Conclusions

- “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?

- Variability vs diurnal demand

[Graph showing variability vs diurnal demand]

Objective/hypothesis

- 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”
What could they have said?

- To determine 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?

- 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?

- Consider mass transfer resistance within biofilm

What should be done next?

- **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
SANCHO Model

- B1: biologically fixed bacteria
- B2: adsorbed bacteria

**Input**
(H1, H2, B3)

**Internal Processes**

**Output**

\[
\begin{align*}
& \text{BDOC} \\
& \text{CO}_2 \\
& \text{Cl}_2 \\
& \text{Mortality}
\end{align*}
\]

\[
\begin{align*}
& \text{Fixed Bacteria} \\
& \text{B1} \\
& \text{Mortality}
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Distribution System</th>
<th>Biologically Active Filter</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ Sh = 0.023 \text{Re}^{0.83} \text{Sc}^{0.33} ]</td>
<td>[ Sh = 1.09 \text{Re}^{2/3} \text{Sc}^{1/3} ]</td>
<td>( d ) = pipe diameter</td>
</tr>
<tr>
<td>[ k_m = \frac{ShD_w}{d} ]</td>
<td>[ k_m = \frac{ShD_w}{d_p} ]</td>
<td>( d_p ) = filter media grain diameter</td>
</tr>
<tr>
<td>[ Sc = \frac{\mu_w}{\rho_wD_w} ]</td>
<td>[ Sc = \frac{\mu_w}{\rho_wD_w} ]</td>
<td>( D_w ) = solute diffusion coefficient in water</td>
</tr>
<tr>
<td>[ Re = \frac{d\rho_w\mu_w}{\mu_w} ]</td>
<td>[ Re = \frac{d\rho_w\mu_w}{\rho_w(1-\epsilon)\mu_w} ]</td>
<td>( \epsilon ) = bed porosity</td>
</tr>
</tbody>
</table>

\( \mu_w \) = water viscosity at 20°C
\( \rho_w \) = water density at 20°C

CEE 679 Kinetics Lecture #19
### TABLE 3  General parameter values used for the model calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>References/Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water temperature</td>
<td>$T$</td>
<td>$20^\circ C$</td>
<td>Simulated summer conditions</td>
</tr>
<tr>
<td>Water viscosity</td>
<td>$\rho_{w}$</td>
<td>$1.0087 \times 10^{-1}$ $kg$ $m^{-3}$</td>
<td>Reynold's, 1996; Zhang et al., 2004</td>
</tr>
<tr>
<td>Water density</td>
<td>$\rho_{w}$</td>
<td>$998.2$ $kg$ $m^{-3}$</td>
<td>Zhang et al., 2004</td>
</tr>
<tr>
<td>Diffusion coefficient of MCAA in water</td>
<td>$D_{MCAA}$</td>
<td>$1.12 \times 10^{-9}$ $m^{2}$ $s^{-1}$</td>
<td>Niquette et al., 2002</td>
</tr>
<tr>
<td>Diffusion coefficient of DCAA in water</td>
<td>$D_{DCAA}$</td>
<td>$1.02 \times 10^{-9}$ $m^{2}$ $s^{-1}$</td>
<td>Niquette et al., 2002</td>
</tr>
<tr>
<td>Diffusion coefficient of TCIA in water</td>
<td>$D_{TCIA}$</td>
<td>$9.75 \times 10^{-10}$ $m^{2}$ $s^{-1}$</td>
<td>Niquette et al., 2002</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total bacterial density on the pipe wall</td>
<td>$\rho$</td>
<td>$10^{-10}$ cells/cm$^3$ - $10^{-3}$ cells/cm$^3$</td>
<td>Slibun et al., 2006; Leblanc et al., 2004; Chang et al., 2003; Olmos et al., 2003; Zhang et al., 2002; Niquette et al., 2000; Dorton &amp; Pipes, 1986; LeChevalier et al., 1987; McGhee, 1991; Riboudes, 1986</td>
</tr>
<tr>
<td>Pipe diameter</td>
<td>$d$</td>
<td>2-36 in; 6 in. for simulations in which other parameters were varied</td>
<td>McGhee, 1991</td>
</tr>
<tr>
<td>Water flow velocity</td>
<td>$u$</td>
<td>0.1-4 fps; 2 fps for simulations in which other parameters were varied</td>
<td>McGhee, 1991</td>
</tr>
<tr>
<td>Pipe distance</td>
<td>$x$</td>
<td>0.1-10 m; 10 m for simulations in which other parameters were varied</td>
<td>McGhee, 1991</td>
</tr>
</tbody>
</table>

![Figure 4: Effect of Haloacetic Acid (HAA) and Haloformic Acid (HFA) on the rate of removal](image-url)
Effect of Zn on HAAs

- Effect of Zinc on the Transformation of HAAs in Drinking Water
  - Wei Wang and Lizhong Zhu

Enzymatic Reactions

- Many ways of illustrating the steps
  - Substrate(s) bond to active site
  - Product(s) form via transition state
  - Product(s) are released
Basic Enzyme Kinetics

- Irreversible
  - Single intermediate
    - The overall rate is determined by the RLS, \( k_2 \)
      \[
      r \equiv -\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[ES]
      \]
    - But we don’t know \([ES]\), so we can get it by the SS mass balance
      \[
      \frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]
      \]
    - Again, we only know \([E_o]\) or \([E_{tot}]\), not free \([E]\), so:
      \[
      0 = k_1([E_o] - [ES])[S] - k_{-1}[ES] - k_2[ES]
      \]

Reactants, products and Intermediates

- Simple Progression of components for simple single intermediate enzyme reaction
  - Shaded block shows steady state intermediates
  - Assumes \([S] \gg [E]\)
  - From Segel, 1975; Enzyme Kinetics
And solving for $[ES]$,

$$k_1[ES][S] + k_{-1}[ES] + k_2[ES] = k_1[E_o][S]$$

$$[ES] = \frac{k_1[E_o][S]}{k_1[S] + k_{-1} + k_2}$$

Michaelis–Menten

- Irreversible
  - Single intermediate

$$r \equiv \frac{d[P]}{dt} = k_2[ES]$$

$$r \equiv \frac{d[P]}{dt} = \frac{k_2[E_o][S]}{k_1[S] + [S]} = \frac{r_{max}[S]}{K_s + [S]}$$
Michaelis Menten Kinetics

- Classical substrate plot

\[
\begin{align*}
\text{Substrate Concentration} & \quad \text{Reaction Rate} \\
0 & \quad 0 \\
20 & \quad 20 \\
40 & \quad 40 \\
60 & \quad 60 \\
80 & \quad 80 \\
100 & \quad 100 \\
\end{align*}
\]

\[
r = \frac{d[P]}{dt} = \frac{r_{max} [S]}{K_s + [S]}
\]

Substrate and growth

- If we consider \( Y \)

\[
r = \frac{d[P]}{dt} = \frac{d[S]}{dt} = \frac{1}{Y} \frac{dX}{dt}
\]

- We can define a microorganism-specific substrate utilization rate, \( U \)

\[
U = \frac{r}{X} = \frac{dX}{dt} \frac{1}{YX} = \frac{\mu}{Y}
\]

- And the maximum rates are then

\[
U_{max} = k = \frac{\mu_{max}}{Y}
\]

\[
U = \frac{1}{X} \frac{d[S]}{dt} = \frac{k[S]}{K_s + [S]}
\]

\[
\mu = \frac{1}{X} \frac{d[X]}{dt} = \frac{\mu_{max} [S]}{K_s + [S]}
\]

CIE 679 Kinetics Lecture #19

David A. Reckhow
Linearizations

- Lineweaver-Burke
  - Double reciprocal plot

Wikipedia version

Voet & Voet version

Das
3 types

- Lineweaver Burk

- Hanes

- Eadie-Hofsteede

Compare predictions
Multi-step

Double intermediate
- Also gives:
  \[ r \equiv \frac{d[P]}{dt} = \frac{r_{\text{max}}[S]}{K_s + [S]} \]

But now:
  \[ r_{\text{max}} = \frac{k_2 k_3 E_o}{k_2 + k_3} \quad K_s = \frac{k_3 (k_{-1} + k_2)}{(k_2 + k_3) k_1} \]

Note what happens when: \( k_3 \gg k_2 \)

To next lecture
Enzymatic Reactions

- Many ways of illustrating the steps
  - Substrate(s) bond to active site
  - Product(s) form via transition state
  - Product(s) are released

Basic Enzyme Kinetics

- Irreversible
  - Single intermediate
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      $$ r \equiv -\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[ES] $$
    - But we don’t know $[ES]$, so we can get it by the SS mass balance
      $$ \frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES] $$
    - Again, we only know $[E_0]$ or $[E_{\text{tot}}]$, not free $[E]$, so:
      $$ 0 = k_1([E_0] - [ES])[S] - k_{-1}[ES] - k_2[ES] $$

Note that some references use $k_2$ for $k_{-1}$, and $k_3$ for $k_2$.
Reactants, products and Intermediates

Simple Progression of components for simple single intermediate enzyme reaction
- Shaded block shows steady state intermediates
- Assumes \([S] \gg [E]\),
- From Segel, 1975; Enzyme Kinetics

![Graph of concentration over time showing reactants, products, and intermediates.](image)

Basic Enzyme Kinetics II

- And solving for \([ES]\),

\[
k_1[ES][S] + k_{-1}[ES] + k_2[ES] = k_i[E_o][S]
\]

\[
[ES] = \frac{k_i[E_o][S]}{k_i[S] + k_{-1} + k_2}
\]

\[
[ES] = \frac{[E_o][S]}{[S] + \frac{k_{-1} + k_2}{k_1}}
\]

CEE 679 Kinetics Lecture #19
Michaelis-Menten

- **Irreversible**
  - Single intermediate

\[ \text{E + S} \xrightarrow{k_1} \text{ES} \xrightarrow{k_2} \text{E} + \text{P} \]

\[ r \equiv \frac{d[P]}{dt} = k_2[ES] \]

\[ [ES] = \frac{[E_o][S]}{[S] + \frac{k_1}{k_2}} \]

\[ r = \frac{d[P]}{dt} = \frac{k_2[E_o][S]}{\frac{k_1}{k_2} + [S]} = \frac{r_{max}[S]}{K_s + [S]} \]

Michaelis-Menten Kinetics

- **Classical substrate plot**

\[ r \equiv \frac{d[P]}{dt} = \frac{r_{max}[S]}{K_s + [S]} \]
Substrate and growth

- If we consider \( Y \)
  \[
  r \equiv \frac{d[P]}{dt} = -\frac{d[S]}{dt} = \frac{1}{Y} \frac{dX}{dt}
  \]

- We can define a microorganism-specific substrate utilization rate, \( U \)
  \[
  U = \frac{dX}{dt} = \frac{r}{YX} \approx \frac{\mu}{Y}
  \]

- And the maximum rates are then
  \[
  U_{\text{max}} = k = \frac{\mu_{\text{max}}}{Y}
  \]

\[
U \equiv 1 \frac{d[S]}{dt} = \frac{k[S]}{K_s + [S]} \quad \text{and} \quad \mu \equiv \frac{1}{X} \frac{d[X]}{dt} = \frac{\mu_{\text{max}} [S]}{K_s + [S]}
\]

Linearizations

- Lineweaver-Burke
  - Double reciprocal plot

\[
\frac{1}{v} = \frac{1}{V_{\text{max}}} + \frac{K_m}{V_{\text{max}}} \quad \text{and} \quad \frac{1}{\mu} = \frac{1}{S} + \frac{K_s}{S}
\]

\[
\text{Slope} = \frac{K_m}{V_{\text{max}}} \quad \text{and} \quad [S] = 0.5 K_M
\]

\[
\text{Slope} = 5 \quad \text{and} \quad [S] = 5 K_M
\]
3 types

- Lineweaver-Burk
- Hanes
- Eadie-Hofstee
Compare predictions

Multi-step

- Double intermediate
  - Also gives:
    \[ r = \frac{d[P]}{dt} = \frac{r_{\text{max}}[S]}{K_s + [S]} \]
  - But now:
    \[ r_{\text{max}} = \frac{k_2 k_3 [E_o]}{k_2 + k_3} \]
    \[ K_s = \frac{k_3 (k_{-1} + k_2)}{(k_2 + k_3) k_1} \]
  - Note what happens when: \( k_3 >> k_2 \)
☐ To next lecture