General Model
Kinetics

Atmosphere

Dissolved Oxygen

Organic N

NH₃

NO₂

NO₃

SOD

CBOD

K₄(K₉)

K₄

K₁(K₉)

K₃(K₉)
Modeling procedures

- Verify model calculations
  - using a simplified example, check computer vs. analytical
- Identify inputs (loads, rate coefficients, transport)
  - reaction coefficients - general
    - all rate constants must be uniform in space and time unless variations are linked to system characteristics
    - rates and formulations should fall within the range reported in the literature (e.g., *Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling*, Bowie et al., US EPA, Athens Environmental Research Laboratory, EPA/600/3-85/040, June 1985., see: [http://www.epa.gov/ORD/WebPubs/surfaceH2O/surface.html](http://www.epa.gov/ORD/WebPubs/surfaceH2O/surface.html) or course [website](#)

Identifying inputs (cont.)

- $k_d, k_r$
  - simplified method:
    - in-stream assessment
      - $k_d = 0.3 \left( \frac{H}{8} \right)^{-0.434}$ d$^{-1}$; for H < 8 ft
      - $k_d = 0.3 \text{ d}^{-1}$ for H > 8 ft

\[
L = L_0 e^{-k_r t}
\]

\[
\ln L = \ln L_0 - k_r t
\]
Identifying inputs (cont.)

- $k_d$, $k_r$ (cont.)
  - Tierney & Young correction for bottle rates

<table>
<thead>
<tr>
<th>Stream slope (ft/mile)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
</tr>
<tr>
<td>10</td>
<td>0.25</td>
</tr>
<tr>
<td>25</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Identifying inputs (cont.)

- Determining bottle rates from Lab data
  - Thomas Method

\[
\beta_0 \approx \frac{1}{6} \left( \beta^{-1} \beta_0^{-2} \right)
\]

\[
k_b \approx L_o^{-1} \beta_0^{-3}
\]
Identifying inputs (cont.)

- Photosynthesis/Respiration (Chapra L.24)
  - chemistry: \(6CO_2 + 6H_2O \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2\)
  - two important issues
    - long term effect: net of P & R
    - short term effect: extent of DO drop during night

- Three common methods
  - Light and Dark bottle method
    - expose aquatic biota to natural light conditions, with "control" in the dark
  - Estimation from Observed Chlorophyll levels
  - Measurement of Diurnal DO Range

Additional notes on WLA (cont.)

- Algal modeling
  - Level I
    - measure P-R: diurnal swings in D.O.
  - Level II
    - measure chlorophyll a, light, light extinction, nutrients "in-situ"
    - calculate P-R
  - Level III
    - assess nutrient loadings, light extinction
    - model nutrient conc., chlorophyll a, P-R
Time variability of Photosynthesis

- Assumed to be proportional to light intensity

\[ P(t) \]

\[ \int_0^{T_P} P(t) \, dt = P_m \frac{2f}{\pi} \]

Light and dark bottle method

- Expose aquatic plants to natural light conditions
- “control” in the dark bottle

\[ P_{net} = \frac{DO_{lf} - DO_{li}}{t} \]
\[ R_{cm} = \frac{DO_{di} - DO_{df}}{t} \]
\[ R_b = R_{cm} - k_d L_{of} \]
\[ P_b = P_{net} - R_{cm} \]
Estimation from observed chlorophyll levels

- Under conditions where algal metabolism is not limited

\[
P = r_{oa} G_{max} 1.066^{T-20} a \Phi_l \approx 0.25a
\]

- Oxygen generated per unit biomass produced (0.1-0.3 mg-O₂/µg-chla)
- Maximum plant growth rate for optimal conditions (1.5-3.0 d⁻¹)
- Concentration of plant biomass (µg-chla/L)
- Light attenuation factor

P-R method

- Respiration is from rates and stoichiometry
- Need chlorophyll level

\[
R = r_{oa} k_{ra} 1.08^{T-20} a \approx 0.025a
\]

- Plant respiration rate (0.05-0.25 d⁻¹)
• To next lecture