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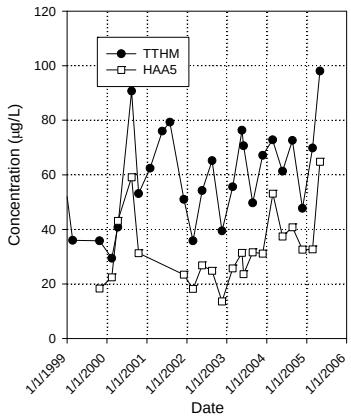
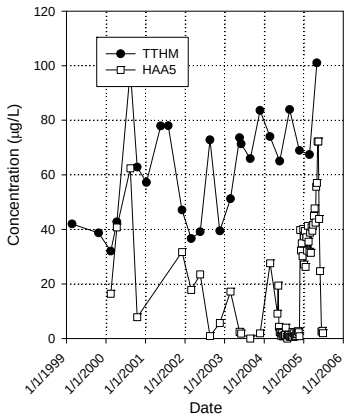
- Biodegradation:
  - dihaloacetic acids degrade more readily than trihaloacetic acids
  - On BAC
    - MHAA>DHAA>THAA
      - Wu & Xie, 2005 [JAWWA 97:11:94]
  - In distribution systems
    - DHAA>MHAA>THAA
      - Many studies

Degradation in Dist. Systems

Town Hall; Norwood, MA



Pier 1; Norwood, MA



Example: Norwood, MA

Degradation of HAAs

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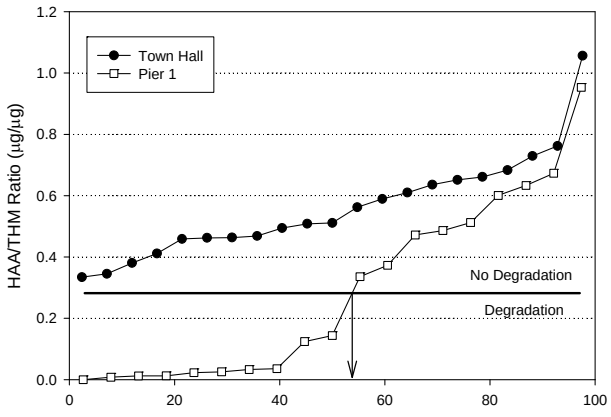
- Norwood, MA example



Why the loss of HAAs?

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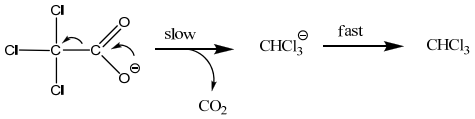
- Homogeneous Chemical Decomposition ?
  - Decarboxylation



    - What is half-life
      - Is it too slow to be very important?
  - Dehalogenation
    - Probably too slow for chlorinated HAAs
- Reaction with reduced pipe materials?
  - Abiotic reductive dehalogenation not likely either, especially for DCAA
- Biodegradation?

A few recent studies

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- Modeling HAA Biodegradation in Biofilters and Distribution Systems
  - Alina S. Grigorescu and Ray Hozalski, University of Minnesota at Minneapolis

Journal AWWA, July 2010, 102(7)67-80

Background conclusion?

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- *"Thus aerobic biodegradation is believed to be the dominant HAA degradation process in ……..water distribution systems"*
  - Citing: Tung & Xie, 2009; Zhang et al., 2009a; 2009b; Bayless & Andrews, 2008

Objective/hypothesis

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- Not really stated, but they did end the intro with:
  - *"In this work, computer simulations were performed to predict the fate of three HAAs (MCAA, DCAA, and TCAA) along a distribution system and within a biologically active filter. Sensitivity analyses were performed to investigate the effects of physical parameters (e.g., fluid velocity) and biological parameters (e.g., biodegradation kinetics, biomass density) on HAA removal"*

Transport Model

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- Loss of HAAs in a pipe
  - One dimensional plug flow

$$C = C_0 e^{-k_{overall}\left(x/U\right)}$$

  - Overall rate is a combination of rate of biodegradation (k_{ra}) and mass transfer (k_{ma})

$$k_{overall} = \frac{1}{1/k_{ma} + 1/k_{ra}}$$

Biodegradation model

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- Monod model

$$\frac{dC}{dt} = -\frac{kXC}{K_M + C}$$

- Simplified for low C

$$\frac{dC}{dt} = -\frac{k}{K_M} XC \equiv -k_r XC$$

Biodegradation model II

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- Biodegradation rate (k_{ra}; in day^{-1}) is the pseudo-first order biodegradation rate constant (k_r; in L/day/µg-protein) times the biofilm density (X; in µg-protein/cm^2) and the specific surface area (a; in m^{-1})

$$k_{ra} = k_r Xa\left(\frac{10cm^2m}{L}\right) = \frac{4k_r X}{d}\left(\frac{10cm^2m}{L}\right)$$

Where d is the pipe diameter in meters

TABLE 1 Summary of kinetic parameter values used in the model calculations

Enrichment Culture or Isolate*	Bacterial Source	k—μg HAA/μg protein	K_M μg/L	k_r—L/d/μg protein
Experimentally determined values†				
MCAA kinetics				
WWM	Activated sludge enriched on MCAA	8.4 ± 1.5	97.7 ± 44.8	0.086
DCAA kinetics				
WWD	Activated sludge enriched on DCAA	47.0 ± 1.8	26.5 ± 5.6	1.77
PAWD	Pennsylvania tap water enriched on DCAA	9.36 ± 0.48	7.79 ± 5.82	1.2
PAWDI	Isolate from PAWD on DCAA	6.48 ± 0.48	77.91 ± 16.14	0.083
EMD2E	United Kingdom tap water enriched on DCAA	32.88 ± 0.72	4.38 ± 2.22	7.51
EMD2	Isolate from EMD2E on DCAA	23.28 ± 0.72	10.42 ± 3.61	2.23
TCAA kinetics				
WWT	Activated sludge enriched on TCAA	6.6 ± 0.6	210.7 ± 37.9	0.03
Estimated values‡				
MCAA kinetics				
PAWM	MCAA-degrading enrichment	ND	ND	0.0588
PAWMI	MCAA-degrading isolate	ND	ND	0.0041
EMM2E	MCAA-degrading enrichment	ND	ND	0.37
EMM2	MCAA-degrading isolate	ND	ND	0.11
TCAA kinetics				
PAWT	TCAA-degrading enrichment	ND	ND	0.0204
PAWTI	TCAA-degrading isolate	ND	ND	0.0014
EMT2E	TCAA-degrading enrichment	ND	ND	0.13
EMT2	TCAA-degrading isolate	ND	ND	0.038

DCAA—dichloroacetic acid, HAA—haloacetic acid, k—maximum specific utilization rate, K_M—substrate concentration at which the biodegradation rate is half of the maximum rate, k_r—pseudo-first-order biodegradation rate constant, MCAA—monochloroacetic acid, ND—not determined, TCAA—trichloroacetic acid

*Initialisms for bacterial strains are not literal. For additional details about these strains, see Zhang et al, 2009b.
†The average k and K_M values were used for calculating the k_r values.
‡The k_r values were calculated by multiplying the calculated k_r values for the MCAA enrichment cultures and isolates by $k_{r,WWM}/k_{r,WWD}$ (0.049) and $k_{r,PAWD}/k_{r,PAWDI}$ (0.017).

Mass Transfer Model I

- Mass transfer constant (k_{ma}) is the mass transfer velocity (k_m; m/s) times the specific surface area; and k_m is related to the Sherwood number

$$k_{ma} = k_m a \qquad k_m = \frac{ShD_w}{d}$$

Compare to equ 7.126 in Clark

  - combining

$$k_{ma} = k_m a = \frac{ShD_w}{d} a = \frac{4ShD_w}{d^2}$$

- Linton & Sherwood (1950) found the following correlation for flow in pipes (fn(Reynolds and Schmidt numbers)):

$$Sh = 0.023\,\mathrm{Re}^{0.83}\,Sc^{0.33}$$

Eq 7.164 in Clark

Mass Transfer Model II

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- The Schmidt number is the ratio of mass to viscous diffusion timescales, and calculated from the viscosity, the density and the diffusion coefficient:

$$Sc = \frac{\mu_w}{\rho_w D_w}$$

Compare to equ 7.82 in Clark

- And the Reynolds number can be calculated from the pipe diameter, velocity, density and viscosity:

$$\mathrm{Re} = \frac{du\rho_w}{\mu_w}$$

Model Predictions

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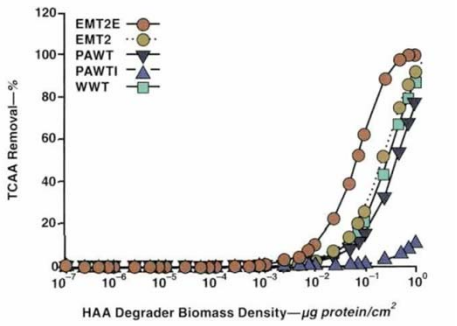
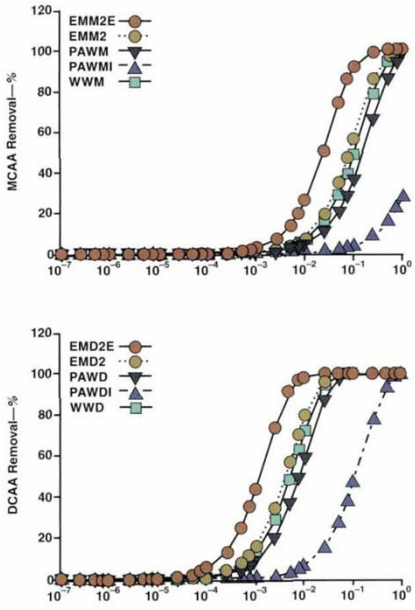


DCAA—dichloroacetic acid, HAA—haloacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

For these simulations, the pipe length was 10 mi, the pipe diameter was 6 in., and the water flow velocity was 2 fps.

Initialisms for bacterial strains are not literal. For additional details about these strains, see Zhang et al, 2009b.

FIGURE 1 Effect of culture and HAA-degrader biomass density on the biodegradation of MCAA, DCAA, and TCAA in a water distribution system



Impact of biomass density

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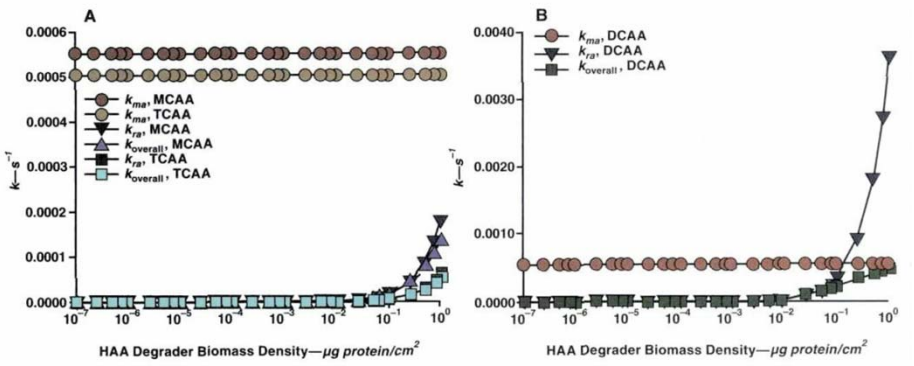
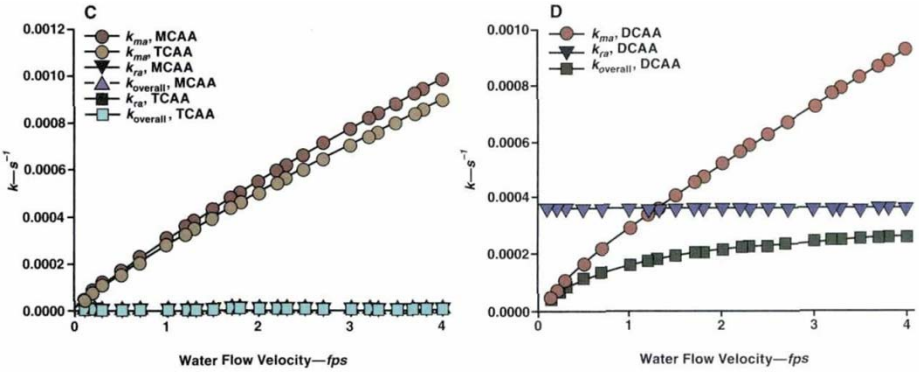


Impact of flow velocity

24



Impact of Pipe Diameter

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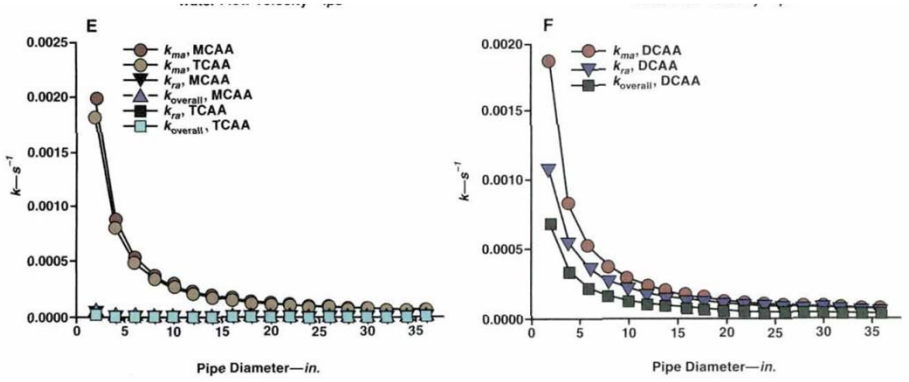

DCAA—dichloroacetic acid, HAA—haloacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

Simulations were performed using the kinetic parameters for Pennsylvania tap water enrichment cultures (i.e., PAWM, PAWD, PAWT). For parts A and B, the water flow velocity was 2 fps, and the pipe diameter was 6 in. For parts C and D, the HAA-degrader biomass density was 0.1 μg protein/cm² and the pipe diameter was 6 in. For parts E and F, the water flow velocity was 2 fps, and the HAA-degrader biomass density was 0.1 μg protein/cm².

Combining

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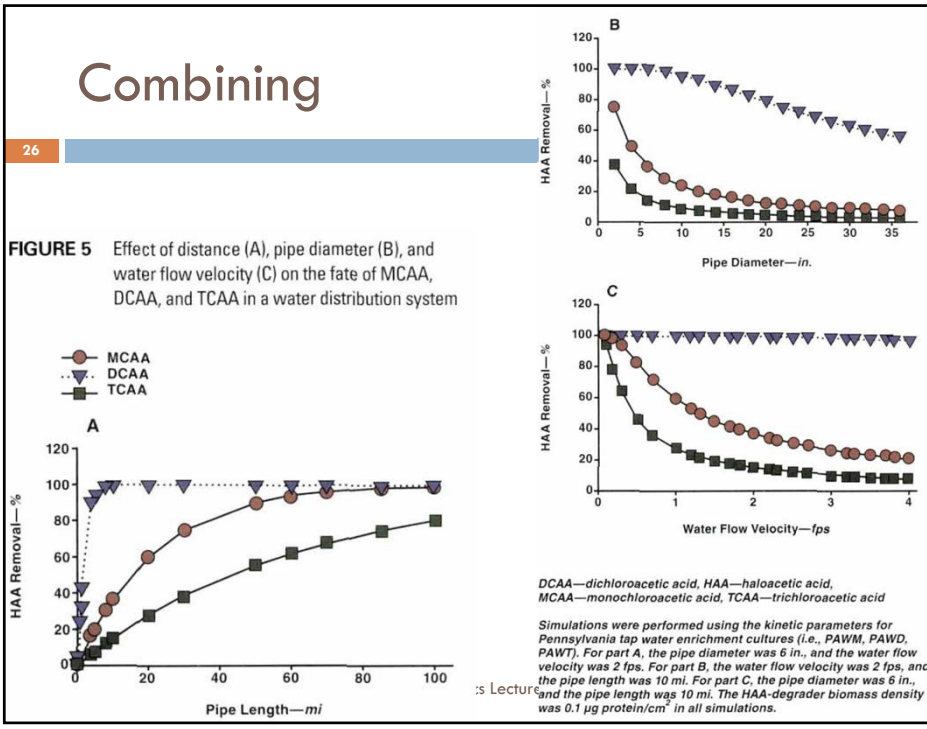
FIGURE 5 Effect of distance (A), pipe diameter (B), and water flow velocity (C) on the fate of MCAA, DCAA, and TCAA in a water distribution system



DCAA—dichloroacetic acid, HAA—haloacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

Simulations were performed using the kinetic parameters for Pennsylvania tap water enrichment cultures (i.e., PAWM, PAWD, PAWT). For part A, the pipe diameter was 6 in., and the water flow velocity was 2 fps. For part B, the water flow velocity was 2 fps, and the pipe length was 10 mi. For part C, the pipe diameter was 6 in., and the pipe length was 10 mi. The HAA-degrader biomass density was 0.1 μg protein/cm² in all simulations.

Conclusions

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- *"Overall the model calculations suggest that biodegradation is…..not likely to play a major role in most water distribution systems"*
  - *"the conditions needed for significant HAA removals in a distribution system (i.e., total biomass densities > 10^5 cells/cm^2 over long distances of pipe) are unlikely in the US water distribution systems where total chlorine residuals typically are high and thus inhibit the development of biofilm on pipe walls"*

But this seems to contradict their introductory conclusion – how to reconcile?

What could they have concluded?

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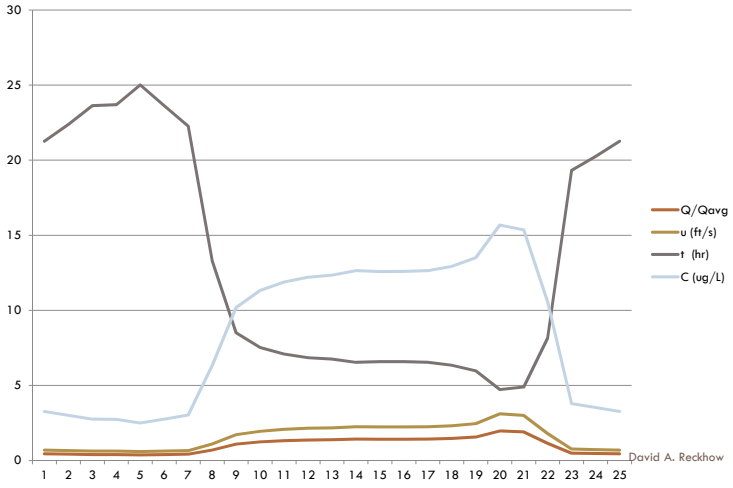
- Variability vs diurnal demand



Objective/hypothesis

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What could they have said?

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- To determined if observed HAA loss could be attributed to biodegradation on pipe walls given known physical and microbial characteristics of distribution systems
- To estimate spatial and temporal variability of HAA concentrations based on a rational physical model of biodegradation in distribution systems

What could they have done?

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- Find some direct evidence for biodegradation of HAAs in distribution systems
  - A product of the enzymatic reaction?
    - Chlorohydroxyacetate?
- Evidence of abiotic reactions?
  - Increase in MCAA?

What else?

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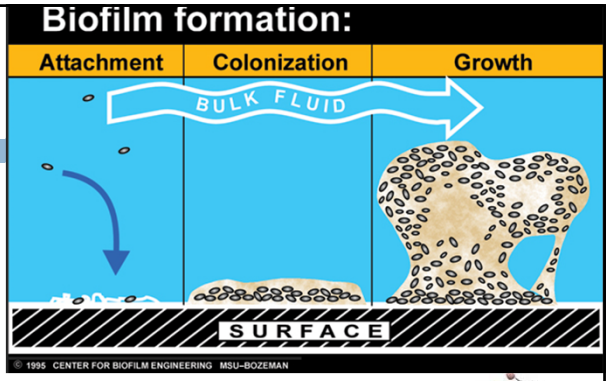
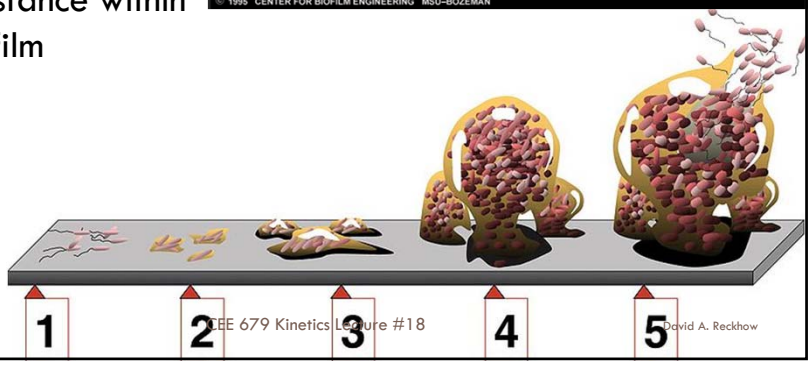
- Consider mass transfer resistance within biofilm





What should be done next?

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- Experimental Work
  - In-situ controlled study of flow velocity vs DCAA loss in a pipe segment?
  - Effect of biocide in above segment?
- Model Refinement
  - Account for internal mass transfer resistance
  - Combine with growth model for HAA degraders

- B1: biologically fixed bacteria
- B2: adsorbed bacteria

SANCHO Model

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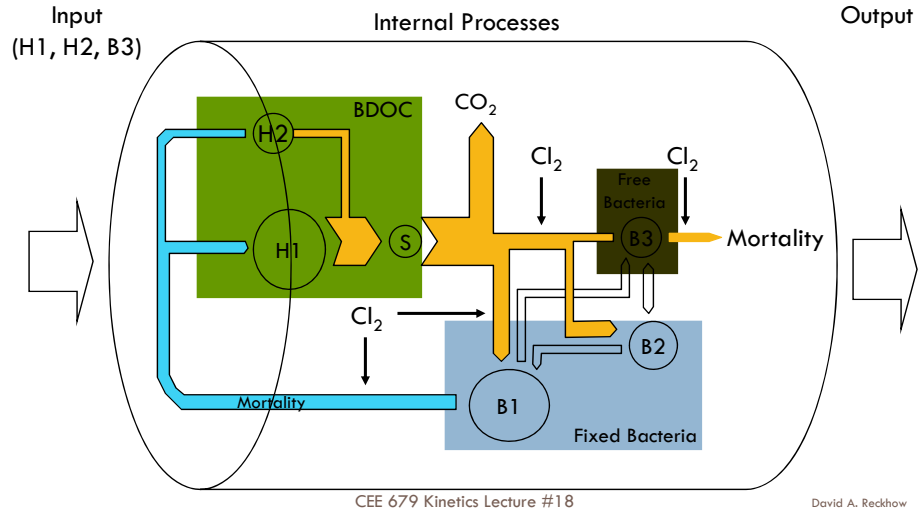

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TABLE 2 Summary of equations used to compute the mass transfer rate constants for the distribution system and biologically active filter

Distribution System	Biologically Active Filter	Notation
$Sh = 0.023\ Re^{0.83}\ Sc^{0.33}$	$Sh = 1.09\epsilon^{-2/3}\ Re^{1/3}\ Sc^{1/3}$	d = pipe diameter
$k_m = \frac{ShD_w}{d}$	$k_m = \frac{ShD_w}{d_p}$	d_p = filter media grain diameter
		D_w = solute diffusion coefficient in water
$Sc = \frac{\mu_w}{\rho_w D_w}$	$Sc = \frac{\mu_w}{\rho_w D_w}$	k_m = mass transfer rate constant
		Re = Reynolds number
		Sc = Schmidt number
$Re = \frac{du\rho_w}{\mu_w}$	$Re = \frac{d_p v \rho_w}{(1-\epsilon)\mu_w}$	Sh = Sherwood number
		u = water flow velocity
		v = filtration rate
		ϵ = bed porosity
		μ_w = water viscosity at 20°C
		ρ_w = water density at 20°C

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TABLE 3 General parameter values used for the model calculations

Parameter	Symbol	Value	References/Observations
Water temperature	T	20°C	Simulated summer conditions
Water viscosity	μ_w 20°C	1.0087×10^{-3} kg m^{-1} s^{-1}	Reynolds & Richards, 1996
Water density	ρ_w 20°C	998.2 kg m^{-3}	Reynolds & Richards, 1996
Diffusion coefficient of MCAA in water	$D_{w,MCAA}$	1.12×10^{-9} m^2 s^{-1}	Zhang et al, 2004
Diffusion coefficient of DCAA in water	$D_{w,MCAA}$	1.02×10^{-9} m^2 s^{-1}	Zhang et al, 2004
Diffusion coefficient of TCAA in water	$D_{w,TCAA}$	9.75×10^{-10} m^2 s^{-1}	Zhang et al, 2004

DCAA—dichloroacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

TABLE 4 Parameter values used to simulate the fate of haloacetic acids in water distribution systems

Parameter	Symbol	Range	References
Total bacterial density on the pipe wall	ρ	10–10^8 cells/cm^2; 10^7 cells/cm^2 for simulations in which other parameters were varied	Silhan et al, 2006; Lehtola et al, 2004; Chang et al, 2003; Ollos et al, 2003; Zhang et al,2002; Niquette et al, 2000; Donlan & Pipes, 1988; LeChevalier et al, 1987
Pipe diameter	d	2–36 in.; 6 in. for simulations in which other parameters were varied	McGhee, 1991; Rhoades, 1986
Water flow velocity	u	0.1–4 fps; 2 fps for simulations in which other parameters were varied	McGhee, 1991
Pipe distance	x	0–100 mi; 10 mi for simulations in which other parameters were varied	

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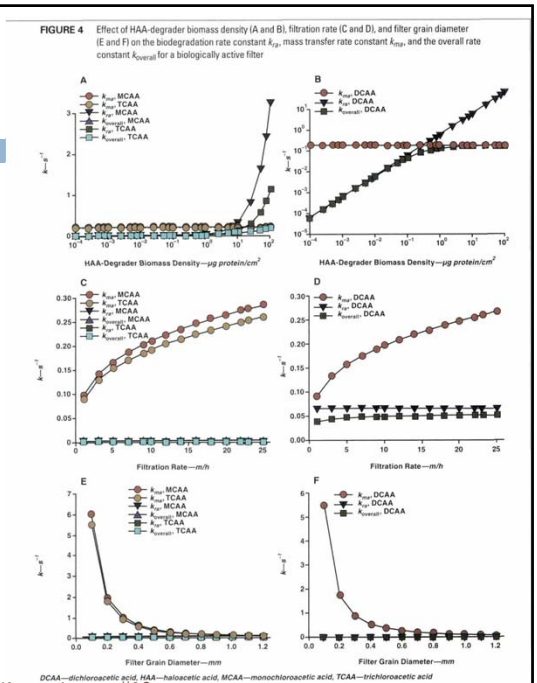

Effect of Zn on HAAs

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- Effect of Zinc on the Transformation of HAAs in Drinking Water
  - Wei Wang and Lizhong Zhu
    - Journal of Hazardous Materials 174:40-46.

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- To next lecture