Important points from previous lecture

• What are the major hydrologic fluxes to and from lakes?
• How can flow from one gaged river be extrapolated to an ungaged river?
• How does one convert flow in cm to units of m$^3$/sec?
• What is the definition of water residence time? Of conservative-chemical-residence time?

Models & Modeling
Model Definitions

- A **simplified** representation of something;
- a description or analogy used to help visualize something that cannot be directly observed;
- a system of postulates, data, and inferences presented as a **mathematical description** of an entity or state of affairs;

Types of Models

- CONCEPTUAL: a non-quantitative description that illustrates the underlying structures, mechanisms or trends;
- all models generally begin as conceptual models;
Types of Models: BOX

- A box model is little more than a conceptual model of flow paths;
- it may or may not have estimates of transfer rates;

Types of Models: Empirical

- Empirical models provide a quantitative, mathematical description of data;
- the mathematical expression in the model may be unrelated to the causal mechanisms.
Concentrations in Rivers

Mass flux (kg/d) = Conc. (kg/m³) • Flow (m³/d)

Often, flow is measured continuously, but concentrations are measured only periodically. Because concentration often is related to flow, a “Q-C” relationship can be used to estimate concentrations that were not measured.

Flow x Conc. = Load
(m³/yr)(g/m³) = g/yr

L = QC
L = Q(12.3lnQ-39)
Types of Models: Mechanistic

- Mechanistic models employ equations based on actual reaction steps or pathways;
- mechanistic models are quantitative;
- models may be used in simulation, design or predictive modes.

Simulation Mode

![Graph showing simulations over years for North and South basins with and without algal uptake.](image-url)
All models are wrong; some are useful
**Chapra Model**

- $c =$ concentration (M L$^{-3}$)
- $W =$ loading (M T$^{-1}$)
- $a =$ assimilation factor (L$^3$ T$^{-1}$)

\[ c = \frac{1}{a} \bullet W \]

**Simplest Mass Balance Model**

\[ V \frac{dC}{dt} = Q_{in} C_{in} - Q \cdot C - k \cdot C \cdot V \]
Steady State Solution

\[ V \frac{dC}{dt} = Q_{in} C_{in} - Q \cdot C - k \cdot C \cdot V \]

\[ \frac{dC}{dt} = 0 \]

\[ Q_{in} C_{in} = \text{Load} = W = C(Q + kV) \]

\[ C = \frac{W}{Q + kV} = \frac{W}{a} \]

Hydrologic Budget

\[ Q_{in} + P + G_{in} - (Q + G_{out} + E) = \frac{dV}{dt} = \Delta S (= 0) \]
Hydrologic Budgets

<table>
<thead>
<tr>
<th>Flux (cm)</th>
<th>Lake Superior</th>
<th>Little Rock Lake</th>
<th>Torch Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{in}$</td>
<td>56.3 (41%)</td>
<td>0</td>
<td>1130 (94%)</td>
</tr>
<tr>
<td>$P$</td>
<td>80.4 (59%)</td>
<td>82.4 (92%)</td>
<td>77.4 (6%)</td>
</tr>
<tr>
<td>$G_{in}$</td>
<td>0</td>
<td>7.5 (8%)</td>
<td>~0</td>
</tr>
<tr>
<td>$E$</td>
<td>39.8 (32%)</td>
<td>50.8 (56%)</td>
<td>55 (4%)</td>
</tr>
<tr>
<td>$Q$</td>
<td>85.6 (68%)</td>
<td>0</td>
<td>1160 (96%)</td>
</tr>
<tr>
<td>$G_{out}$</td>
<td>0</td>
<td>39.1 (44%)</td>
<td>~0</td>
</tr>
</tbody>
</table>
Chapra Model

\[ V \frac{dC}{dt} = Q_{in} C_{in} - Q \cdot C - k \cdot C \cdot V \]

Chapra model again

\[
\frac{dC}{dt} = 0 \quad \text{Steady State}
\]

\[
Q_{in} C_{in} = \text{Load} = W = C(Q + kV)
\]

\[
C = \frac{W}{Q + kV} = \frac{W}{a}
\]
Kinetics: Points to learn

- Rate laws (zero-, first-, second-, pseudo-first-order, Monod, reversible or “deficit”);
- Methods to assess rate law (graphical [integral], differential);
- Temperature dependence
  - Arrhenius equation
  - θ values
  - Q_{10}
Timestep Effects

SO$_4^{2-}$ (µM)

Year


1-month 2-month 6-month 12-month Measured values

LRL Conceptual Model

Atmospheric Deposition $W_A$

Groundwater Discharge $W_{GWin}$

Lake SO$_4^{2-}$

Groundwater Discharge $W_{GWout}$

Algal Sedimentation $W_{alg}$

Microbial Sulfate reduction $W_{bac}$
Sulfate Reduction

Common Rate Laws

\[
\frac{dC}{dt} = k \quad \text{Zero order}
\]

\[
\frac{dC}{dt} = kC \quad \text{First order}
\]

\[
\frac{dC}{dt} = kC^2 \quad \text{Second order}
\]

\[
\frac{dC}{dt} = V_m \cdot \frac{C}{K_m + C} \quad \text{Michaelis-Menten}
\]
Differential Evaluation

\[ \log\left(\frac{dC}{dt}\right) \]

\[ n=1.7, \; k=0.04 \text{ hr}^{-1} \]
\[ r^2=0.46, \; P < 0.05 \]

Second Order Reaction

\[ \frac{1}{[SO_4^{2-}]} \]

\[ n=2, \; k=0.0062 \text{ L mole}^{-1} \text{ hr}^{-1} \]
\[ r^2=0.65, \; P < 0.01 \]
Evaluation of rate constant

\[ \ln[\text{SO}_4^{2-}] \text{vs. Time (hr)} \]

- \( k = 0.36 \text{ hr}^{-1} \)
- \( r^2 = 0.39, \ P < 0.05 \)

Michaelis-Menten Kinetics

- \( V_m = 11 \ \mu\text{M hr}^{-1} \)
- \( K_m = 20 \ \mu\text{M} \)
- \( r^2 = 0.84 \)
Integration revisited

\[ \ln(C/Co) = n = 1, \ k = 0.54 \ \text{hr}^{-1} \]
\[ r^2 = 0.81, \ P < 0.01 \]

Temperature dependence of rates

Rate (nmol cm$^{-3}$ hr$^{-1}$)

Temperature (°C)

\[ r^2 = 0.81, P < 0.01 \]
Temperature Corrections

\[ k = A \exp \left( \frac{-E_A}{RT} \right) \]

Arrhenius Equation

\[ \frac{k_1}{k_2} = \exp \left( \frac{E_A}{RT} \right) \]

\[ \theta = \exp \left( \frac{E_A}{RT_1} \right) \]

\[ Q_{10} = \theta^{10} = \frac{k_{T+10}}{k_T} \]

Temperature dependence of rates

Fig. A. Rates of nitric oxide reaction in solution showed large responses to changes in temperature. However, rates were in line with those measured in initial tests. B. An Arrhenius plot of the data without correction was almost all (temperatures) indicated that the activation energy may not have been constant over the entire temperature range. A regression with all data points yields a Q_{10} value of only 2.6, lower than many reported in the literature.
Process equations:

1. Sulfate reduction (SR, kg yr\(^{-1}\))

\[
SR = k \cdot \theta^{T-20} \cdot [SO_4^{2-}] \cdot A
\]

\(k = 0.37 \text{ m yr}^{-1}\)
\(\theta = 1.041 \ (Q_{10} = 1.5)\)

2. Biological uptake, settling (BU, kg yr\(^{-1}\))

\[
BU = NPP \cdot \left( \frac{S_{\text{algae}}}{C_{\text{algae}}} \right) \cdot A
\]