Updated: 4 November 2019

Print version

CEE 370 Environmental Engineering Principles

Lecture #24

Water Quality Management II: Rivers

Reading: Mihelcic & Zimmerman, Chapter 7 (7.7 focus)

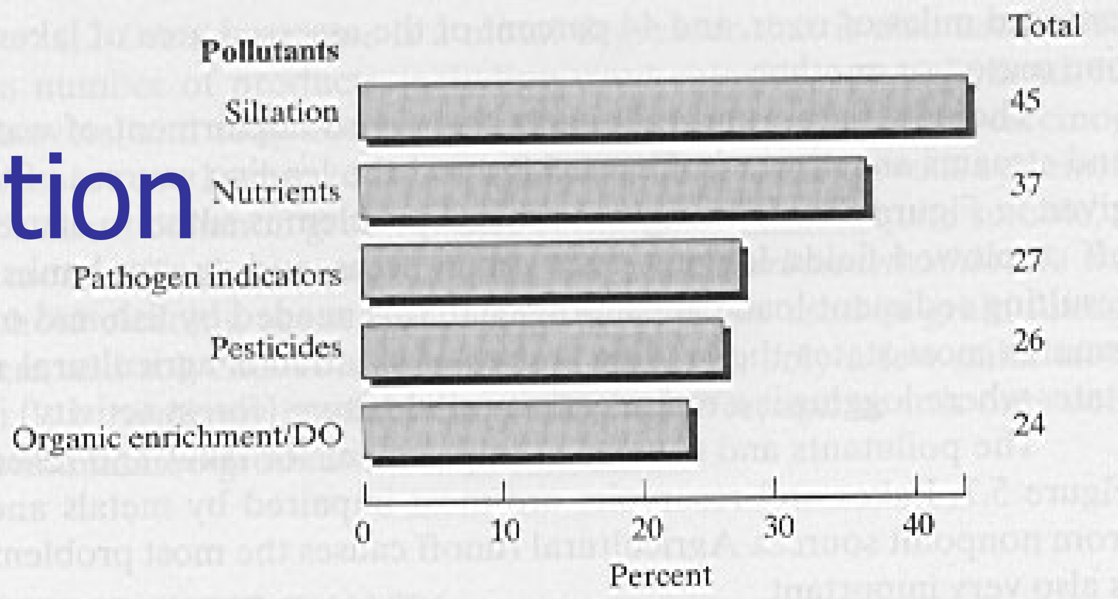
Reading: Davis & Cornwall, Chapt 5-3

Reading: Davis & Masten, Chapter 9-3

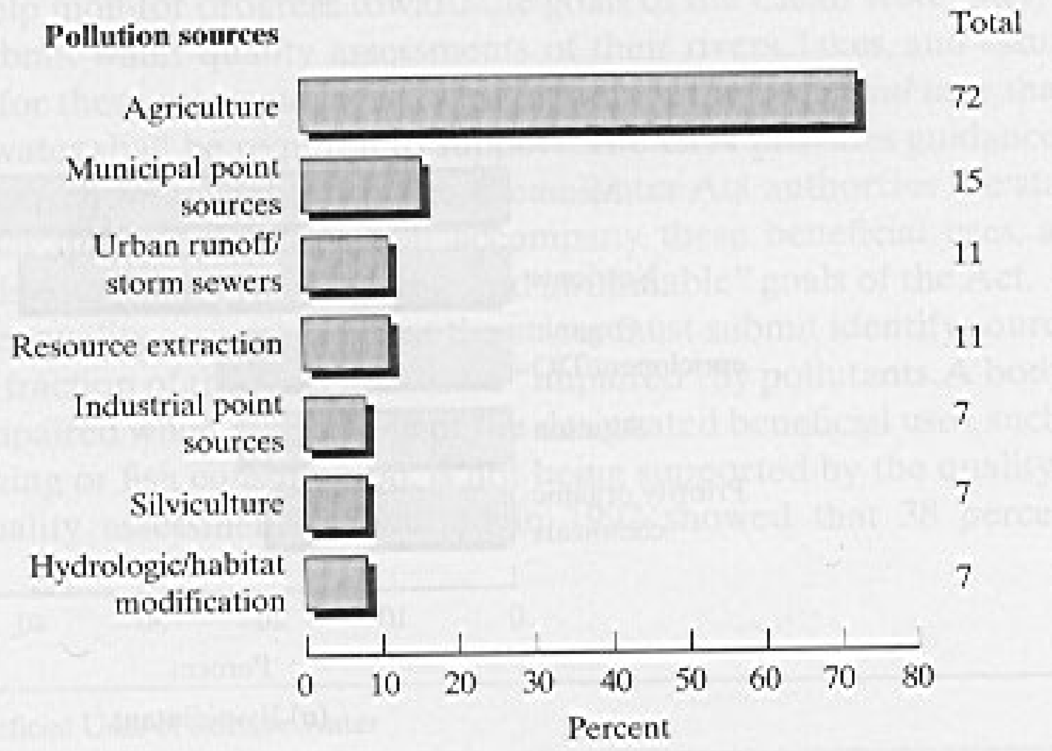
River Pollution

- Percent impaired by pollutant
- Percent impaired by sources

From Masters, section 5.4



(*a*) By pollutant



General Aspects of WQ Models

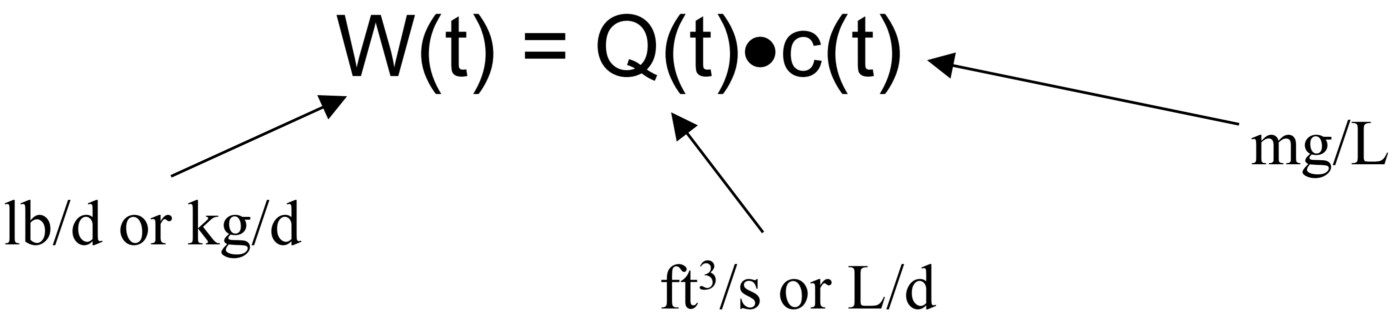
- Pollutants
  - Conservative
    Doesn't Undergo Degradation
  - Non-conservative
- Approach
  - Deterministic
    Based on mechanisms
  - Stochastic
    Incorporates randomness
- Time Variability
  - Steady State
    Unchanging with time
  - Dynamic

Waste Loading

- Point Sources
  - Municipal WW
  - Industrial WW
  - Tributaries
- Non-point Sources
  - Agricultural
  - Silvicultural
  - Atmospheric
  - Urban & Suburban Runoff

Loading Calculations

Point Sources - General Concepts



$$W(t) = Q(t) \bullet c(t)$$

lb/d or kg/d

ft^3/s or L/d

mg/L

Important Conversion Factors:

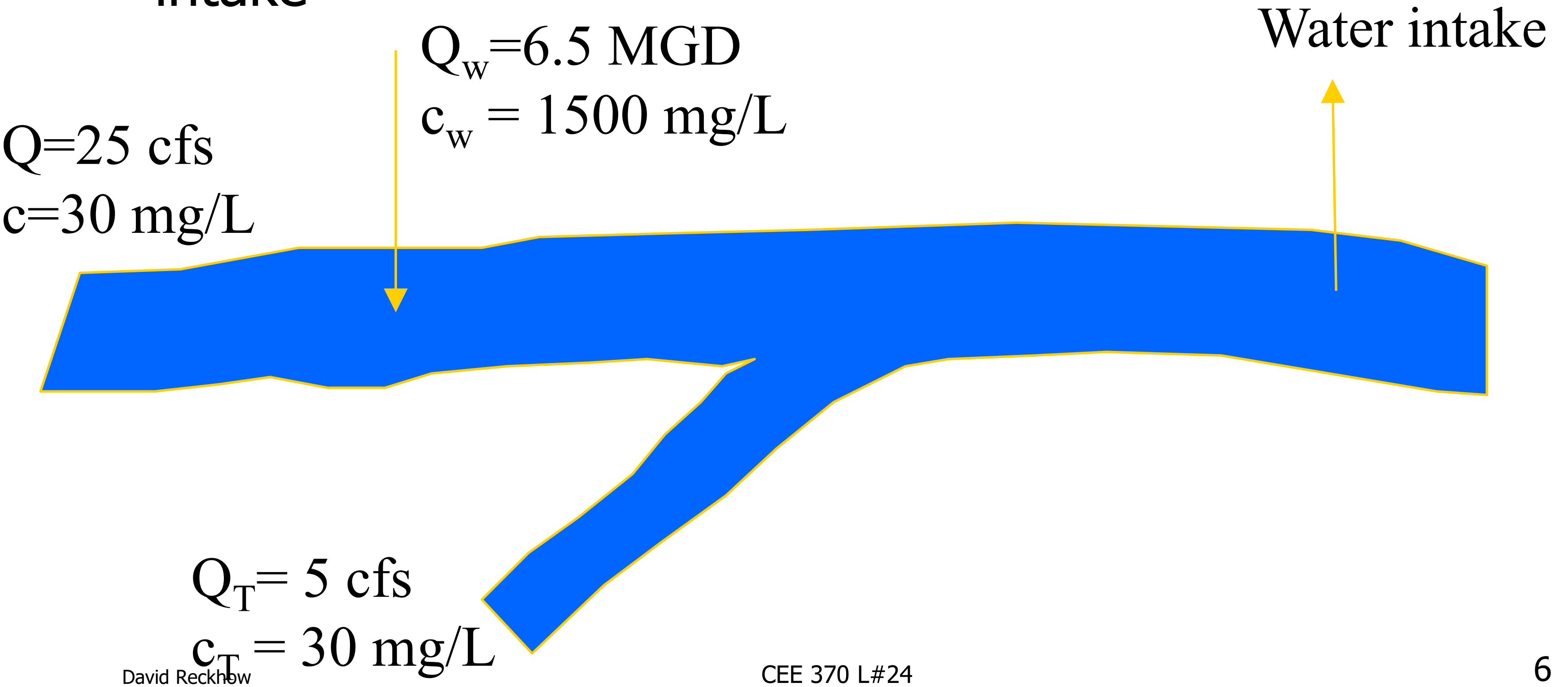
$$8.34 \frac{lb \bullet liters}{mg \bullet MG}$$

$$5.39 \frac{lb \bullet liters \bullet \sec}{mg \bullet ft^3 \bullet day}$$

$$2.45 \frac{Kg \bullet liters \bullet \sec}{mg \bullet ft^3 \bullet day}$$

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



Example 24.1

- A waste is discharged into a river
  - Waste characteristics
    - $CBOD_5 = 200$ mg/L
    - $k_L = 0.1\ day^{-1}$
    - $Q_w = 1\ m^3/s$
  - Upstream river characteristics
    - $CBOD_{ultimate} = 2$ mg/L
    - $Q_u = 9\ m^3/s$
- What is the $CBOD_{ultimate}$ at the point of mixing?

$$BOD_t \equiv y_t = L_o(1 - e^{-k_1 t})$$

See pg. 267 in Mehelcic

Loading

$$Loading = W(t) = Qc_{in}(t)$$

- Point Sources
  - Municipal Wastewater
  - Industrial Wastewater
  - Tributaries
- Non-point sources
  - agricultural
  - silvicultural
  - atmospheric
  - urban & suburban runoff
  - groundwater

Well defined origin
easily measured
more constant

Diffuse origin
more transient
often dependent on precipitation

Reported Values Of Selected Waste Input Parameters In The United States (Table 1.3 from Thomann & Mueller)

Variable	Units[a]	Municipal Influent[b]	CSO[c]	Urban Runoff[d]	Agriculture (lb/mi^2-d)[e]	Forest (lb/mi^2-d)[e]	Atmosphere (lb/mi^2-day)[f]
Average daily flow	gcd	125					
Total suspended solids	mg/L	300	410	610	2500	400	
CBOD5[g]	mg/L	180	170	27	40	8	
CBODU[g]	mg/L	220	240				
NBOD[g]	mg/L	220	290				
Total nitrogen	mg-N/L	50	9	2.3	15	4	8.9-18.9
Total phosphorus	mg-P/L	10	3	0.5	1.0	0.3	0.13-1.3
Total coliforms	10^6/100 mL	30	6	0.3			
Cadmium	µg/L	1.2	10	13			0.015
Lead	µg/L	22	190	280			1.3
Chromium	µg/L	42	190	22			0.088
Copper	µg/L	159	460	110			
Zinc	µg/L	241	660	500			1.8
Total PCB	µg/L	0.9	0.3	-			0.002-0.02

Footnotes for T&M Table 1.3

[a] Units apply to municipal, CSO (combined sewer overflow), and urban runoff sources; gcd = gallons per capita per day.

[b] Thomann (1972); heavy metals and PCB, HydroQual (1982).

[c] Thomann (1972); total coli, Tetra Tech, (1977); heavy metals Di Toro et al. (1978): PCB. Hydroscience (1978).

[d] Tetra Tech (1977): heavy metals, Di Toro et al. (1978).

[e] Hydroscience (1976a).

[f] Nitrogen and phosphorus, Tetra Tech (1982): heavy metals and PC13, HydroQual (1982).

[g] CBOD5 = 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: $Q_R = cIA$

Drainage Area $[L^2]$

Runoff flow $[L^3/T]$

Rainfall Intensity $[L/T]$

Runoff coefficient

0.1-0.3 for rural areas (1 person/acre)

0.7-0.9 for heavy commercial areas

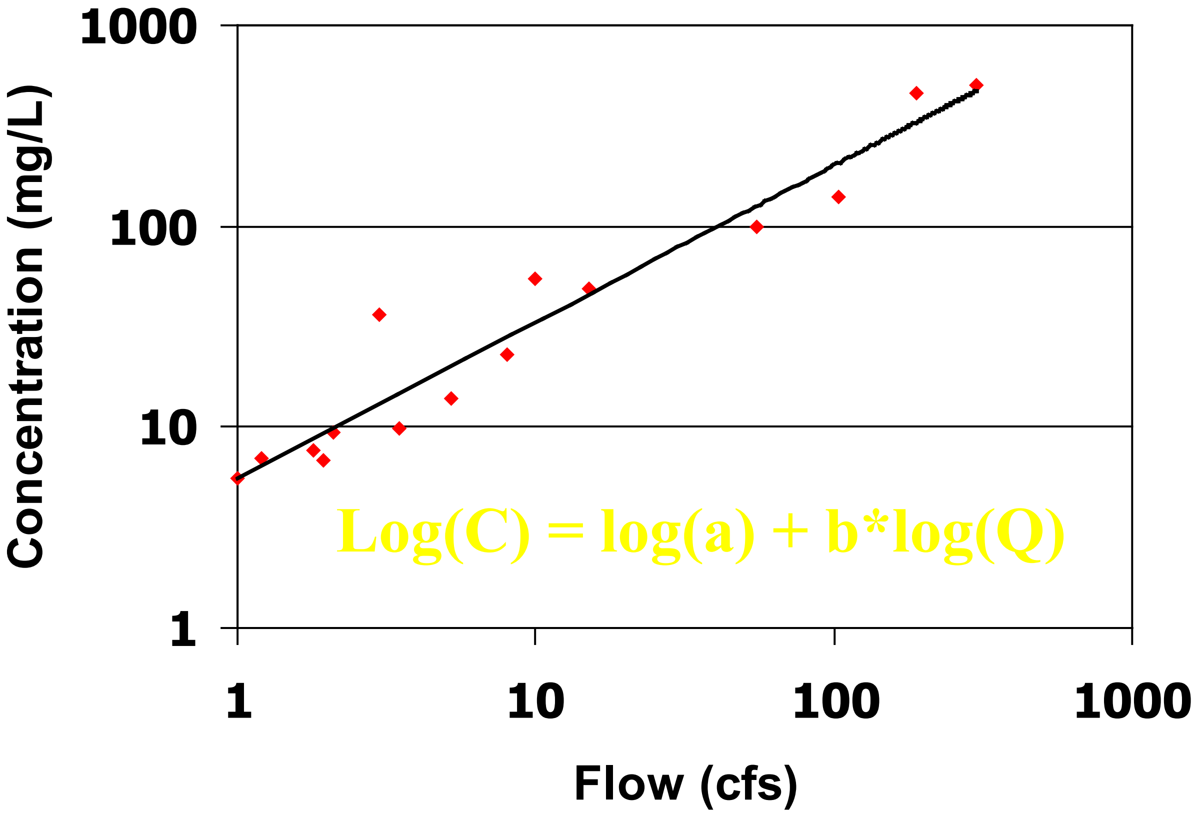
Note:

1 acre-in/hr ≈1 cfs

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
- $c=aQ^b$



Loading Example: #3.1 from T&M

- Data: Runoff from 100 mi^2 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 mi^2 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.

Item	**(at) Atmospheric**	**(ag) Agricultural**	**(ur) Urban Runoff**	**Wastewater Treatment Plant Influent**	**Wastewater Treatment Plant Resid. Fract.**
Fow		30% precip.	50% precip.	125 gcd	1.00
CBOD5		40 lb/mi^2-d	27 mg/L	180 mg/L	0.15
Total coliform		100/100 mL	3x10^5/100mL	3x10^6/100mL	0.0001
Lead	1.3 lb/mi^2-d		280 µg/L	22 µg/L	0.05

Solution to loading problem

- Flow contributions

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

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

$$Q(wwtp) = 100{,}000cap\frac{125gal}{cap-d}\frac{1MG}{10^6\,gal}$$
$$= 12.5MGD\left(\frac{1.548cfs}{MGD}\right)$$
$$= 19.4cfs$$

Solution to loading problem (cont.)

- CBOD5 loading

$$W(ag) = 100mi^2\left(40\frac{lb}{mi^2d}\right)$$

$$= 4000\frac{lb}{d}$$

$$W(ur) = 11.1cfs(27mg/L)5.4\frac{lb/d}{cfs-mg/L}$$

$$= 1620\frac{lb}{d}$$

$$W(wwtp) = 12.5MGD(180mg/L)0.15\left(\frac{8.34lb/d}{MGD*mg/L}\right)$$

$$= 2810\frac{lb}{d}$$

Solution to loading problem (cont.)

- Lead loading

$$W(atm) = 100mi^2\left(1.3\frac{lb}{mi^2 d}\right)0.1$$

$$= 13\frac{lb}{d}$$

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

$$= 16.8\frac{lb}{d}$$

$$W(wwtp) = 12.5MGD(22\mu g/L)0.05\left(\frac{8.34lb/d}{MGD{*}mg/L}\right)\frac{10^{-3}mg}{\mu g}$$

$$= 0.11\frac{lb}{d}$$

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.

$$O_2(aq) \rightarrow O_2(g)$$

Example 4.7 from Ray

Solution to DO example

$$\Delta G^\circ_{rxn} = \Delta G^\circ_{O_2(g)} - \Delta G^\circ_{O_2(aq)} = (0\ \frac{\text{kcal}}{\text{mol}}) - (-3.9\ \frac{\text{kcal}}{\text{mol}})$$

$$\Delta G^\circ_{rxn} = 3.9\ \frac{\text{kcal}}{\text{mol}}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{p_{O_2}}{[O_2(aq)]}$$

$$[O_2(aq)] = 4\ \frac{\text{mg}\ O_2}{\text{L}}\ \text{x}\ \frac{\text{g}\ O_2}{1000\ \text{mg}\ O_2}\ \text{x}\ \frac{\text{mol}\ O_2}{32\ \text{g}\ O_2} = 1.25\ \text{x}\ 10^{-4}\ \text{M}$$

Solution (cont.)

$$\Delta G = -3.9\frac{\text{kcal}}{\text{mol}} \text{ x } \frac{1000 \text{ cal}}{\text{kcal}} + \left(1.987\frac{\text{cal}}{\text{K-mol}}\right)(298\,\text{K}) \ln\left(\frac{0.209 \text{ atm}}{1.25 \text{ x } 10^{-4} \text{ M}}\right)$$

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

Since ΔG 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

Reaction	Name	K_h, mol/L-atm	$pK_h = -\log K_h$
$CO_2(g) = CO_2(aq)$	Carbon dioxide	3.41×10^{-2}	1.47
$NH_3(g) = NH_3(aq)$	Ammonia	57.6	-1.76
$H_2S(g) = H_2S(aq)$	Hydrogen sulfide	1.02×10^{-1}	0.99
$CH_4(g) = CH_4(aq)$	Methane	1.50×10^{-3}	2.82
$O_2(g) = O_2(aq)$	Oxygen	1.26×10^{-3}	2.90

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?

Example 4.1 from Ray

Solution O_2 Solubility Ex.

At 5⁰C the solubility is:

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

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

At 25⁰C the solubility is:

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

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

Gas Transfer: kinetics

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

where,

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

k_La = 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_La 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.

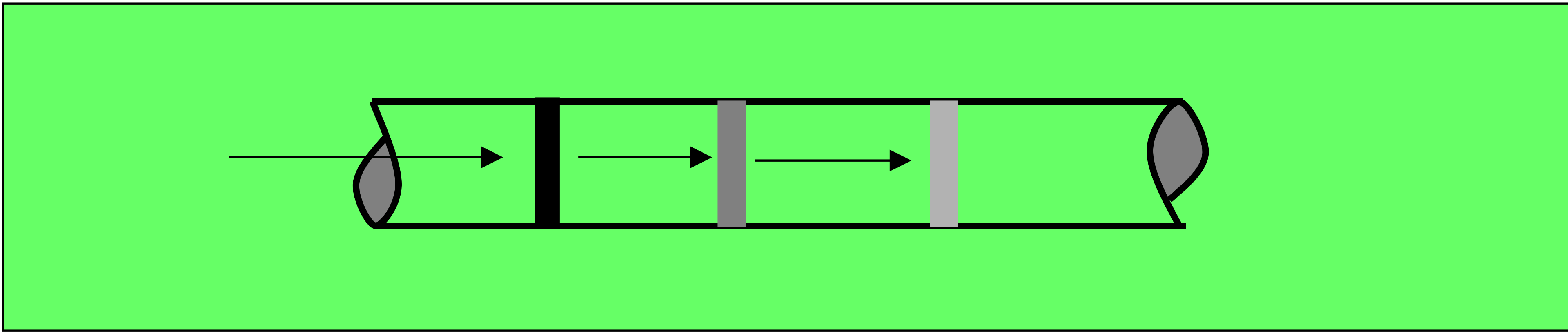
Analyzing Gas Transfer Data

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

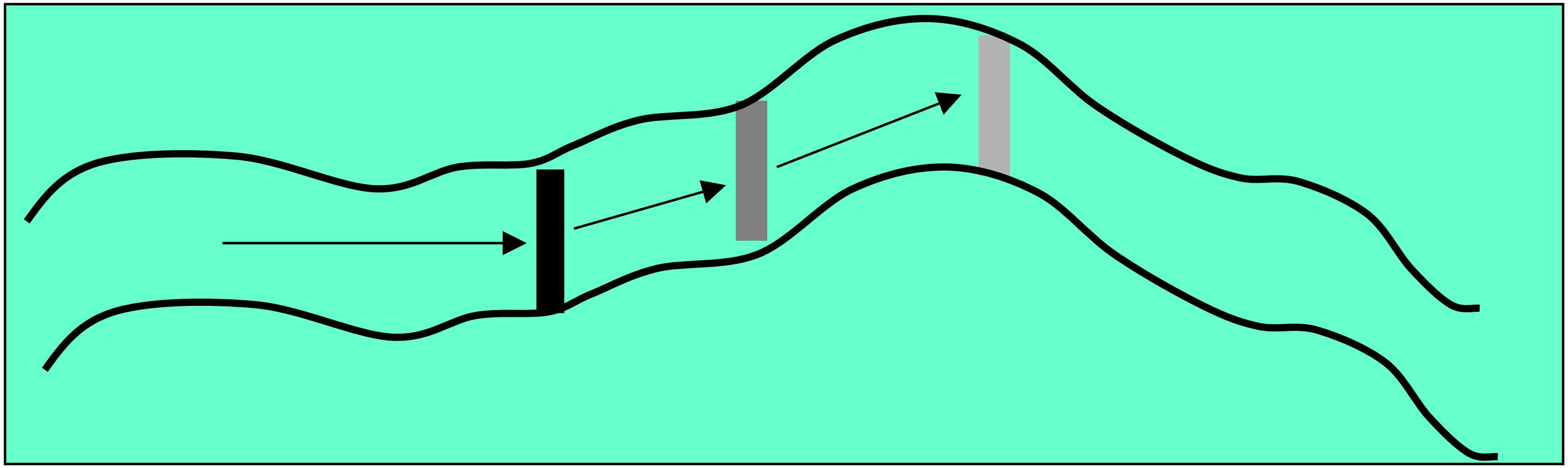
$$\ln\frac{\left(C_s - C_t\right)}{\left(C_s - C_o\right)} = -k_L a t$$

Simple Plug Flow River Model

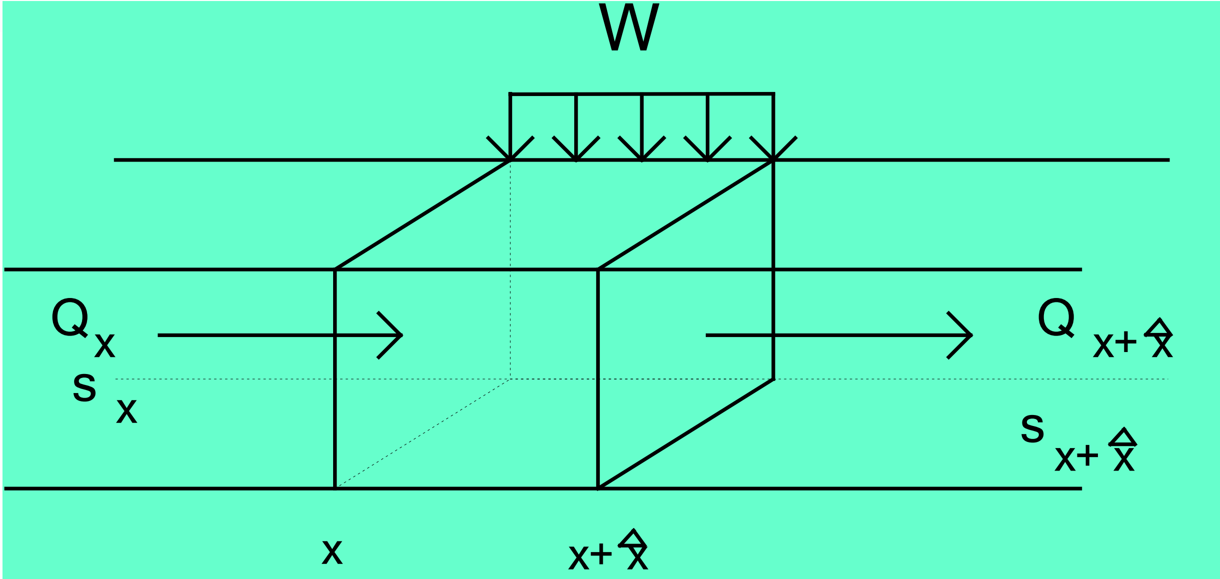
Pipe: Plug Flow Reactor



River: Plug Flow Model



Model Formulation



[accumulation] = [loadings] ± [transport] ± [reactions]

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

Reaction Term:

$$r = k$$
$$r = ks$$
$$r = ks^2$$

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"

$$s = s_o e^{-k\frac{x}{u}}$$

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:

$$L_t = L_o e^{-k_1 t}$$

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

$$BOD_t \equiv y_t = L_o - L_t$$

And combining we get:

$$BOD_t \equiv y_t = L_o(1 - e^{-k_1 t})$$

Equ 9-6 in D&M

$$BOD_u \equiv BOD_{ultimate} \equiv BOD_\infty \equiv L_0$$

BOD Modeling in a River I

- We use BOD_u (ultimate BOD) for all calculations that involve dissolved oxygen in natural waters
  - This is because all of the BOD (not just the BOD_5) is able to consume oxygen
- Since BOD is always measured as BOD_5, we must first convert it to BOD_u before we can use it in DO models
  - You need the bottle constant (k_b) to do this:

$$BOD_u = \frac{BOD_5}{1 - e^{-k_b(5 days)}}$$

BOD Modeling in a River II

- Since BOD is lost by simple 1st order decay (causing deoxygenation at rate, k_d)

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

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

$$L_x = L_o e^{-(k_d + k_s)\left(x/u \right)}$$

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]

DO Deficit Mass Balance

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 BOD_u (ultimate BOD).

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

where

t = time, [days]

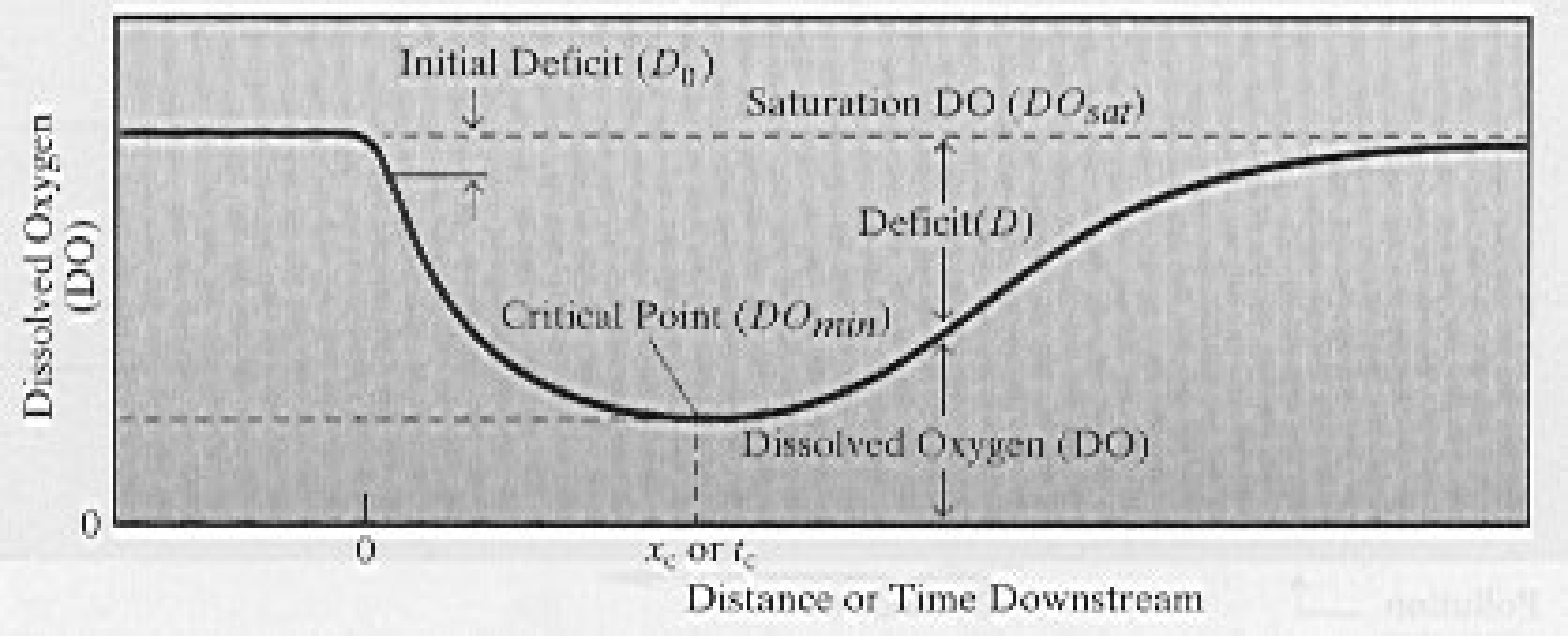
L = ultimate stream BOD, [mg/L]

k_1 = deoxygenation constant, [day^{-1}]

k_2 = reaeration constant, [day^{-1}]

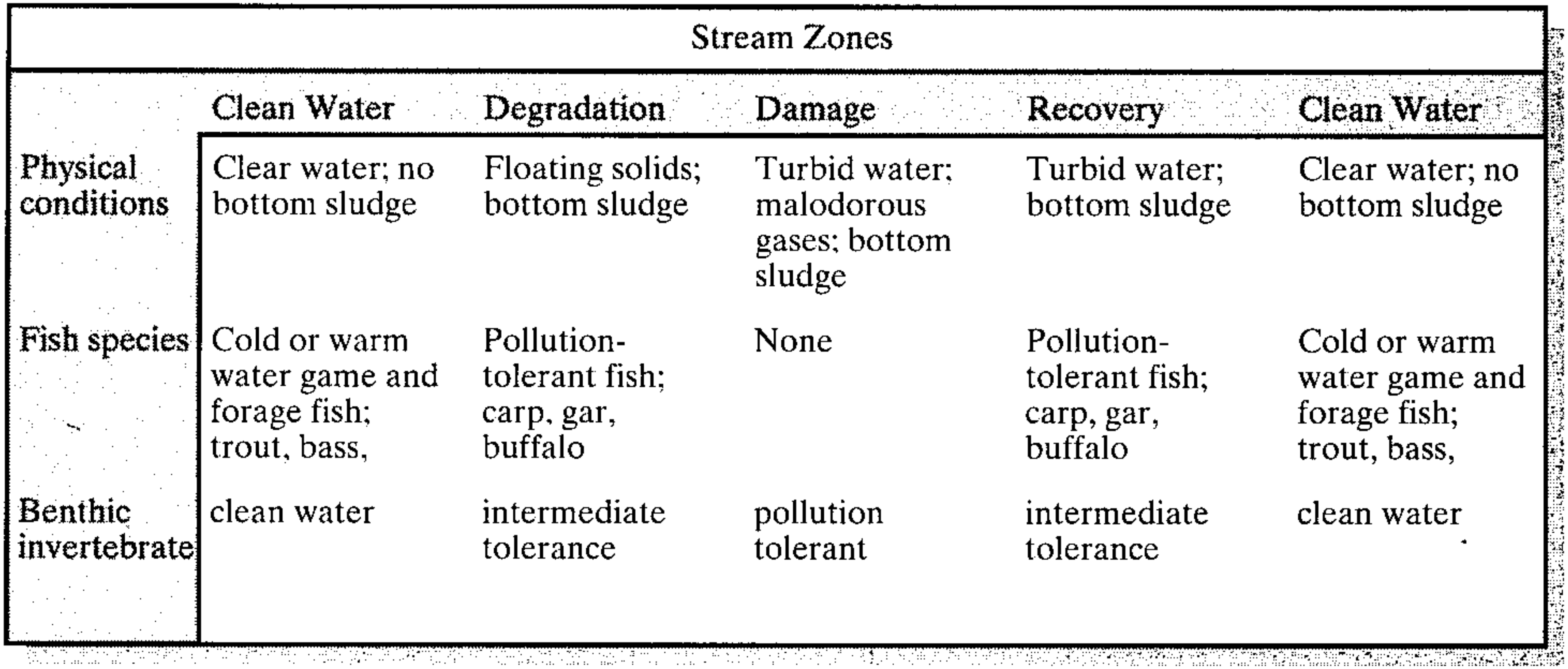
DO sag curve

- Note critical point, deficit



M&Z Fig 7.22a

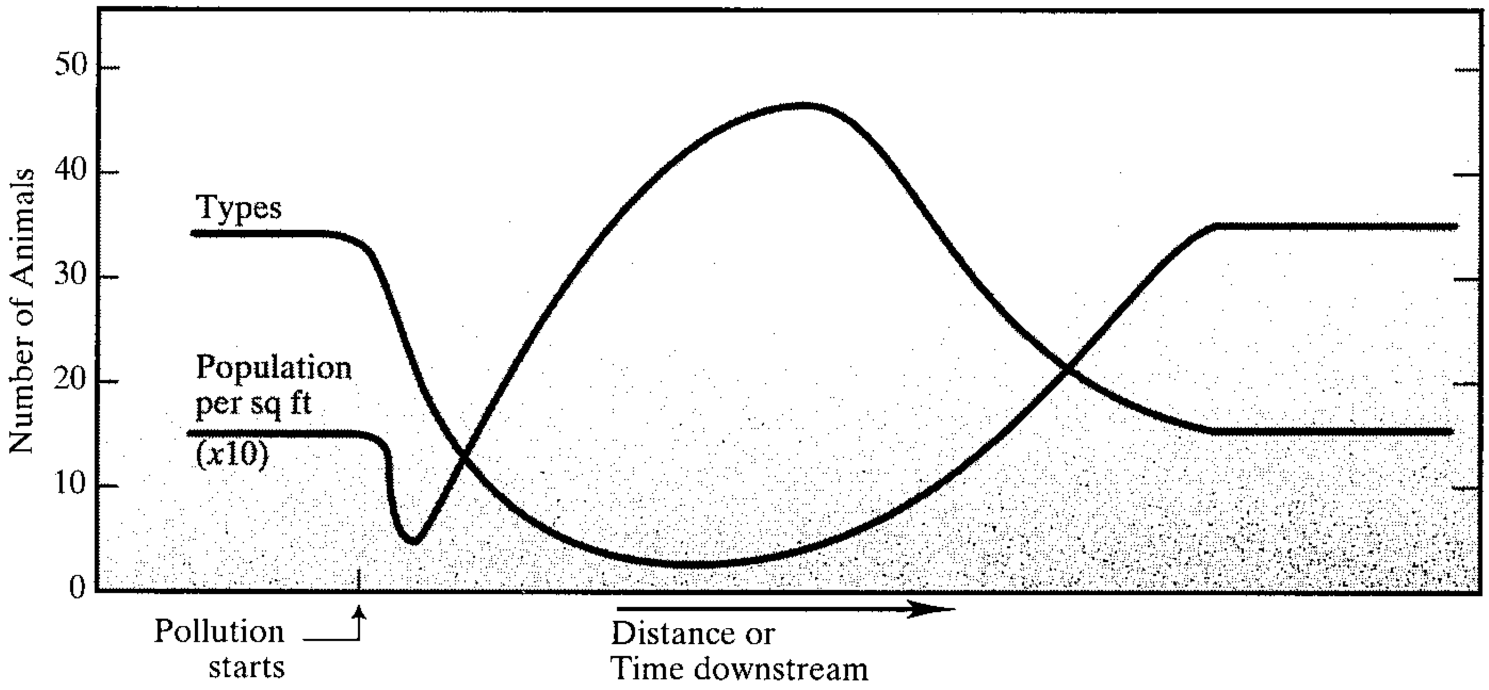
Characteristics



	Stream Zones				
	Clean Water	**Degradation**	**Damage**	**Recovery**	**Clean Water**
Physical conditions	Clear water; no bottom sludge	Floating solids; bottom sludge	Turbid water; malodorous gases; bottom sludge	Turbid water; bottom sludge	Clear water; no bottom sludge
Fish species	Cold or warm water game and forage fish; trout, bass,	Pollution-tolerant fish; carp, gar, buffalo	None	Pollution-tolerant fish; carp, gar, buffalo	Cold or warm water game and forage fish; trout, bass,
Benthic invertebrate	clean water	intermediate tolerance	pollution tolerant	intermediate tolerance	clean water

Ecology

- Diversity and population



M&Z Fig 7.22d

Gas Transfer: kinetics

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

$$\frac{dC}{dt} = -k_L a\left(C_S - C\right)$$

where,

K_La = gas transfer coefficient, [time^{-1}]

C = concentration at time t, [mol/L or mg/L]

C_s = saturation concentration from Henry's Law.

And defining the deficit, D as: $D \equiv C_S - C$

$$\frac{dD}{dt} = k_L aD$$

K_La 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

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

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

- Integrating and using the appropriate boundary conditions

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

Equ 9-36 in D&M

- Sometimes called the “DO sag” equation

Streeter Phelps

- Can be applied to any travel time (t), including the critical time (t_c)

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

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

where

D_a = Initial stream DO deficit, [mg/L]; same as D_o

L_a = Initial stream BOD_{ult}, [mg/L]; same as L_o

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 rate (K_2) is often represented as k_a or k_r

Reaeration Rates (d^{-1})

(U in ft/s; H in ft)

(U in m/s; H in m)

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

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

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

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

$$k_2 = 11.6\frac{U}{H^{1.67}}$$

- Owens formula
  - British
  - shallow streams

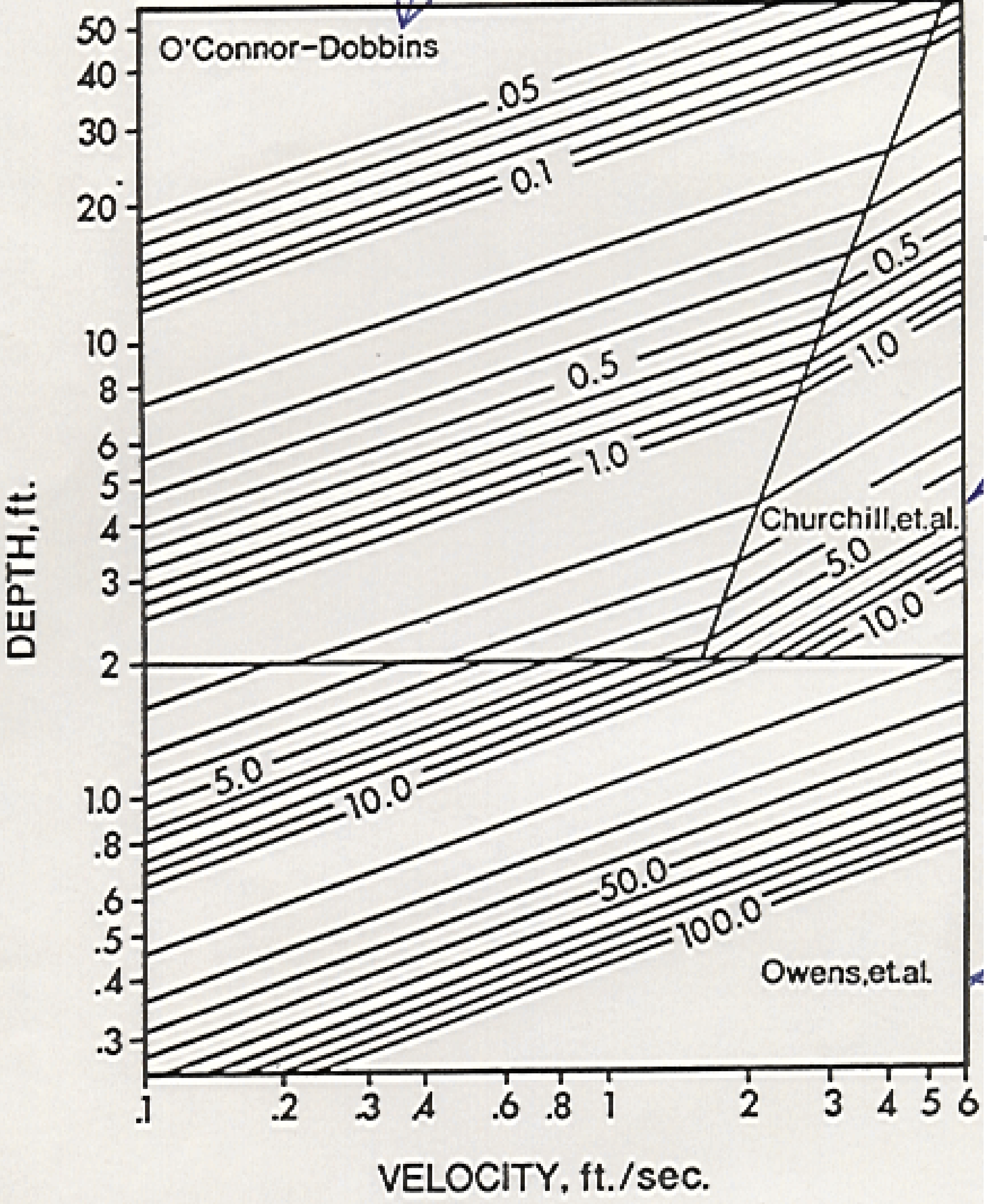
$$k_2 = 21.6\frac{U^{0.67}}{H^{1.85}}$$

(<u>Principles of Surface Water Quality Modeling and Control</u>, by Thomann & Mueller)

<u>For k_2</u>

$$k_T = k_{20^o C}\theta^{T-20^o C}$$

D&M cites: θ=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

Equ 9-30 in D&M

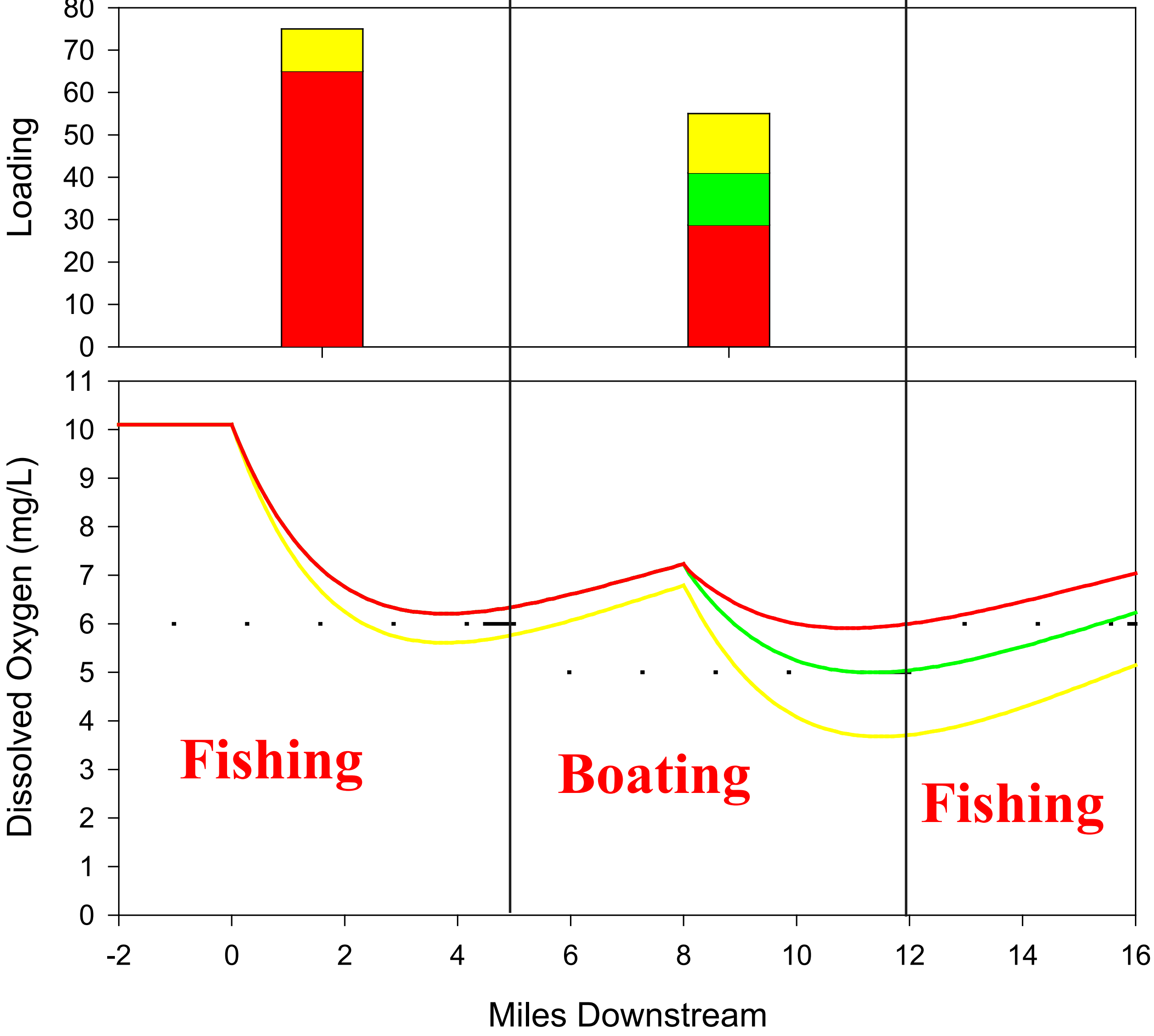
$$k_d = k_b + \frac{U}{H}\eta$$

Note the units of η are essentially "sec/day" as U/H is in sec^{-1} and k is in d^{-1}

- Where η 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"

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

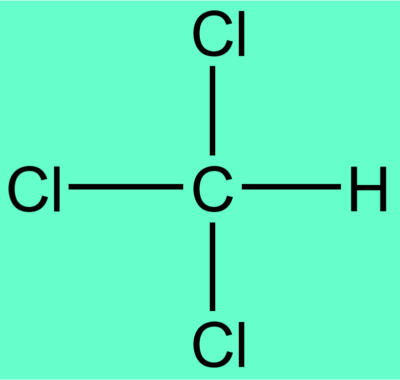
- BOD degradation
  - Tied to DO loss
- Specific compound processes
  - Biodegradation (microbial)
  - Volatilization
  - Photolysis
  - Hydrolysis
  - Settling

$$k = k_h + k_v + k_p + k_m + k_s$$

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. Lets 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:

$Q_{WW} = 4$ MGD

$U = 0.5$ ft/s

$Q_U = 80$ cfs

Chloroform loss rate = $0.80 d^{-1}$

There is no chloroform in the Millers River upstream of Erving.

Example: Preliminary Calcs.

Conversion of Units

$$Q_{ww} = 4\,MGD * 1.547\,{}^{cfs}\!/_{MGD} = 6.2cfs$$

$$U = 0.5\,ft/s = 8.2mi/d$$

Determination of Chloroform concentration at the point of mixing

$$\begin{aligned} C_o &= \frac{Q_{ww}C_{ww} + Q_u C_u}{Q_{ww} + Q_u} \\ &= \frac{(6cfs)100\mu g/L + (80cfs)0\mu ug/L}{6.2cfs + 80cfs} \\ &= 7.2\mu g/L \end{aligned}$$

Sample problem solution

$$k = k_h + k_v + k_p + k_m + k_s = 0.8 d^{-1}$$

Using “C” here instead of “S”

$$C = C_o e^{-k\left(x/U\right)}$$

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

$$= 4.4\,\mu g / L$$

Some important computer models

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

- To next lecture