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
Water Quality Management Plan

Specify Use

Establish Criteria

Determine Cause/Effect

Cost/Benefit Analysis

Social/other non-monetary impact analysis

Identify Alternatives

Often based on empirical models

Modeling

All models are wrong; some are useful
**Chapra Model**

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

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

**Simplest Mass Balance Model**

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

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

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

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

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

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

1-10 1-month
2-2-month
3-6-month
4-12-month
5-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

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

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

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

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

\[ \text{ln}[\text{SO}_4^{2-}] / [\text{SO}_4^{2-}]_0 = -0.36 \text{ hr}^{-1} \]
\[ r^2 = 0.39, P < 0.05 \]

Michaelis-Menten Kinetics

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

\[ \ln(C/Co) = 0 \]

\[ n=1, k=0.54 \text{ hr}^{-1}, r^2=0.81, P < 0.01 \]

Temperature dependence of rates

\[ \text{Rate (nmol cm}^3 \text{ hr}^{-1}) \]

\[ 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \quad 30 \quad 35 \]

Temperature (°C)
Temperature Corrections

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

**Arrhenius Equation**

\[ \frac{k_1}{k_2} = \Theta^{T_2 - T_1} \]

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

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

**Free Energy**

\[ E_A = \text{Activation Energy} \]

\[ \Delta G^0 \]

**Course of Reaction, \( \xi \)**

Temperature dependence of rates

**Fig. 1.** A series of diluted solutions were prepared at various temperatures. The results are shown in the graph. The Arrhenius plot indicates a linear relationship between the reaction rate and temperature.

**Fig. 2.** The Arrhenius plot of the data with a concentration of 0.1 M at different temperatures shows a straight line. The reaction rate increases with increasing temperature, as predicted by the Arrhenius equation.

**Fig. 3.** A plot of the log of the reaction rate versus the reciprocal of the temperature shows a linear relationship, confirming the Arrhenius behavior of the reaction.
Process equations:

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

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

\[k = 0.37 \text{ m yr}^{-1}\]
\[\theta = 1.041 \text{ (Q}_{10} = 1.5)\]

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

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

SO\(_4^{2-}\) Model for LRL

Change in lake SO\(_4^{2-}\) = Sum(Inputs) – Sum(Outputs) ± Reaction

\[
V \frac{dC_{SO_4^{2-}}}{dt} = \text{Loading-Outflow± (SulfateReduction+BiologicalUptake)}
\]

\[
V \frac{dC_{SO_4^{2-}}}{dt} = W - QC - k\theta^{T-R} \cdot C_{SO_4^{2-}} \cdot A - NPP \cdot \frac{S_{algae}}{C_{algae}}
\]
Nitrogen in Lake Superior

- Atmos. Deposition
- Denitrification
- River inflows
- Outflow
- Sedimentation
- Porewater diffusion

1 state variable, 6 processes
Copper Cycle

Cu(aq) → Biotic uptake → Cu(p)

Sorption

Precipitation → Dissolution (leaching) → Resuspension → Setting