Lecture #24
Water Quality Management II: Rivers

Reading: Mihelcic & Zimmerman, Chapter 7 (7.7 focus)
Reading: Davis & Cornwall, Chapt 5-3
Reading: Davis & Masten, Chapter 9-3
River Pollution

- Percent impaired by pollutant
- Percent impaired by sources

From Masters, section 5.4
General Aspects of WQ Models

- Pollutants
  - Conservative
  - Non-conservative

- Approach
  - Deterministic
  - Stochastic

- Time Variability
  - Steady State
  - Dynamic

- Doesn't Undergo Degradation
- Based on mechanisms
- Unchanging with time
Waste Loading

- **Point Sources**
  - Municipal WW
  - Industrial WW
  - Tributaries

- **Non-point Sources**
  - Agricultural
  - Silvicultural
  - Atmospheric
  - Urban & Suburban Runoff
Loading Calculations

Point Sources - General Concepts

\[ W(t) = Q(t) \cdot c(t) \]

- \( W(t) \) in lb/d or kg/d
- \( Q(t) \) in ft\(^3\)/s or L/d
- \( c(t) \) in mg/L

Important Conversion Factors:

- \( \frac{lb \cdot liters}{mg \cdot MG} = 8.34 \)
- \( \frac{lb \cdot liters \cdot sec}{mg \cdot ft^3 \cdot day} = 5.39 \)
- \( \frac{Kg \cdot liters \cdot sec}{mg \cdot ft^3 \cdot day} = 2.45 \)
Chloride Problem

- Determine the required industrial reduction in chloride (a conservative substance) to maintain a desired chloride concentration of 250 mg/L at the intake.

\[
Q = 25 \text{ cfs} \\
c = 30 \text{ mg/L} \\
Q_w = 6.5 \text{ MGD} \\
c_w = 1500 \text{ mg/L} \\
Q_T = 5 \text{ cfs} \\
c_T = 30 \text{ mg/L}
\]
Example 24.1

- A waste is discharged into a river
  - Waste characteristics
    - $\text{CBOD}_5 = 200 \text{ mg/L}$
    - $k_L = 0.1 \text{ day}^{-1}$
    - $Q_w = 1 \text{ m}^3/\text{s}$
  - Upstream river characteristics
    - $\text{CBOD}_{\text{ultimate}} = 2 \text{ mg/L}$
    - $Q_u = 9 \text{ m}^3/\text{s}$
- What is the $\text{CBOD}_{\text{ultimate}}$ at the point of mixing?

See pg. 267 in Mehelic
Loading

Point Sources
- Municipal Wastewater
- Industrial Wastewater
- Tributaries

Non-point sources
- Agricultural
- Silvicultural
- Atmospheric
- Urban & suburban runoff
- Groundwater

Loading: \[ W(t) = Qc_{in}(t) \]

Well defined origin
- Easily measured
- More constant

Diffuse origin
- More transient
- Often dependent on precipitation
<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Municipal Influent</th>
<th>CSO</th>
<th>Urban Runoff</th>
<th>Agriculture (lb/mi²-d)</th>
<th>Forest (lb/mi²-d)</th>
<th>Atmosphere (lb/mi²-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average daily flow</td>
<td>gcd</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>mg/L</td>
<td>300</td>
<td>410</td>
<td>610</td>
<td>2500</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>CBOD₅</td>
<td>mg/L</td>
<td>180</td>
<td>170</td>
<td>27</td>
<td>40</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>CBODU</td>
<td>mg/L</td>
<td>220</td>
<td>240</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBOD</td>
<td>mg/L</td>
<td>220</td>
<td>290</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>mg-N/L</td>
<td>50</td>
<td>9</td>
<td>2.3</td>
<td>15</td>
<td>4</td>
<td>8.9-18.9</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>mg-P/L</td>
<td>10</td>
<td>3</td>
<td>0.5</td>
<td>1.0</td>
<td>0.3</td>
<td>0.13-1.3</td>
</tr>
<tr>
<td>Total coliforms</td>
<td>10⁶/100 mL</td>
<td>30</td>
<td>6</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>µg/L</td>
<td>1.2</td>
<td>10</td>
<td>13</td>
<td></td>
<td></td>
<td>0.015</td>
</tr>
<tr>
<td>Lead</td>
<td>µg/L</td>
<td>22</td>
<td>190</td>
<td>280</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>Chromium</td>
<td>µg/L</td>
<td>42</td>
<td>190</td>
<td>22</td>
<td></td>
<td></td>
<td>0.088</td>
</tr>
<tr>
<td>Copper</td>
<td>µg/L</td>
<td>159</td>
<td>460</td>
<td>110</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>µg/L</td>
<td>241</td>
<td>660</td>
<td>500</td>
<td></td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>Total PCB</td>
<td>µg/L</td>
<td>0.9</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td>0.002-0.02</td>
</tr>
</tbody>
</table>
Footnotes for T&M Table 1.3

aUnits apply to municipal, CSO (combined sewer overflow), and urban runoff sources; gcd = gallons per capita per day.
bThomann (1972); heavy metals and PCB, HydroQual (1982).
cThomann (1972); total coli, Tetra Tech, (1977); heavy metals Di Toro et al. (1978): PCB. Hydroscience (1978).
eHydroscience (1976a).
gCBOD5 = 5 day carbonaceous biochemical oxygen demand (CBOD); CBODU = ultimate CBOD; NBOD = nitrogenous BOD.
Loading: Flow as a function of precipitation

Non point sources are difficult to characterize

- Empirical approach: export coefficients (see Table 3.1 in T&M)
- Mechanistic approach: relate to meteorology, topology, etc.

- Flow: use the rational formula: \[ Q_r = cIA \]

- Runoff flow \([L^3/T]\)
- Runoff coefficient
  - 0.1-0.3 for rural areas (1 person/acre)
  - 0.7-0.9 for heavy commercial areas

Note:
1 acre-in/hr \(\approx\) 1 cfs

Drainage Area \([L^2]\)
Rainfall Intensity \([L/T]\)
Loading: conc. as a function of flow

It is common for pollutant concentrations from uncontrolled sources (e.g. tributaries) to be correlated with flow

- establish a log-log relationship
- \( c = aQ^b \)

\[
\log(C) = \log(a) + b\log(Q)
\]
Loading Example: #3.1 from T&M

Data: Runoff from 100 mi² of agricultural lands drains to a point in a river where a city of 100,000 people is located. The city has a land area of 10 mi² and its sanitary sewers are separated from its storm drains. A sewage treatment plant discharges to the river immediately downstream of the city. The area receives an annual rainfall of 30 in. of which 30% runs off the agricultural lands and 50% drains off the more impervious city area.

Problem: Using the loading data from Table 1.3 and the residual fractions cited in the table below, compare the contributions of the atmospheric, agricultural and urban sources to annual average values of flow, CBOD5, total coliform bacteria, and lead in the river. Neglect any decay mechanisms for all parameters.

<table>
<thead>
<tr>
<th>Item</th>
<th>(at) Atmospheric</th>
<th>(ag) Agricultural</th>
<th>(ur) Urban Runoff</th>
<th>Wastewater Treatment Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Influent</td>
</tr>
<tr>
<td>Flow</td>
<td>30% precip.</td>
<td>50% precip.</td>
<td>125 gcd</td>
<td>1.00</td>
</tr>
<tr>
<td>CBOD5</td>
<td>40 lb/mi²-d</td>
<td>27 mg/L</td>
<td>180 mg/L</td>
<td>0.15</td>
</tr>
<tr>
<td>Total coliform</td>
<td>100/100 mL</td>
<td>3x10⁷/100mL</td>
<td>3x10⁸/100mL</td>
<td>0.0001</td>
</tr>
<tr>
<td>Lead</td>
<td>1.3 lb/mi²-d</td>
<td>280 µg/L</td>
<td>22 µg/L</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Solution to loading problem

- Flow contributions

\[ Q(\text{ag}) = 100mi^2 \left(\frac{30\text{in}}{\text{yr}}\right)0.3 \left(\frac{5280\text{ft}}{\text{mi}}\right)^2 \left(\frac{1\text{ft}}{12\text{in}}\right) \left(\frac{1\text{yr}}{365\text{d}}\right) \left(\frac{1\text{d}}{86,400\text{s}}\right) \]
\[ = 66.3\text{cfs} \]

\[ Q(\text{ur}) = 10mi^2 \left(\frac{30\text{in}}{\text{yr}}\right)0.5 \left(\frac{5280\text{ft}}{\text{mi}}\right)^2 \left(\frac{1\text{ft}}{12\text{in}}\right) \left(\frac{1\text{yr}}{365\text{d}}\right) \left(\frac{1\text{d}}{86,400\text{s}}\right) \]
\[ = 11.1\text{cfs} \]

\[ Q(\text{wwtp}) = 100,000\text{cap} \left(\frac{125\text{gal}}{\text{cap - d}}\right) \left(\frac{1\text{MG}}{10^6\text{gal}}\right) \]
\[ = 12.5\text{MGD} \left(\frac{1.548\text{cfs}}{\text{MGD}}\right) \]
\[ = 19.4\text{cfs} \]
Solution to loading problem (cont.)

CBOD5 loading

\[ W(\text{ag}) = 100 \times 10^2 \left(\frac{40 \text{ lb}}{\text{mi}^2 \text{d}}\right) \]

\[ = 4000 \frac{\text{lb}}{\text{d}} \]

\[ W(\text{ur}) = 11.1 \text{cfs} \left(27 \text{mg} / \text{L}\right) 5.4 \frac{\text{lb}}{\text{d}} \frac{\text{cfs} - \text{mg} / \text{L}}{\text{cfs} - \text{mg} / \text{L}} \]

\[ = 1620 \frac{\text{lb}}{\text{d}} \]

\[ W(\text{wwtp}) = 12.5 \text{MGD} \left(180 \text{mg} / \text{L}\right) 0.15 \left(\frac{8.34 \text{lb}}{\text{d}} \frac{\text{MGD} \times \text{mg} / \text{L}}{\text{MGD} \times \text{mg} / \text{L}}\right) \]

\[ = 2810 \frac{\text{lb}}{\text{d}} \]
Solution to loading problem (cont.)

Lead loading

\[ W(\text{atm}) = 100m^2 \left( 1.3 \frac{lb}{m^2 \cdot d} \right) 0.1 \]
\[ = 13 \frac{lb}{d} \]

\[ W(\text{ur}) = 11.1 \text{cfs} \left( 280 \mu g / L \right) 5.4 \left( \frac{lb}{d \cdot \text{cfs}} \right) \left( \frac{10^{-3} \text{mg}}{\mu g} \right) \]
\[ = 16.8 \frac{lb}{d} \]

\[ W(\text{wwtp}) = 12.5 \text{MGD} \left( 22 \mu g / L \right) 0.05 \left( \frac{8.34 \text{lb/d}}{\text{MGD} \cdot \text{mg/L}} \right) 10^{-3} \frac{\text{mg}}{\mu g} \]
\[ = 0.11 \frac{lb}{d} \]
DO Example

A polluted stream with a temperature of 25°C has a dissolved oxygen concentration of 4 mg/L. Use Gibbs free energy to determine if oxygen from the atmosphere is dissolving into the water, the oxygen is at equilibrium, or oxygen from the stream is going into the atmosphere.

\[ \text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) \]

Example 4.7 from Ray
Solution to DO example

\[ \Delta G_{\text{rxn}}^\circ = \Delta G_{\text{O}_2(\text{g})}^\circ - \Delta G_{\text{O}_2(\text{aq})}^\circ = (0 \text{ kcal/mol}) - (-3.9 \text{ kcal/mol}) \]

\[ \Delta G_{\text{rxn}}^\circ = 3.9 \text{ kcal/mol} \]

\[ \Delta G = \Delta G^\circ + RT \ln \frac{p_{\text{O}_2}}{[\text{O}_2(\text{aq})]} \]

\[ [\text{O}_2(\text{aq})] = 4 \text{ mg O}_2 \text{ L} \times \frac{\text{g O}_2}{1000 \text{ mg O}_2} \times \frac{\text{mol O}_2}{32 \text{ g O}_2} = 1.25 \times 10^{-4} \text{ M} \]
Solution (cont.)

\[
\Delta G = -3.9 \text{ kcal/mol} \times \frac{1000 \text{ cal}}{\text{kcal}} + \left(1.987 \frac{\text{cal}}{\text{K} \cdot \text{mol}} \right)(298 \text{ K}) \ln \left( \frac{0.209 \text{ atm}}{1.25 \times 10^{-4} \text{ M}} \right)
\]

\[
\Delta G = 491 \frac{\text{cal}}{\text{mol}} > 0
\]

Since \( \Delta G \) is positive, the reaction will proceed in the reverse direction as written. From the atmosphere to the water.
Gas Transfer: Equilibria

**Henry’s Law**

\[ C_{aq} = K_H' p_{gas} \]

where,
- \( C_{aq} \) = concentration of species A at equilibrium, [mol/L or mg/L]
- \( K_H' \) = Henry's Law constant for species A, [mol/L-atm or mg/L-atm]
- \( p_{gas} \) = partial pressure gas A exerts on the liquid, [atm]
# Henry’s Law Constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Name</th>
<th>$K_h$, mol/L-atm</th>
<th>$pK_h = -\log K_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2(g) = \text{CO}_2(aq)$</td>
<td>Carbon dioxide</td>
<td>$3.41 \times 10^{-2}$</td>
<td>1.47</td>
</tr>
<tr>
<td>$\text{NH}_3(g) = \text{NH}_3(aq)$</td>
<td>Ammonia</td>
<td>57.6</td>
<td>-1.76</td>
</tr>
<tr>
<td>$\text{H}_2\text{S}(g) = \text{H}_2\text{S}(aq)$</td>
<td>Hydrogen sulfide</td>
<td>$1.02 \times 10^{-1}$</td>
<td>0.99</td>
</tr>
<tr>
<td>$\text{CH}_4(g) = \text{CH}_4(aq)$</td>
<td>Methane</td>
<td>$1.50 \times 10^{-3}$</td>
<td>2.82</td>
</tr>
<tr>
<td>$\text{O}_2(g) = \text{O}_2(aq)$</td>
<td>Oxygen</td>
<td>$1.26 \times 10^{-3}$</td>
<td>2.90</td>
</tr>
</tbody>
</table>
Example: Solubility of $O_2$ in Water

Although the atmosphere we breathe is comprised of approximately 20.9 percent oxygen, oxygen is only slightly soluble in water. In addition, the solubility decreases as the temperature increases. Thus, oxygen availability to aquatic life decreases during the summer months when the biological processes which consume oxygen are most active. Summer water temperatures of 25 to 30°C are typical for many surface waters in the U.S. Henry's Law constant for oxygen in water is 61.2 mg/L-atm at 5°C and 40.2 mg/L-atm at 25°C. What is the solubility of oxygen at 5°C and at 25°C?
Solution $O_2$ Solubility Ex.

At $5^\circ C$ the solubility is:

$$C_{O_2}(5^\circ C) = K_{H,O_2} P_{O_2} = 61.2 \frac{mg}{L-\text{atm}} \times 0.209 \text{ atm}$$

$$C_{O_2}(5^\circ C) = 12.8 \frac{mg}{L}$$

At $25^\circ C$ the solubility is:

$$C_{O_2}(25^\circ C) = K_{H,O_2} P_{O_2} = 40.2 \frac{mg}{L-\text{atm}} \times 0.209 \text{ atm}$$

$$C_{O_2}(25^\circ C) = 8.40 \frac{mg}{L}$$
Gas Transfer: kinetics

- For a typical water system, the change in concentration of the gas with time can be expressed as:

\[
\frac{dC}{dt} = -k_L a (C_s - C_t)
\]

where,

- \(k_L a\) = gas transfer coefficient, [time\(^{-1}\)]
- \(C_t\) = concentration at time \(t\), [mol/L or mg/L]
- \(C_s\) = saturation concentration from Henry's Law.

- \(k_L a\) is actually the gas transfer coefficient \(k_L\) times the specific surface area, \(a\), where \(a\) is the bubble surface area divided by the bubble volume. It is quite difficult to determine the two parameters separately. Since they are normally used together a separate determination is not necessary.
Analyzing Gas Transfer Data

The above equation can be separated and integrated from $C = C_o$ at $t = 0$ to $C = C_t$ at $t = t$, yielding:

$$\ln \left( \frac{C_s - C_t}{C_s - C_o} \right) = -k_L at$$
Simple Plug Flow River Model

Pipe: Plug Flow Reactor

River: Plug Flow Model
Model Formulation

\[
[\text{accumulation}] = [\text{loadings}] \pm [\text{transport}] \pm [\text{reactions}]
\]

\[
V \frac{ds}{dt} = (Qs)_x - (Qs)_{x+\Delta x} - rV
\]

Reaction Term:

\[
\begin{align*}
 r &= k \\
 r &= ks \\
 r &= ks^2
\end{align*}
\]

Which becomes:

\[
\frac{\partial s}{\partial t} = -\frac{1}{A} \frac{\partial (Qs)}{\partial x} - ks
\]
Plug Flow Model Solution

at steady state, and at constant flow between inputs:

\[ U \frac{ds}{dx} = -ks \]

and solving for "s"

\[ s = S_0 e^{-k \frac{x}{u}} \]
BOD Modeling

Both in a **BOD test** and in a **flowing river**, "L" is modeled as a simple 1st order decay:

\[ \frac{dL}{dt} = -k_1 L \]

Which leads to:

\[ L_t = L_0 e^{-k_1 t} \]

And when considering a **BOD test**, we use the following definition:

\[ BOD_t \equiv y_t = L_0 - L_t \]

And combining we get:

\[ BOD_t \equiv y_t = L_0 (1 - e^{-k_1 t}) \]

\[ BOD_u \equiv BOD_{\text{ultimate}} \equiv BOD_\infty \equiv L_0 \]
We use BOD\textsubscript{u} (ultimate BOD) for all calculations that involve dissolved oxygen in natural waters.

- This is because all of the BOD (not just the BOD\textsubscript{5}) is able to consume oxygen.

Since BOD is always measured as BOD\textsubscript{5}, we must first convert it to BOD\textsubscript{u} before we can use it in DO models.

- You need the bottle constant (k\textsubscript{b}) to do this:

\[
BOD_u = \frac{BOD_5}{1 - e^{-k_b(5\text{days})}}
\]
Since BOD is lost by simple 1\textsuperscript{st} order decay (causing deoxygenation at rate, $k_d$)

$$L_x = L_0 e^{-k_d \left( \frac{x}{u} \right)}$$

And if BOD is also lost due to settling we must include the settling rate ($k_s$)

$$L_x = L_0 e^{-\left( k_d + k_s \right) \left( \frac{x}{u} \right)}$$
BOD example

- A municipal WWTP discharges its effluent into a moderate size river. What is the CBOD$_u$ at a point 30 km downstream of the point of discharge?

  - River geometry
    - Width = 20 m
    - Depth = 5 m
  - River (upstream)
    - Flow = 9 m$^3$/sec
    - CBOD$_u$ = 0 mg/L
  - Wastewater
    - Flow = 1 m$^3$/sec
    - CBOD$_u$ = 30 mg/L
    - $k_1 = 0.3$ d$^{-1}$
DO Deficit

\[ D = DO_{sat} - DO_{act} \]

where

\( D \) = oxygen deficit, [mg/L]
\( DO_{sat} \) = saturation value of dissolved oxygen, [mg/L]
\( DO_{act} \) = actual dissolved oxygen value for the stream, [mg/L]
Let us assume that the rate of oxygen entering the stream through the atmosphere is proportional to the dissolved oxygen deficit in the stream. Similarly, let us assume that the rate of oxygen consumed or leaving the stream is proportional to the amount of organic matter in the stream, expressed as $\text{BOD}_u$ (ultimate BOD).

\[
\frac{dD}{dt} = k_1 L - k_2 D
\]

where

- $t$ = time, [days]
- $L$ = ultimate stream BOD, [mg/L]
- $k_1$ = deoxygenation constant, [day$^{-1}$]
- $k_2$ = reaeration constant, [day$^{-1}$]
DO sag

![Graph showing dissolved oxygen (DO) concentration over distance or time downstream.]

- Initial Deficit ($D_0$)
- Saturation DO ($DO_{sat}$)
- Deficit ($D$)
- Critical Point ($DO_{min}$)
- Dissolved Oxygen (DO)

Distance or Time Downstream

$0 \quad x_c$ or $t_c$
### Characteristics

<table>
<thead>
<tr>
<th>Physical conditions</th>
<th>Stream Zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Water</td>
<td>Degradation</td>
</tr>
<tr>
<td>Clear water; no bottom sludge</td>
<td>Floating solids; bottom sludge</td>
</tr>
<tr>
<td>Fish species</td>
<td></td>
</tr>
<tr>
<td>Cold or warm water game and forage fish; carp, gar, buffalo</td>
<td>Pollution-tolerant fish; carp, gar, buffalo</td>
</tr>
<tr>
<td>Benthic invertebrates</td>
<td>clean water</td>
</tr>
</tbody>
</table>
Gas Transfer: kinetics

For a typical water system, the change in concentration of the gas with time can be expressed as:

\[
\frac{dC}{dt} = -k_L a (C_S - C)
\]

where,
- \(K_L a\) = gas transfer coefficient, \([\text{time}^{-1}]\)
- \(C\) = concentration at time \(t\), \([\text{mol/L or mg/L}]\)
- \(C_S\) = saturation concentration from Henry's Law.

And defining the deficit, \(D\) as:

\[
D \equiv C_S - C
\]

\[
\frac{dD}{dt} = k_L a D
\]

\(K_L a\) is actually the gas transfer coefficient \(K_L\) times the specific surface area, \(a\), where \(a\) is the bubble surface area divided by the bubble volume. It is quite difficult to determine the two parameters separately. Since they are normally used together a separate determination is not necessary.
Streeter Phelps Equation

- Rate of change in deficit is equal to the deoxygenation rate minus the reaeration rate

\[ \frac{dD}{dt} = k_d L - k_r D \]

- Integrating and using the appropriate boundary conditions

\[ D_t = \frac{k_d L_a}{k_r - k_d} \left( e^{-k_d t} - e^{-k_r t} \right) + D_a \left( e^{-k_r t} \right) \]

- Sometimes called the “DO sag” equation

Equ 7.14 in M&Z or Equ 9-35 in D&M

Equ 9-36 in D&M
Can be applied to any travel time \((t)\), including the critical time \((t_c)\)

\[
D_t = \frac{k_d L_a}{k_r - k_d} \left( e^{-k_d t} - e^{-k_r t} \right) + D_a \left( e^{-k_r t} \right)
\]

**Equ 7.15 in M&Z or Equ 9-36 in D&M**

where

- \(D_a\) = Initial stream DO deficit, [mg/L]; same as \(D_0\)
- \(L_a\) = Initial stream BOD\(_{ult}\), [mg/L]; same as \(L_0\)
- \(k_d\) = deoxygenation constant, [day\(^{-1}\)]; same as \(k_1\)
- \(k_r\) = reaeration constant, [day\(^{-1}\)]; same as \(k_2\)
Critical Time

- The most stress is placed on the aquatic life in a stream when the DO is at a minimum, or the deficit, D, is a maximum.
- This occurs when \( dD/dt = 0 \). We can obtain the time at which the deficit is a maximum by taking the derivative of the DO sag equation with respect to t and setting it equal to zero, then solving for t. This yields,

\[
t_c = \frac{1}{k_r - k_d} \ln \left[ \frac{k_r}{k_d} \left( 1 - D_a \frac{k_r - k_d}{k_d L_a} \right) \right]
\]

Equ 7.17 in M&Z or Equ 9-38 in D&M

\( t_c \) = time at which maximum deficit (minimum DO) occurs, [days]
Critical Time

- When $k_r = k_d$, a different form must be used:

$$t_c = \frac{1}{k_d} \left( 1 - \frac{D_a}{L_a} \right)$$

Equ 9-39 in D&M
Reaeration Rates (d⁻¹)

- **O’Connor-Dobbins formula**
  - based on theory
  - verified with some deep waters

- **Churchill formula**
  - Tennessee Valley
  - deep, fast moving streams

- **Owens formula**
  - British
  - shallow streams

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**(Principles of Surface Water Quality Modeling and Control, by Thomann & Mueller)**

Reaeration rate \( (K_2) \) is often represented as \( k_a \) or \( k_r \)

\[
k_2 = 12.9 \frac{U^{0.5}}{H^{1.5}}
\]

\[
k_2 = 3.9 \frac{U^{0.5}}{H^{1.5}}
\]

\[
k_2 = 11.6 \frac{U}{H^{1.67}}
\]

\[
k_2 = 21.6 \frac{U^{0.67}}{H^{1.85}}
\]

For \( k_2 \)

\[
k_T = k_{20^\circ C} \theta^{T-20^\circ C}
\]

D&M cites: \( \theta = 1.024 \)
The method of Covar (1976)

Values for $k_a$ ($k_2$, $k_r$) are in units of $d^{-1}$.
Deoxygenation Rates (d⁻¹)

- Sometimes based on $k_b$ from the BOD test
  - OK for deep, slow moving streams
- Use adjusted values when turbulence is high
  - Fast, shallow streams

Where $\eta$ is the bed activity coefficient
- 0.1 for stagnant or deep water
- 0.6 for rapidly flowing water
- And $k_b$ is the “bottle” rate from lab tests, sometimes just referred to as “k”

\[ k_d = k_b + \frac{U}{H} \eta \]

Equ 9-30 in D&M
Note the units of $\eta$ are essentially “sec/day” as $U/H$ is in sec⁻¹ and $k$ is in d⁻¹
Wasteload Allocation (WLA)

- Successive reductions in waste loading
- Must meet water quality criteria for each river section
- Results in allowable waste loading for each discharger
  - NPDES permit is written based on the WLA
- See also: Fig 1.2 from Thomann & Mueller
Reactions

- BOD degradation
  - Tied to DO loss

- Specific compound processes
  - Biodegradation (microbial)
  - Volatilization
  - Photolysis
  - Hydrolysis
  - Settling

\[ k = k_h + k_v + k_p + k_m + k_s \]

Normally expressed as 1st order rate constants
Example Problem 24.2

Small amounts of chloroform are commonly discharged from municipal and industrial wastewater treatment plants. Let's assume on a given day the concentration in the effluent at Erving, MA is 100 μg/L. What is the concentration of chloroform in the Millers River 5 miles downstream of the Erving outfall, as it approaches the Connecticut River?

Important Information:

\[ Q_{WW} = 4 \text{ MGD} \]
\[ U = 0.5 \text{ ft/s} \]
\[ Q_U = 80 \text{ cfs} \]

Chloroform loss rate = 0.80d\(^{-1}\)

There is no chloroform in the Millers River upstream of Erving.
Example: Preliminary Calcs.

Conversion of Units

\[ Q_{ww} = 4 \text{ MGD} \times 1.547 \frac{\text{cfs}}{\text{MGD}} = 6.2 \text{ cfs} \]

\[ U = 0.5 \text{ ft/s} = 8.2 \text{ mi/d} \]

Determination of Chloroform concentration at the point of mixing

\[ C_o = \frac{Q_{ww} C_{ww} + Q_u C_u}{Q_{ww} + Q_u} \]

\[ = \frac{(6 \text{ cfs})100 \mu g / L + (80 \text{ cfs})0 \mu g / L}{6.2 \text{ cfs} + 80 \text{ cfs}} \]

\[ = 7.2 \mu g / L \]
Sample problem solution

\[ k = k_h + k_v + k_p + k_m + k_s = 0.8 d^{-1} \]

Using “C” here instead of “S”

\[
C = C_0 e^{-k \left( \frac{x}{U} \right)}
\]

\[
= 7.2 \mu g / L \left[ e^{-0.8 d^{-1} \left( \frac{5 mi}{8.2 mi/d} \right)} \right]
\]

\[
= 4.4 \mu g / L
\]
Some important computer models

- Available from the EPA Center for Environmental Modeling (Athens, GA)
  - QUAL 2E (rivers, DO)
  - WASP
  - TOXI WASP
  - MINTEQ (chemistry)
To next lecture