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CEE 370
Environmental Engineering Principles

Lecture #25

Water Quality Management III: Lakes & toxic models

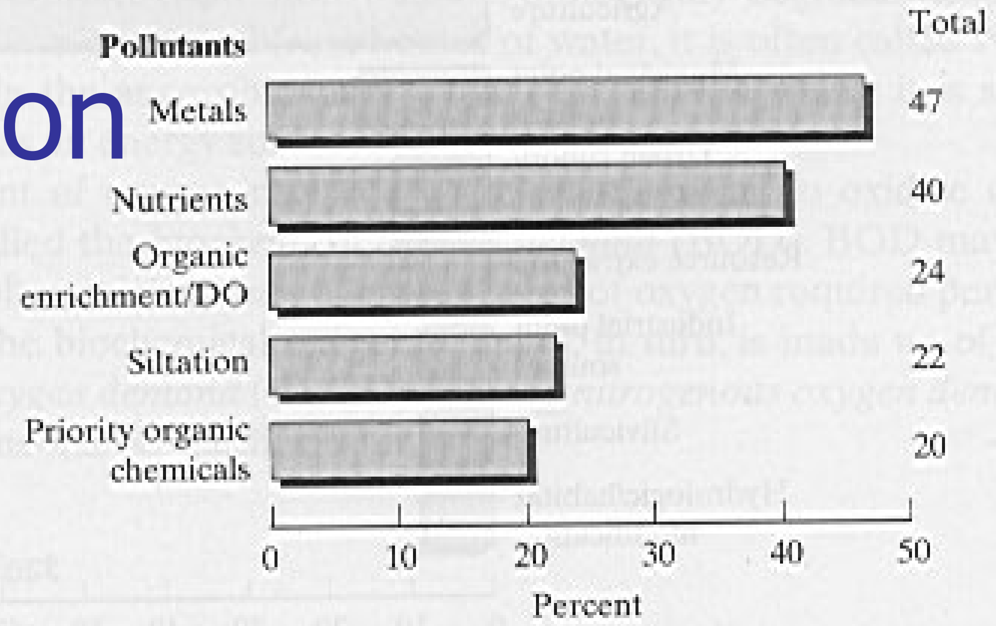
Reading: Mihelcic & Zimmerman, Chapter 7 & 3.10

Reading: Davis & Cornwall, Chapt 5-4

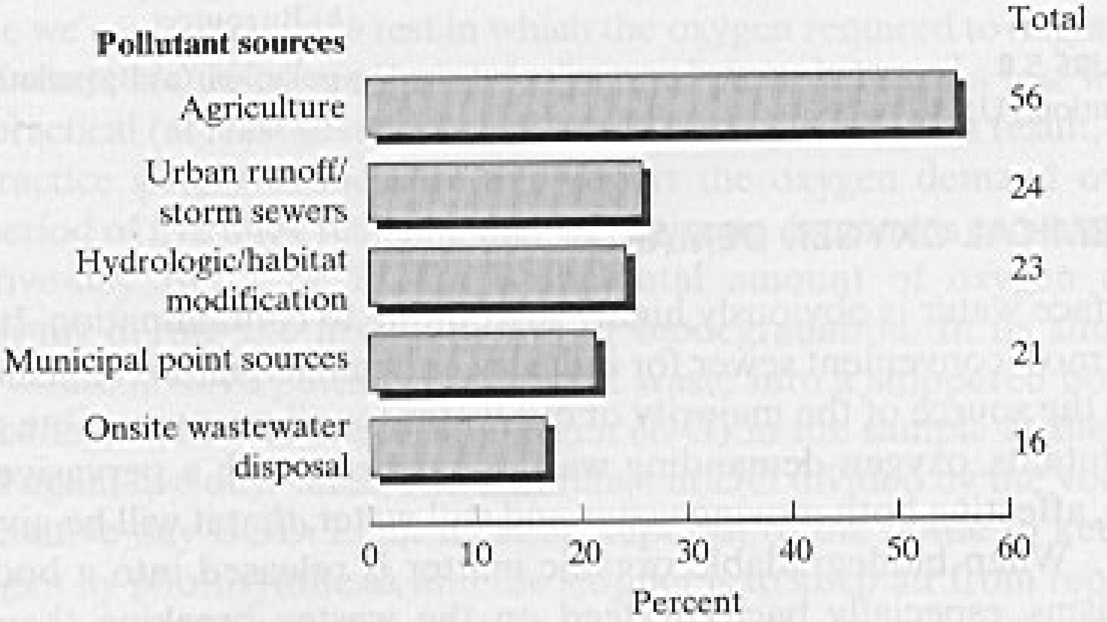
Reading: Davis & Masten, Chapter 5-6 & 9-4

Lake Pollution

- Percent impaired by pollutant
- Percent impaired by sources



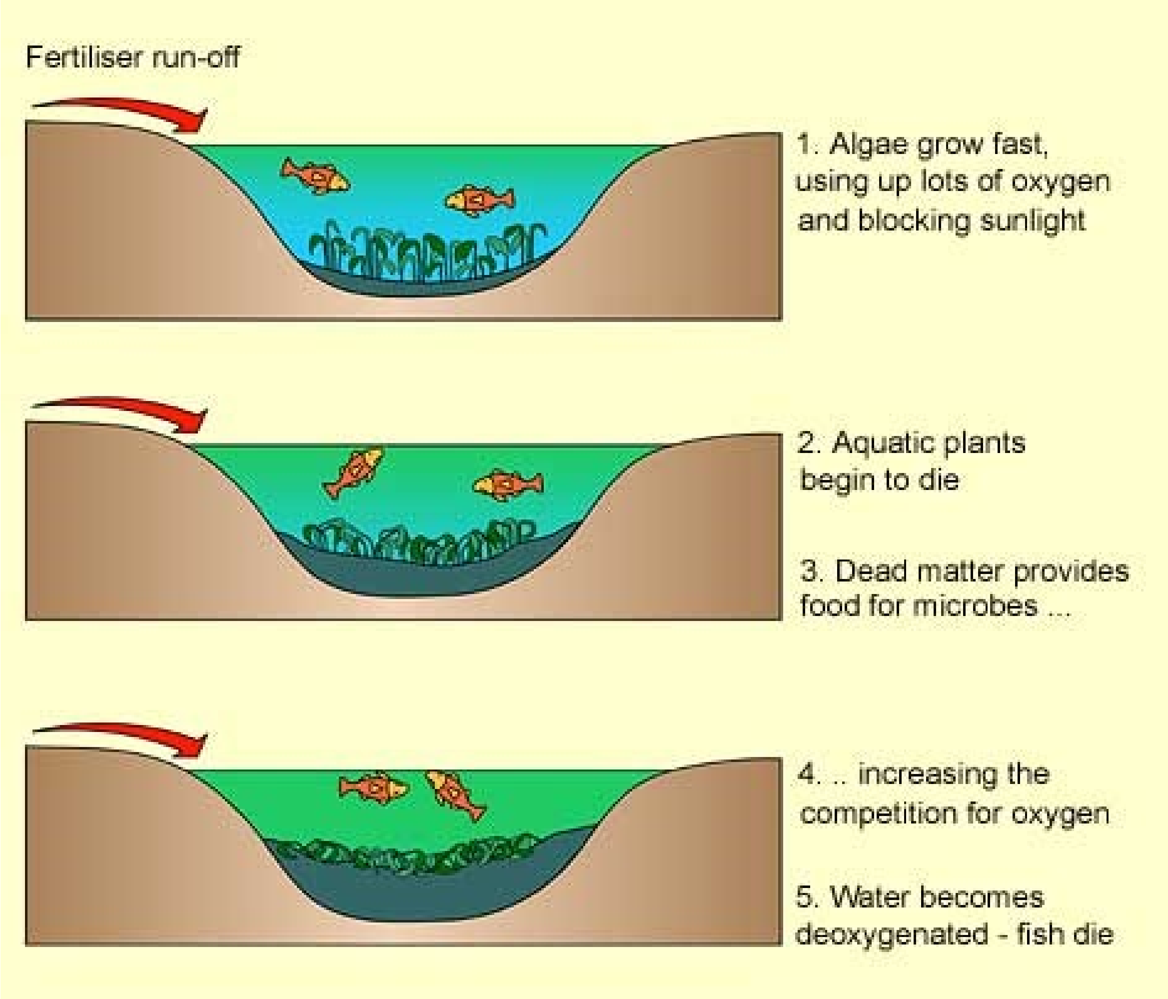
(*a*) By pollutant



From Masters, section 5.4

Lake life cycle

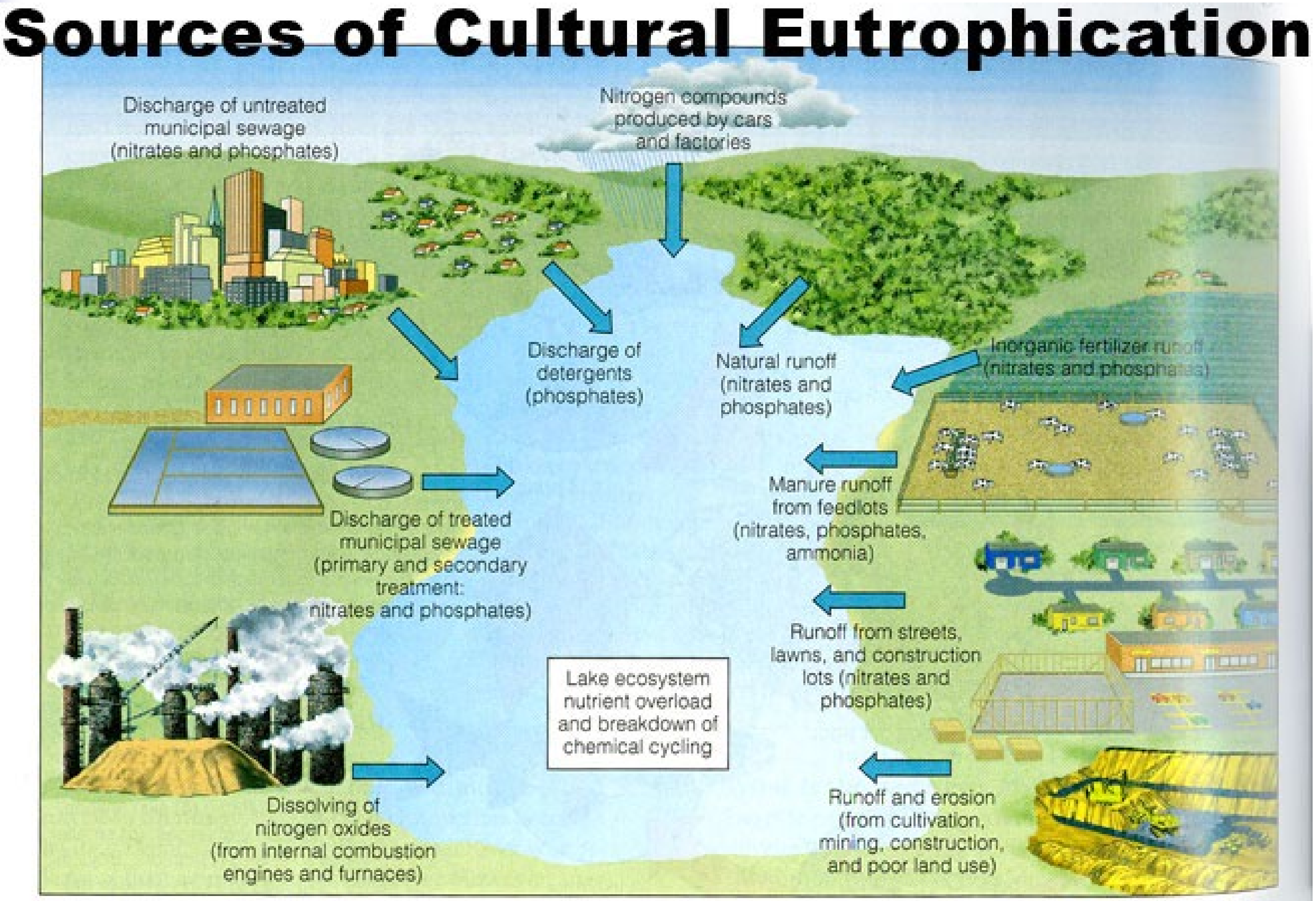
- Succession in lakes
  - Oligotrophic
  - Mesotrophic
  - Eutrophic
  - Other
    - Dystrophic
    - Hyper-eutrophic



Lake Eutrophication

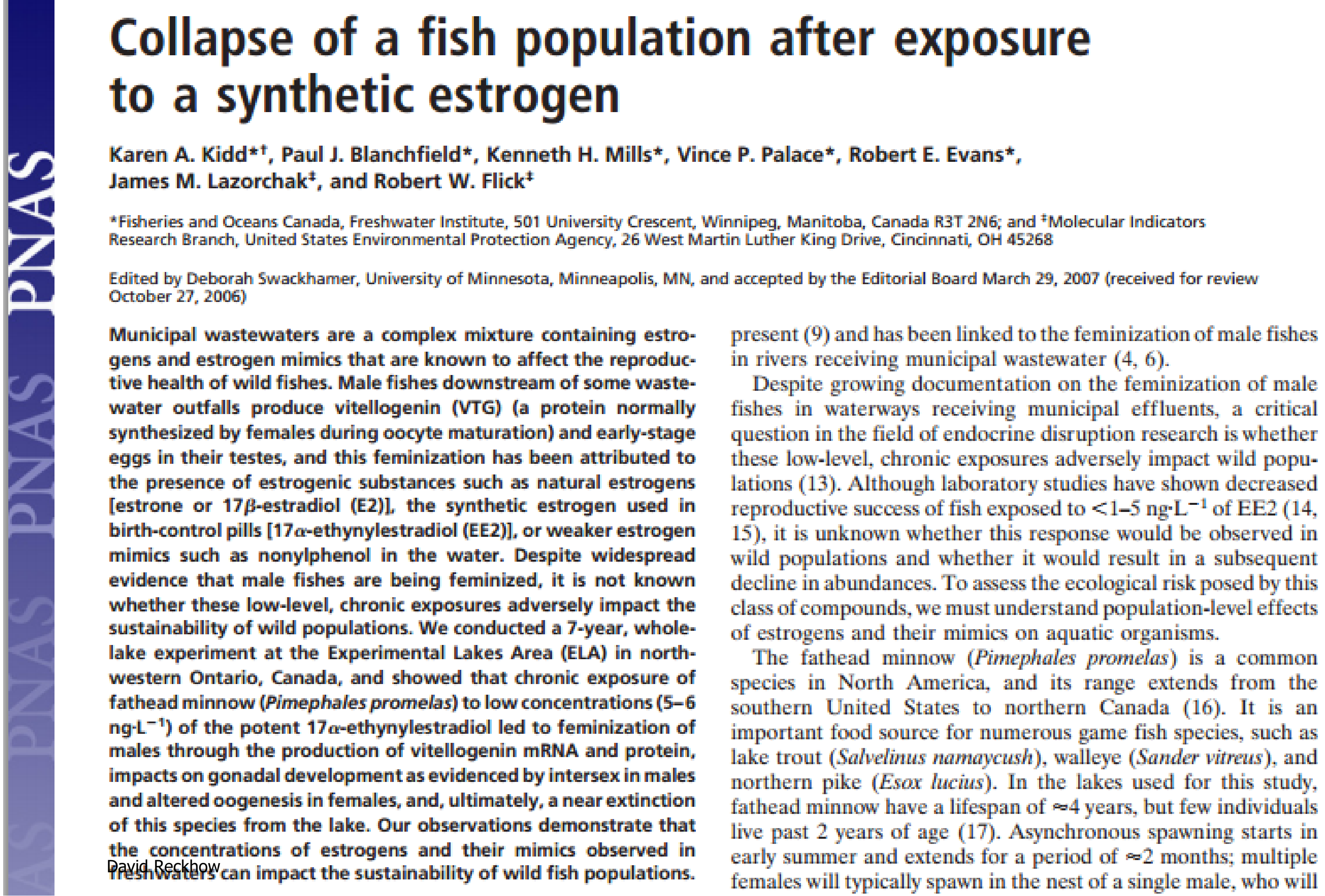
- As lakes age, they become more productive
  - Natural processes: natural Eutrophication
  - Pollutant loading: cultural Eutrophication
- Limiting nutrient
  - Liebig’s law of minimum
  - Redfield Ratio
    - C:N:P in most phytoplankton is 106:16:1
    - When P<16*N, it limit’s growth

Nutrient loading and Eutrophication



Sources of Cultural Eutrophication

Estrogen lake study



Collapse of a fish population after exposure to a synthetic estrogen

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Municipal wastewaters are a complex mixture containing estrogens and estrogen mimics that are known to affect the reproductive health of wild fishes. Male fishes downstream of some wastewater outfalls produce vitellogenin (VTG) (a protein normally synthesized by females during oocyte maturation) and early-stage eggs in their testes, and this feminization has been attributed to the presence of estrogenic substances such as natural estrogens [estrone or 17β-estradiol (E2)], the synthetic estrogen used in birth-control pills [17α-ethynylestradiol (EE2)], or weaker estrogen mimics such as nonylphenol in the water. Despite widespread evidence that male fishes are being feminized, it is not known whether these low-level, chronic exposures adversely impact the sustainability of wild populations. We conducted a 7-year, whole-lake experiment at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada, and showed that chronic exposure of fathead minnow (*Pimephales promelas*) to low concentrations (5–6 ng·L^{-1}) of the potent 17α-ethynylestradiol led to feminization of males through the production of vitellogenin mRNA and protein, impacts on gonadal development as evidenced by intersex in males and altered oogenesis in females, and, ultimately, a near extinction of this species from the lake. Our observations demonstrate that the concentrations of estrogens and their mimics observed in freshwaters can impact the sustainability of wild fish populations.

present (9) and has been linked to the feminization of male fishes in rivers receiving municipal wastewater (4, 6).

Despite growing documentation on the feminization of male fishes in waterways receiving municipal effluents, a critical question in the field of endocrine disruption research is whether these low-level, chronic exposures adversely impact wild populations (13). Although laboratory studies have shown decreased reproductive success of fish exposed to <1–5 ng·L^{-1} of EE2 (14, 15), it is unknown whether this response would be observed in wild populations and whether it would result in a subsequent decline in abundances. To assess the ecological risk posed by this class of compounds, we must understand population-level effects of estrogens and their mimics on aquatic organisms.

The fathead minnow (*Pimephales promelas*) is a common species in North America, and its range extends from the southern United States to northern Canada (16). It is an important food source for numerous game fish species, such as lake trout (*Salvelinus namaycush*), walleye (*Sander vitreus*), and northern pike (*Esox lucius*). In the lakes used for this study, fathead minnow have a lifespan of ≈4 years, but few individuals live past 2 years of age (17). Asynchronous spawning starts in early summer and extends for a period of ≈2 months; multiple females will typically spawn in the nest of a single male, who will

Concern over drinking water

- Drugs?

Organic Compounds: Types?

- Natural Compounds
  - Fulvics
  - Proteins, carbohydrates, etc
- Domestic WW Organics
- Industrial Synthetic Organics
  - Plasticizers: phthalates
  - solvents: tetrachloroethylene
  - waxes: chlorinated parafins
  - others: PCB’s
- Hydrocarbons & oil derivatives
  - includes products of combustion: PAH’s
- Agricultural Chemicals
  - pesticides: DDT, kepone, mirex
- Pharmaceuticals, etc
  - Anti-epileptics
  - Beta-blockers
  - X-ray contrast media
  - antibiotics
- Home & Personal Care Products
  - triclosan
  - Musks, flame retardants
- Endocrine Disrupters
  - Steroidal estrogens
- Natural process byproducts
  - Conjugated pharmaceuticals
- Engineered process byproducts
  - disinfection byproducts, etc

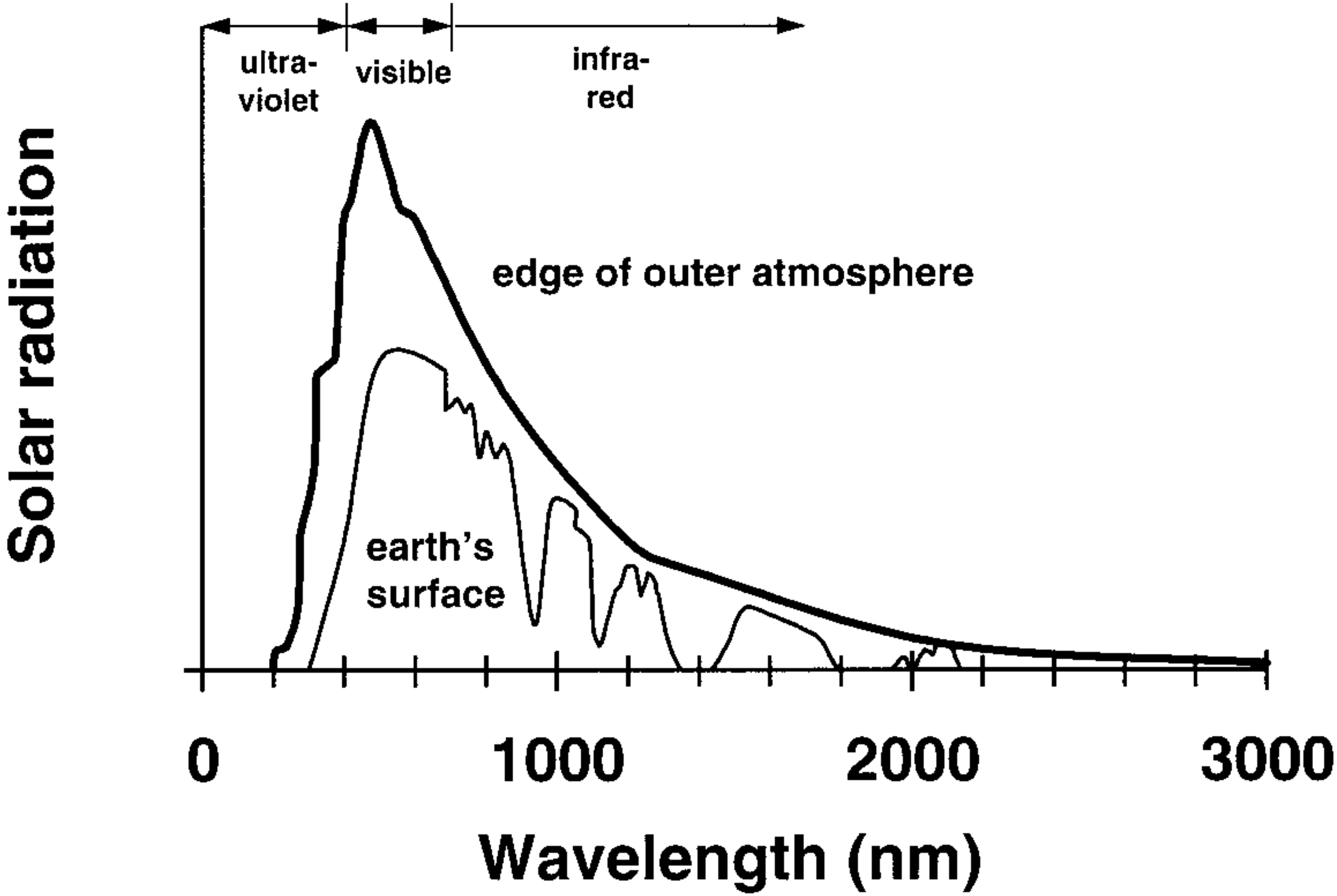
Pollutant loss in lakes

- Photolysis
  - Destruction by solar light energy
- Biodegradation
  - Metabolism by microorganism
- Hydrolysis
  - Chemical decomposition
- Volatilization
  - Loss to the atmosphere
- Adsorption and settling
  - Loss to particles that end up buried in sediments

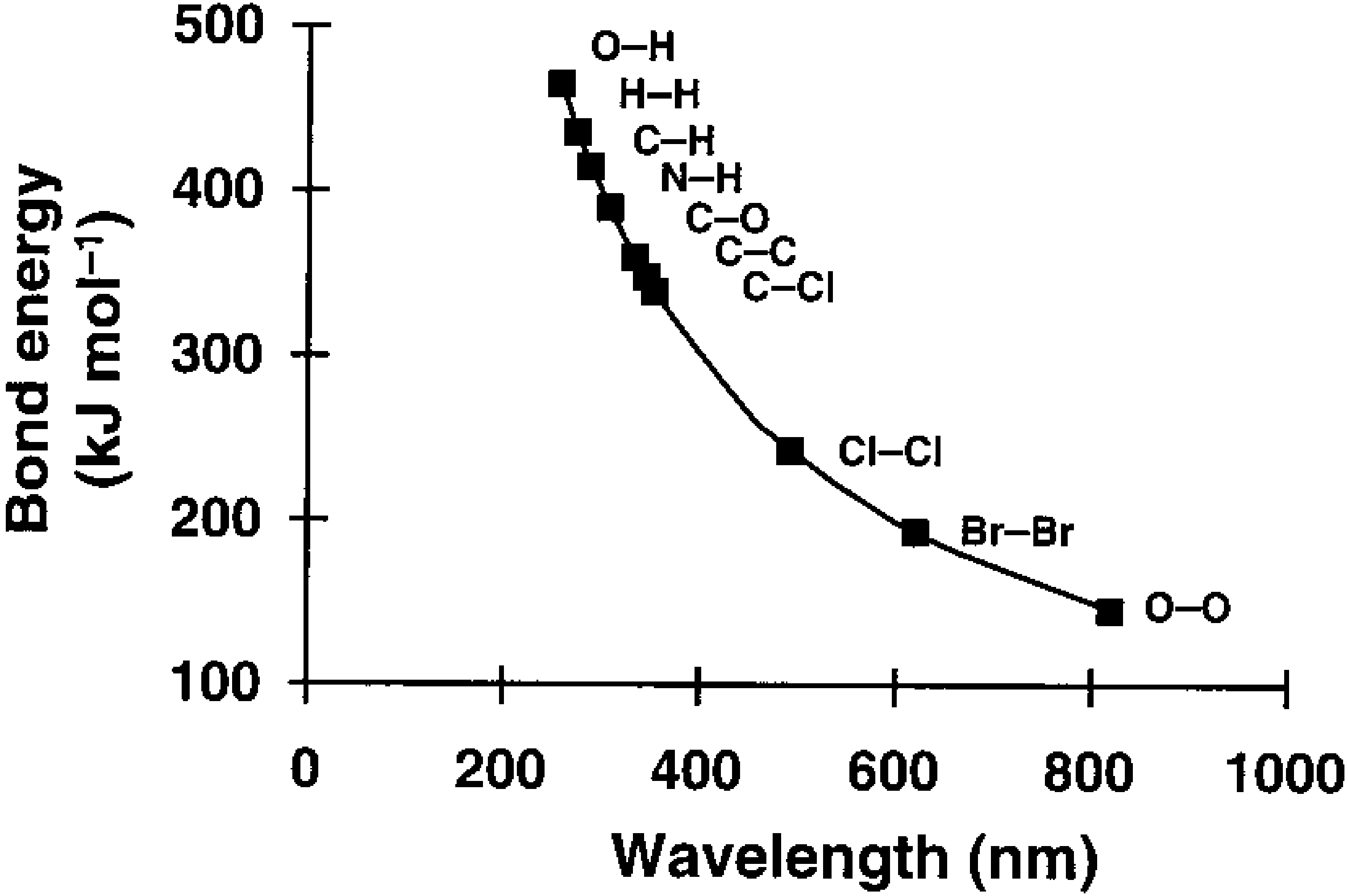
Photolysis

- Chemical breakdown initiated by light energy
- two types
  - direct photolysis
  - sensitized (or indirect) photolysis
- Several steps
  - some solar light reaches water surface
  - some of this light penetrates to the solute
  - some of this is absorbed by the solute
  - some of absorbed light is capable of causing a reaction

Solar Radiation



Susceptible bonds?



Biotransformation

- Microbially mediated transformation of organic and inorganic contaminants
- Biochemical processes:
  - <u>Metabolism</u>: toxicant is used for synthesis or energy
  - <u>Cometabolism</u>: not “used”, but transformed anyway
- Chemical Effects:
  - <u>Detoxication</u>: Toxic to Non-toxic
    - mineralization
  - <u>Activation</u>: Non-toxic to Toxic

Refer to lecture #17

Bio kinetics

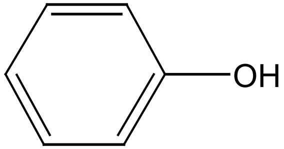
$$k_m = \frac{\mu_{\max} X}{Y\left(k_s + c\right)}$$

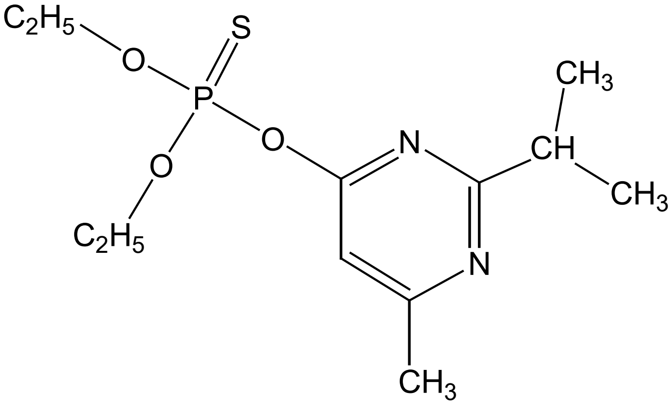
- Michaelis-Menten equation:
  - μ_{max}= maximum growth rate (yr^{-1})
  - X=microbial biomass (#cells/m^3)
  - Y= yield coefficient (cells produced per mass toxicant removed, #cells/µg)
  - k_s= half-saturation constant (µg/m^3)
  - k_b= rate of biotransformation (yr^{-1})
- If $c << k_s$, then:

$$k_m = \frac{\mu_{\max} X}{Y k_s} = k_{m2} X$$

Bio kinetics (cont.)

- Wide environmental range
  - phenol: k_m=4.0 d^{-1}
  - diazinon: k_m=0.016 d^{-1}
- Temperature correction
  - θ=1.04-1.095





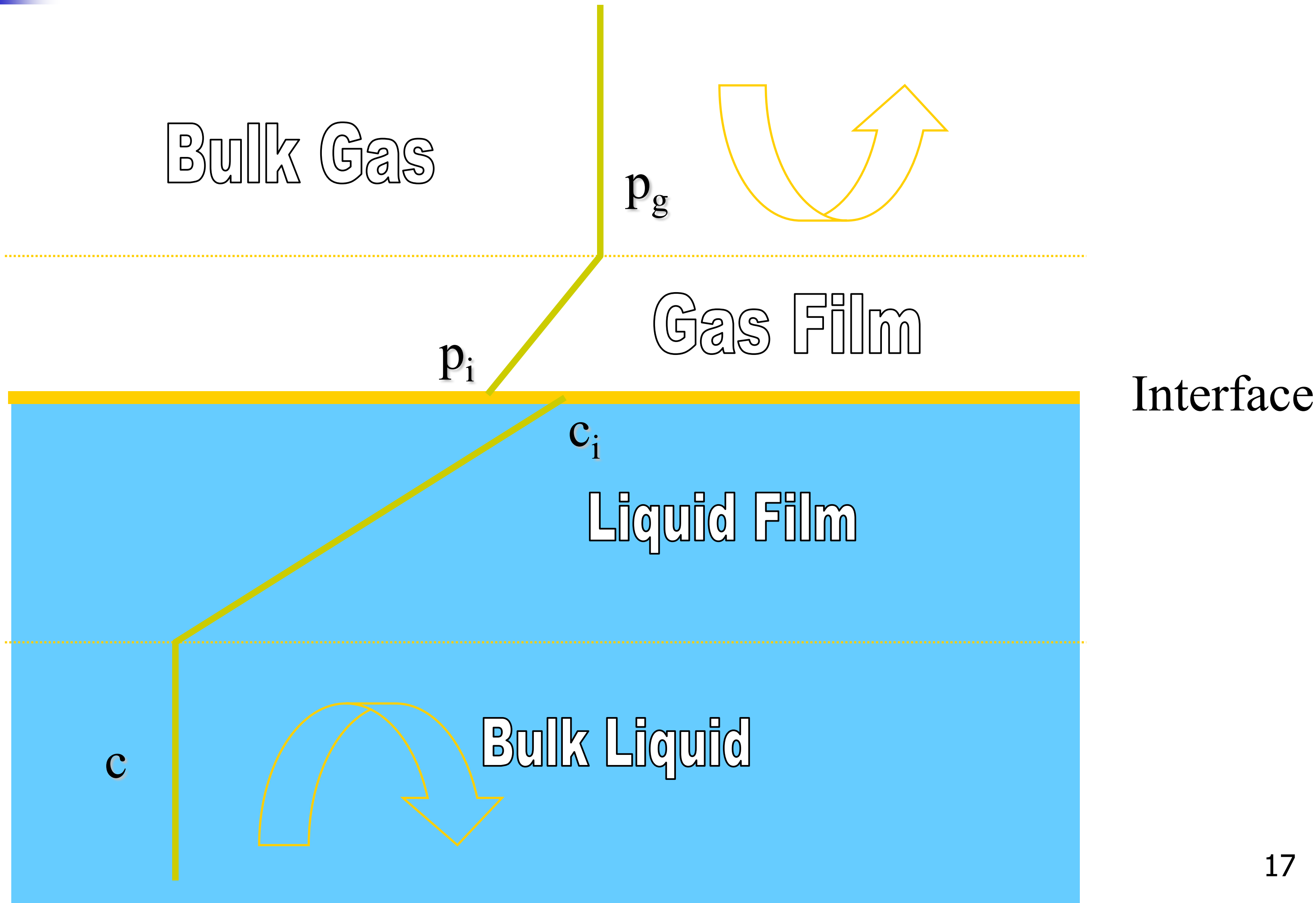
$$\left(k_m\right)_T = \left(k_m\right)_{20}\theta^{T-20}$$

Hydrolysis

- Reaction with water and its constituents
  - H_2O $k_h = k_n$
  - OH^- $k_h = k_b[OH^-]$
  - H^+ $k_h = k_a[H^+]$
- Autodissociation $K_w = [OH^-][H^+]$
- Combining: $k_h = k_b[OH^-] + k_n + k_a[H^+]$
  - or:

$$k_h = k_b \frac{K_w}{10^{-pH}} + k_n + k_a 10^{-pH}$$

Volatilization: The two film theory



Bulk Gas

p_g

Gas Film

p_i

Interface

c_i

Liquid Film

c

Bulk Liquid

Two film model

- Flux from the bulk liquid to the interface

$$J_l = K_l(c_i - c)$$

- Flux from the interface ot the bulk gas

Mass transfer velocities (m/d)

$$J_g = \frac{K_g}{RT_a}(p_g - p_i)$$

  - And the K's are related to the molecular diffusion coefficients by:

$$K_l = \frac{D_l}{z_l} \qquad K_g = \frac{D_g}{z_g}$$

Whitman's 2 film model (cont.)

- According to Henry's law: $p_i = H_e c_i$
- And relating this back to the bulk concentration

$$p_i = H_e \left(\frac{J_l}{K_l} + c \right)$$

- now solving and equating the fluxes, we get:

$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

The net transfer velocity across the air-water interface (m/d)

Whitman’s 2 film model (cont.)

- Which can be rewritten as:

$$v_v = K_l \frac{H_e}{\underbrace{H_e}_{\text{Contaminant specific}} + \underbrace{RT_a\left(K_l/K_g\right)}_{\text{Environment specific}}}$$

- Now, applying it to toxicants
  - $p_g \cong 0$
- And converting to the appropriate units:

$$k_v = \frac{v_v}{H}$$

Volatilization: Parameter estimation

- Liquid film mass transfer coefficient (d^{-1})

$$K_l = K_{l,O_2}\left(\frac{32}{M}\right)^{0.25}$$

Compound molecular weight

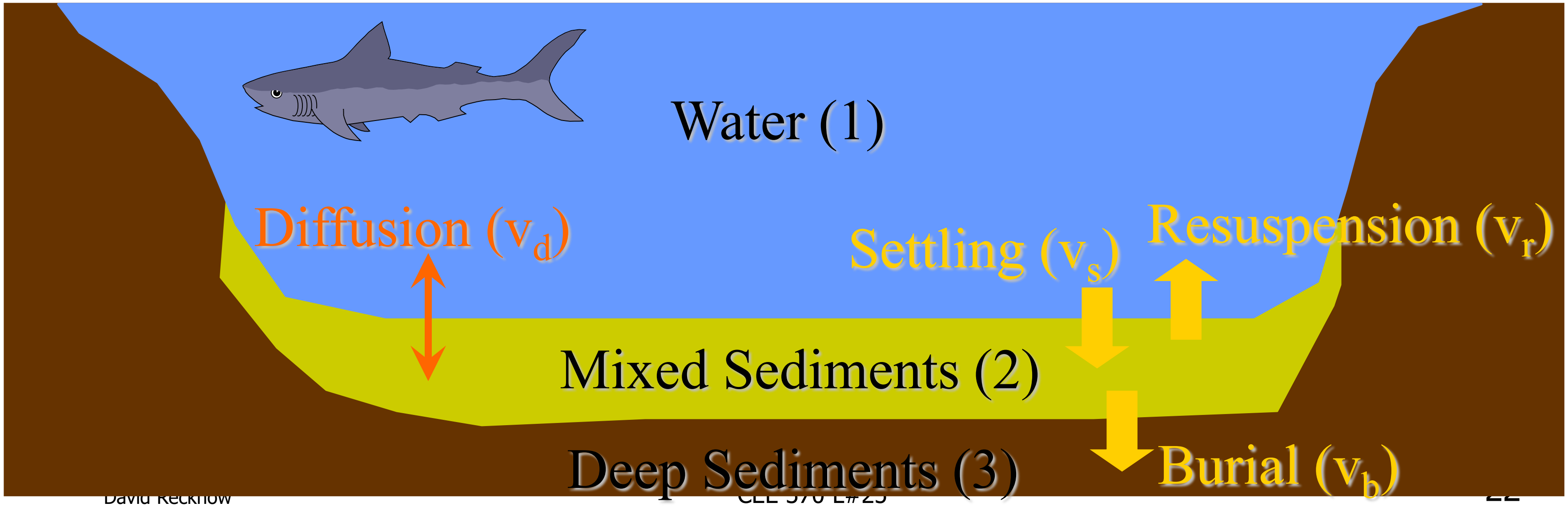
- Gas film mass transfer coefficient (d^{-1})

$$K_g = 168U_W\left(\frac{18}{M}\right)^{0.25}$$

Wind velocity (mps)

Toxics Model: CSTR with sediments

- Internal Transport Processes (between compartments)
  - dissolved: diffusion
  - particulate: settling, resuspension & burial
- Expressed as velocities (e.g., m/yr)



Sorption

Functionally identical to M&Z equ# 3.32

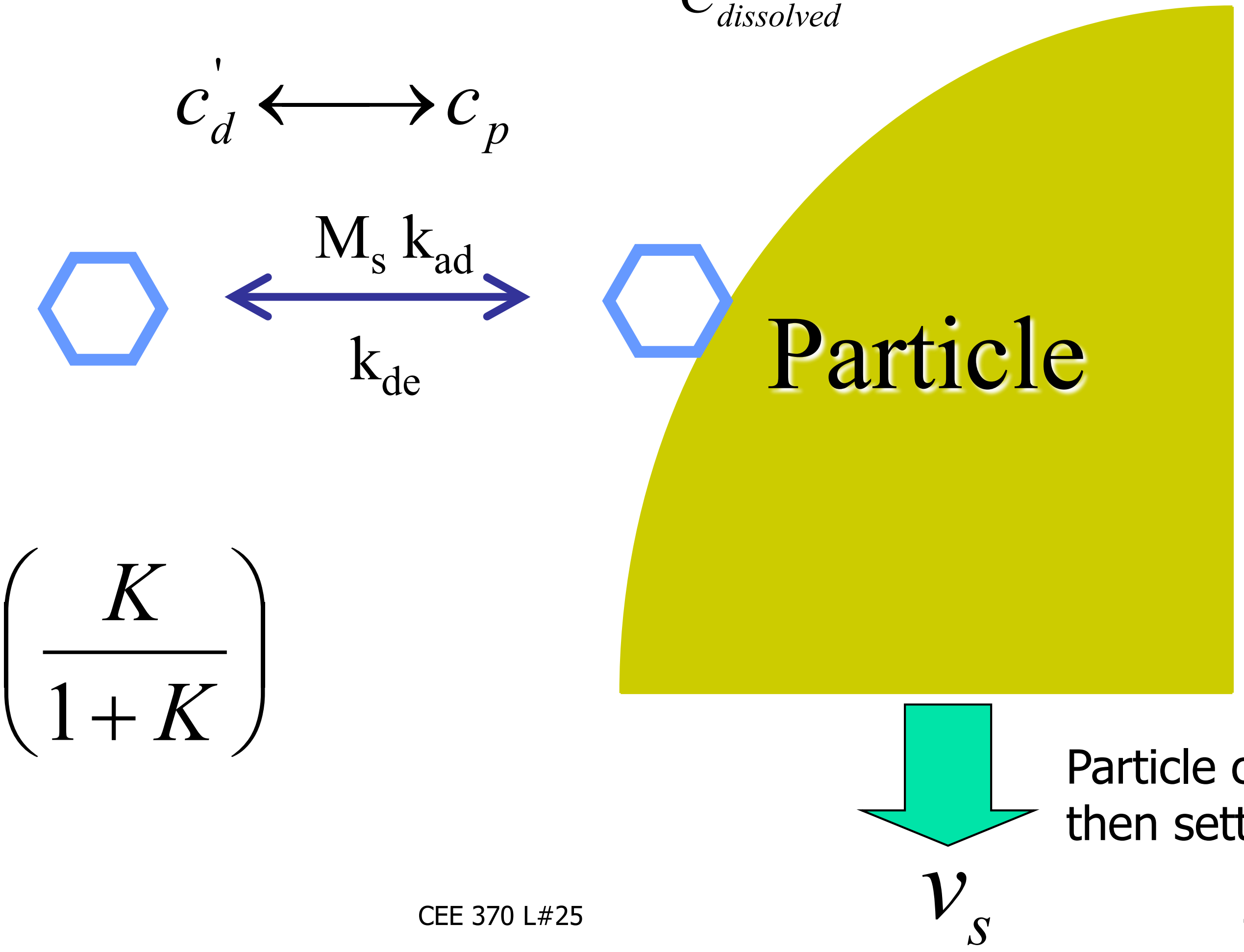
$$K = \frac{q}{C}$$

- Linear Isotherm

$$K = \frac{C_{particulate}}{C_{dissolved}}$$

$$c_d^{'} \longleftrightarrow c_p$$

See M&Z, section 3.10

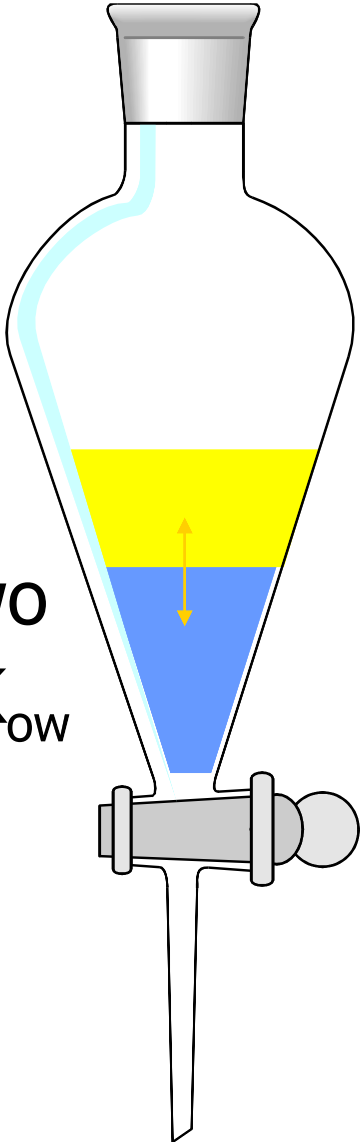


$$k_s = v_s\left(\frac{K}{1+K}\right)$$

Particle can then settle

Also in Lecture #16 biomagnification &
Lecture #22 on groundwater retardation

Octanol:water partitioning



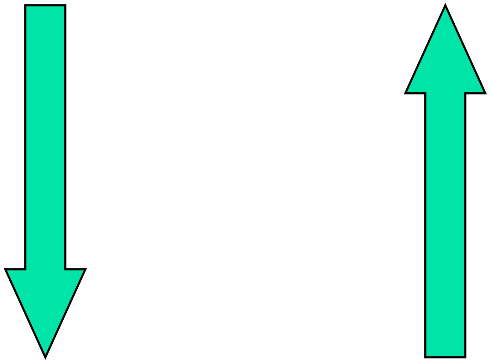
- 2 liquid phases in a separatory funnel that don’t mix
  - octanol
  - water
- Add contaminant to flask
- Shake and allow contaminant to reach equilibrium between the two
- Measure concentration in each (K_{ow} is the ratio)
- Correlate to environmental K

$$K = fn(K_{ow})$$

From Lecture #16

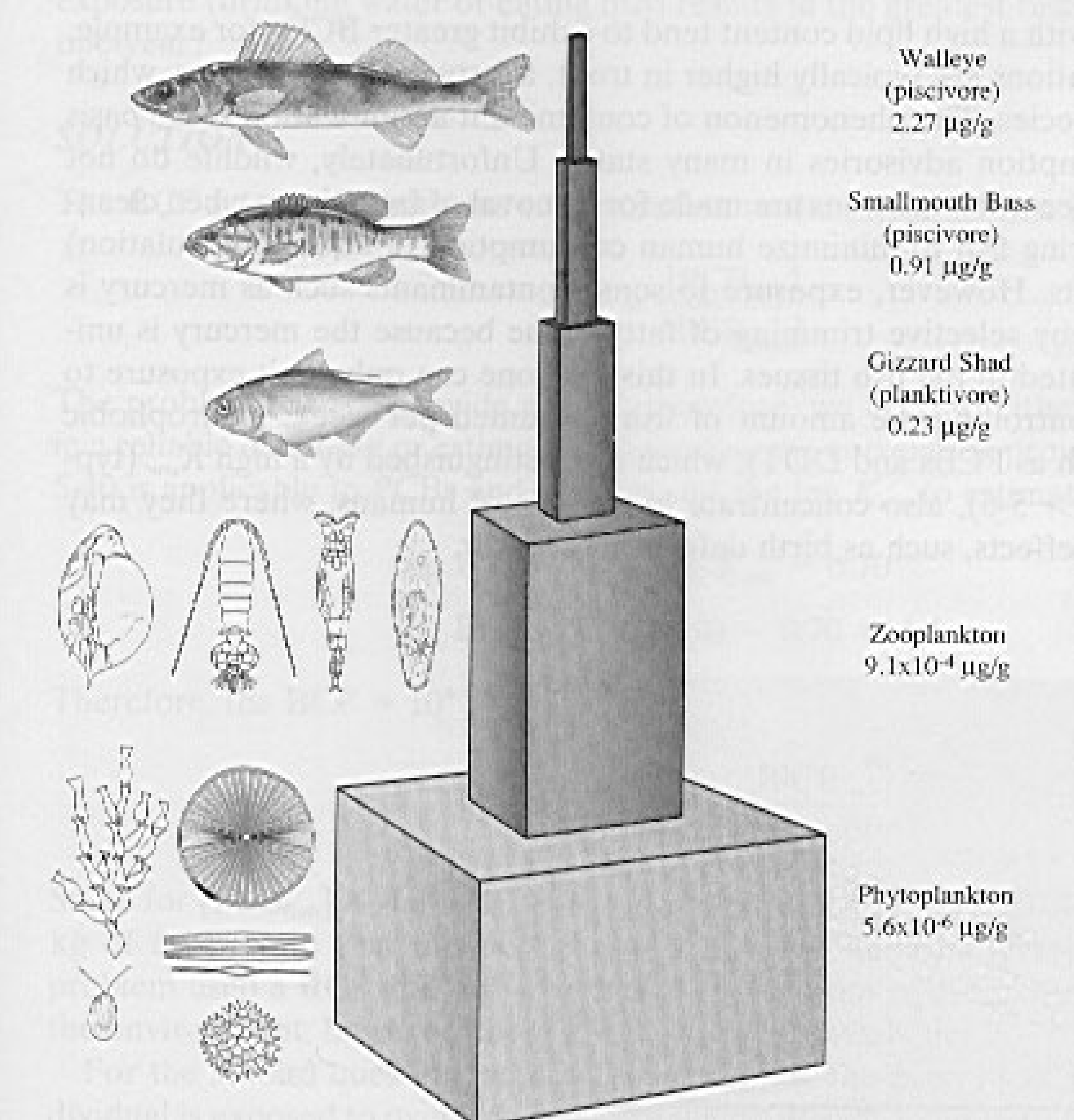
Bioaccumulation

- Mercury in food chain
  - Data from Onondaga Lake



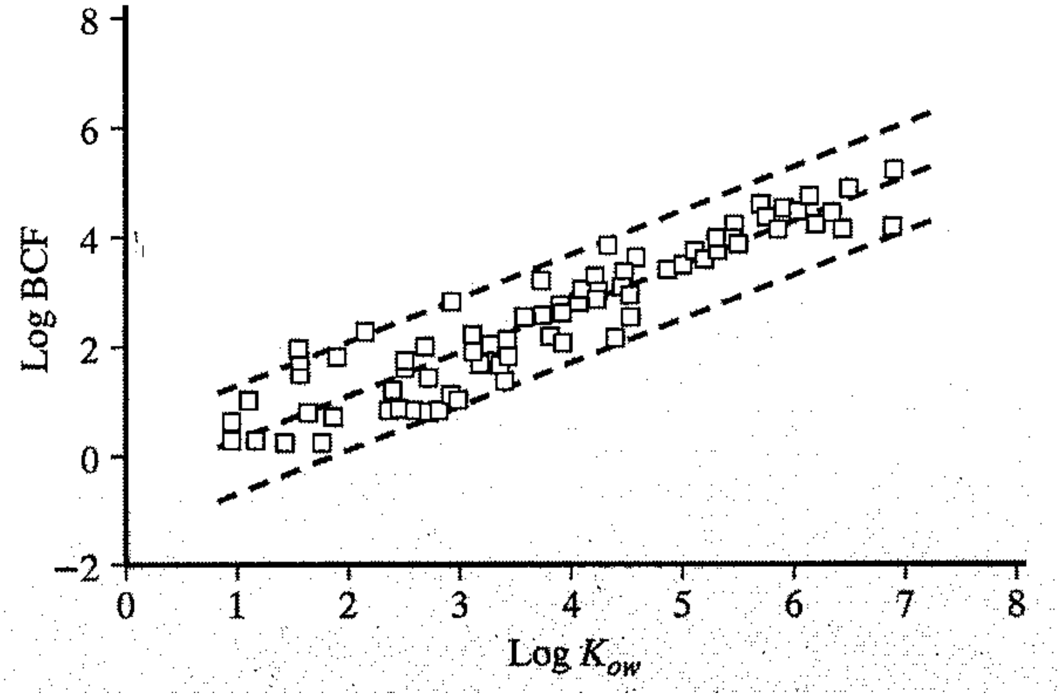
Biomass (box size)

Concentration (Shading)



Lab to Field

- Octanol water partition coefficients and bioconcentration factors

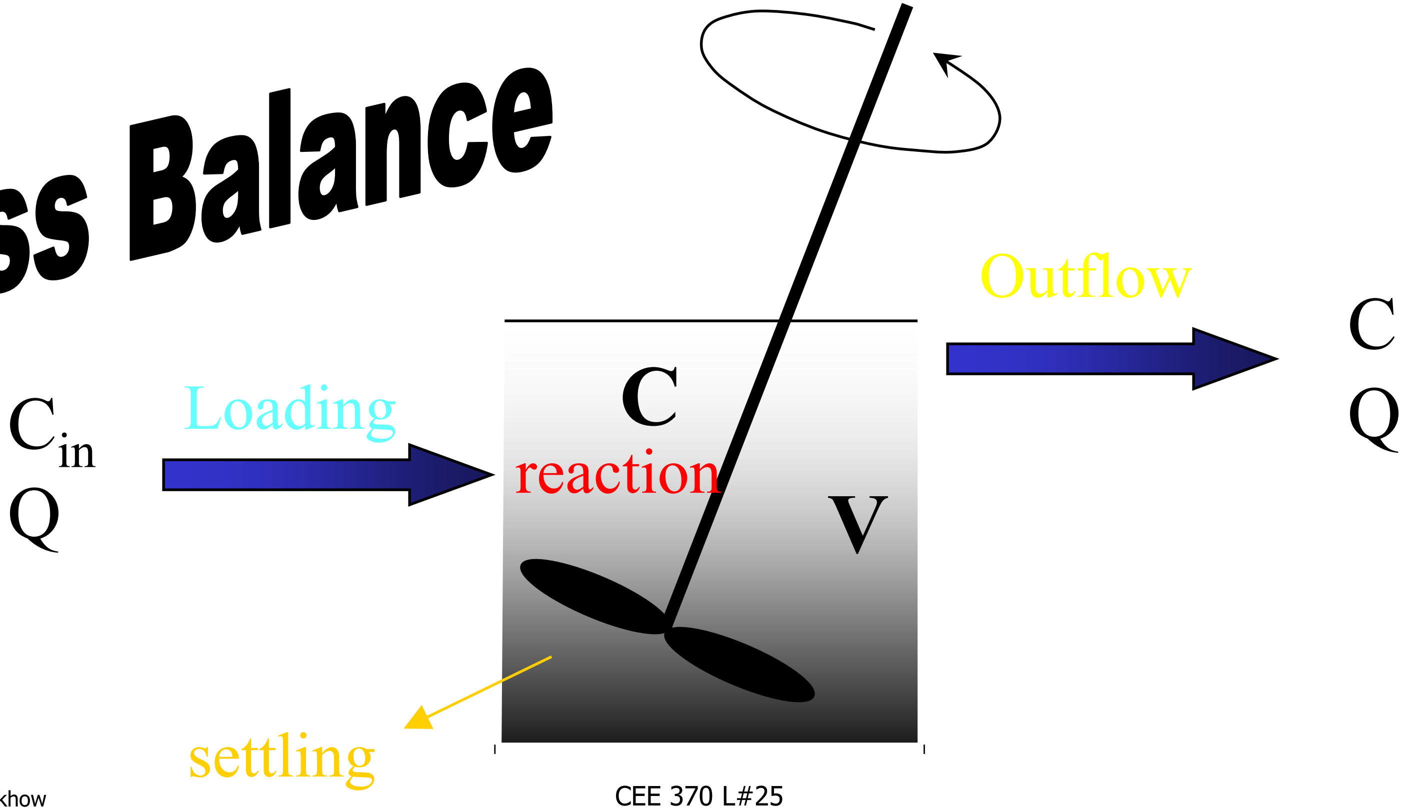


Completely-mixed lake or CMFR

- Often useful to assume perfect mixing
  - same concentration throughout system

$$\mathit{Accumulation} = \mathit{loading} - \mathit{outflow} - \mathit{reaction} - \mathit{settling}$$

Mass Balance



Other Terms in the Mass Balance

- Outflow

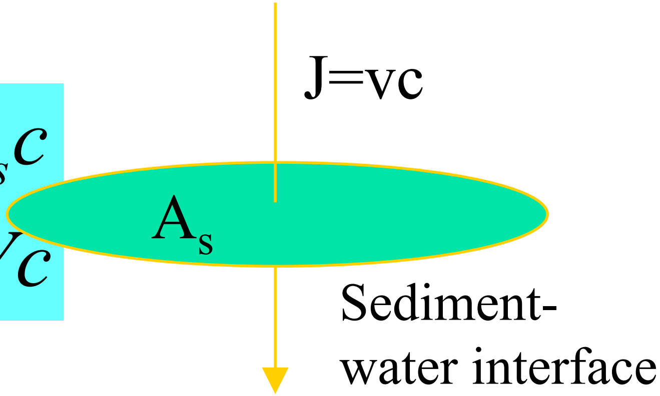
$$Outflow = Qc$$

- Reaction

$$Reaction = kM = kVc$$

- Settling

$$Settling = vA_s c$$
$$= k_s Vc$$



Note HW#6, problem 2

Since: $k_s = v/H$ $V = A_s H$

Combining all terms:

$$V\frac{dc}{dt} = W(t) - Qc - kVc - vA_s c$$

- Units for each term: mass/time
- Dependent variable: c
- Independent variable: t
- Forcing function: W(t), the way in which the external world “forces” the system
- Parameters: V, Q, k, v, A_s

Steady State Case

With Settling

- mass balance

$$\overbrace{V\frac{dc}{dt} = 0} = W(t) - Qc - kVc - vA_s c$$

W

- solution

$$c = \frac{W}{Q + kV + vA_s}$$

or

$$c = \frac{W}{a}$$

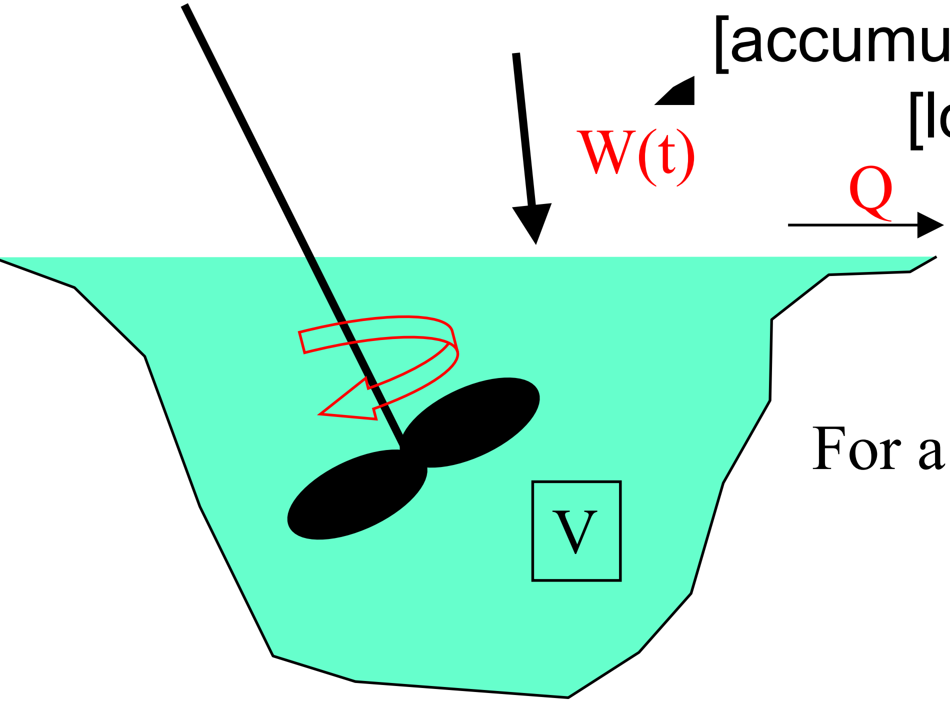
- assimilation factor

Where:

$$a = Q + kV + vA_s$$

The assimilation or “cleansing” factor

Simple lake model without settling



[accumulation] =

[loadings] ± [transport] ± [reactions]

$$V\frac{dc}{dt} = W(t) - Qc - kVc^n$$

For a 1st order reaction (n=1):

$$\frac{dc}{dt} + \alpha c = \frac{W(t)}{V}$$

Where: $\alpha = \frac{Q}{V} + k$

Steady State Solution: $$c = \frac{\overline{W}}{Q + kV}$$

Lake Model: Steady State Example

A lake has the following characteristics:

$$Volume = 50{,}000\ m^3$$
$$\text{Mean Depth} = 2\ \text{m}$$
$$\text{Inflow} = \text{Outflow} = 7500\ \text{m}^3 d^{-1}$$
$$\text{Temperature} = 25^{\text{o}}\,C$$

The lake receives the input of a pollutant from three sources: a factory discharge of 50 kg d^{-1}, a flux from the atmosphere of 0.6 g m^{-2} d^{-1}, and the inflow stream that has a concentration of 10 mg/L. If the pollutant decays at the rate of 0.25/d at 20°C

a. compute the assimilation factor
b. steady state concentration
c. show breakdown for each term

Lake Model: Solution

First correct the decay rate for temperature

$$k = 0.25\theta^{25-20} = 0.25(1.05)^{25-20}$$
$$= 0.319d^{-1}$$

Now the assimilation factor

$$a = Q + kV$$
$$= 7500 + 0.319(50{,}000)$$
$$= 23{,}454m^3d^{-1}$$

Lake Model: Solution (cont.)

The surface area of the lake is:

$$A_s = \frac{V}{H} = \frac{50{,}000}{2} = 25{,}000 m^2$$

The atmospheric and inflow load is then:

$$W_{atmosphere} = JA_s = 0.6(25{,}000) = 15{,}000 g/d$$

$$W_{inflow} = 7500(10) = 75{,}000 g/d$$

Combining all loads:

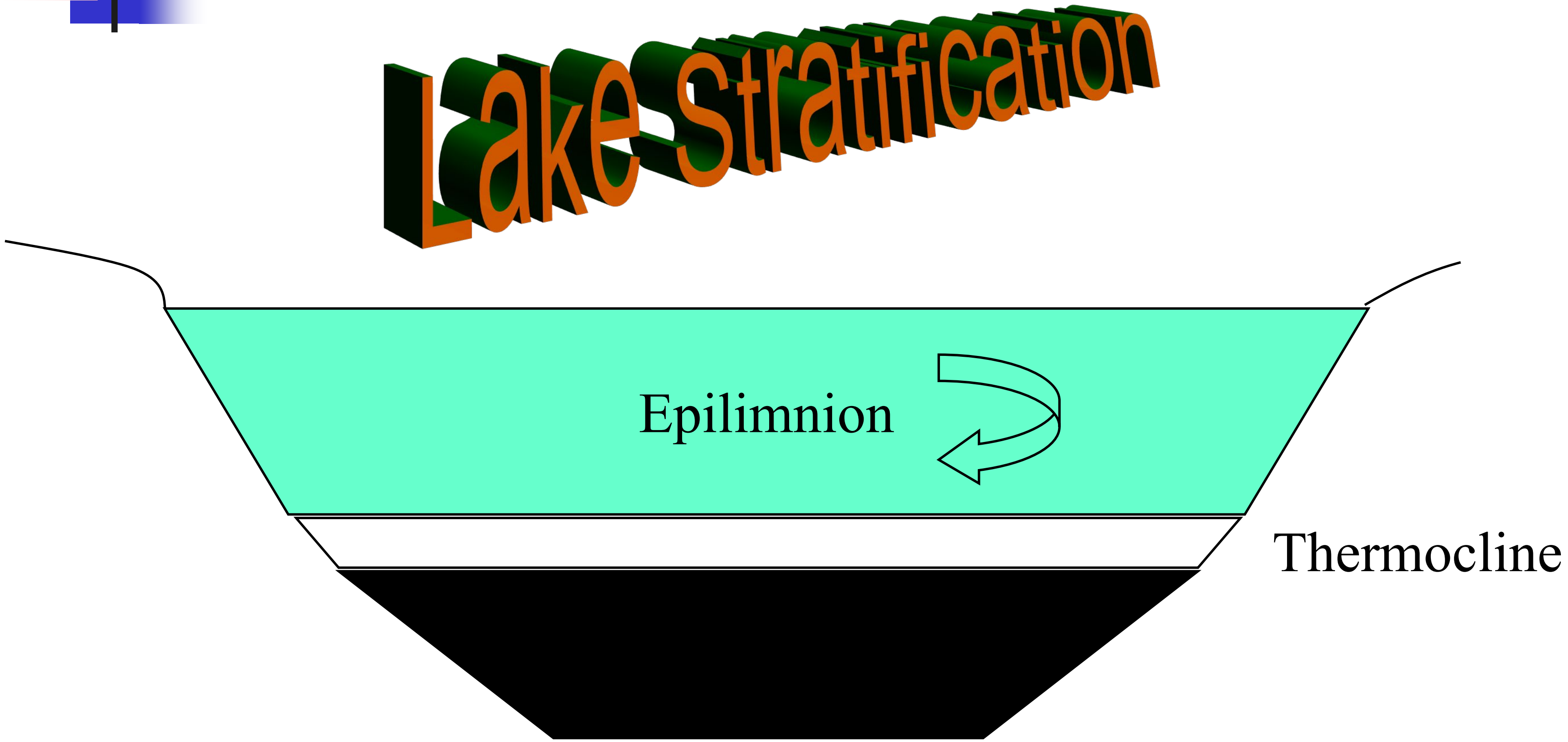
$$\begin{aligned} W &= W_{factory} + W_{atmosphere} + W_{inflow} \\ &= 50{,}000 + 15{,}000 + 75{,}000 \\ &= 140{,}000 g/d \end{aligned}$$

Lake Model: Solution (cont.)

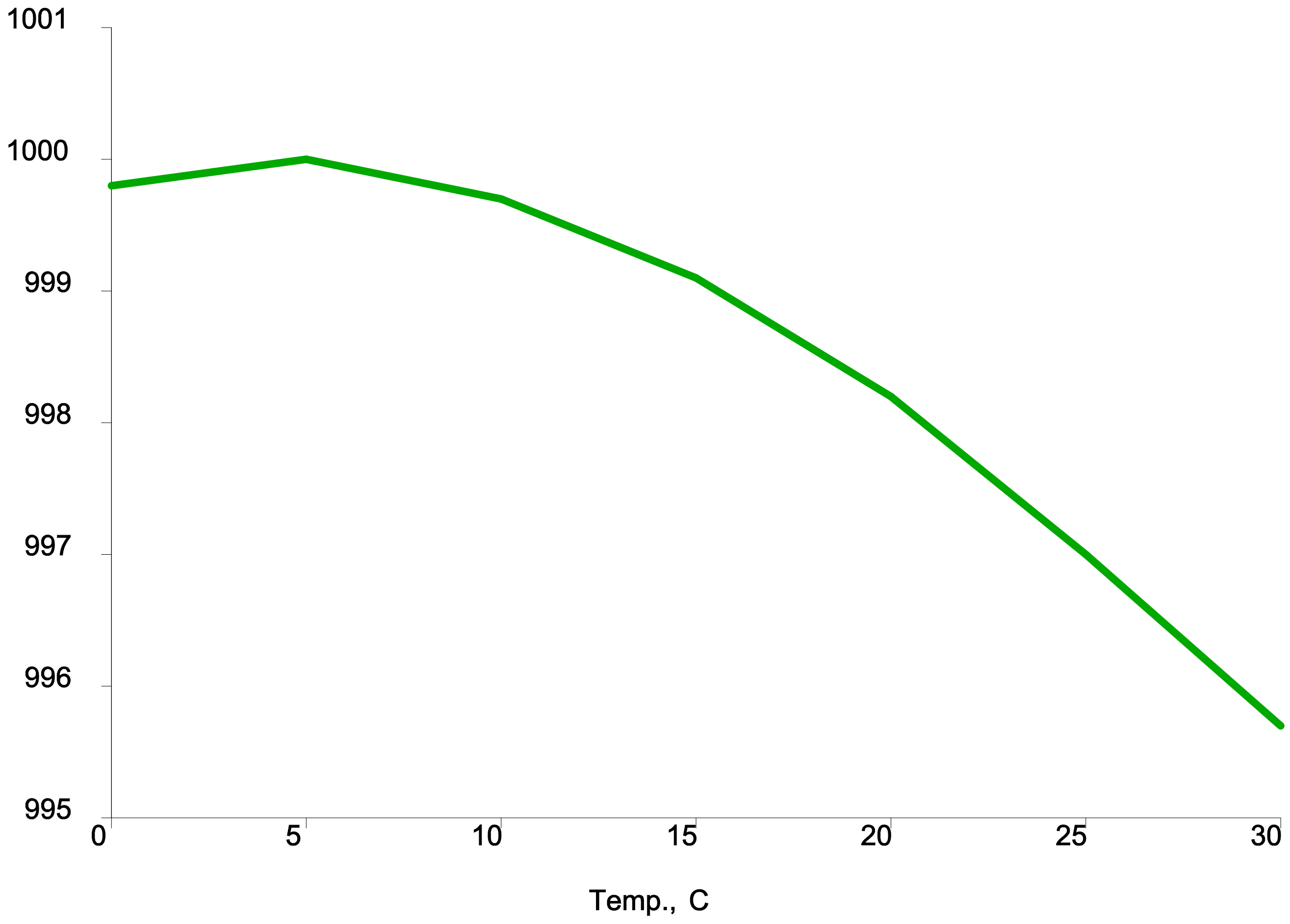
And finally, the concentration:

$$\begin{aligned} c &= \frac{W}{a} \\ &= \frac{140{,}000\, g/d}{23{,}454\, m^3/d} \\ &= 5.97\, mg/L \end{aligned}$$

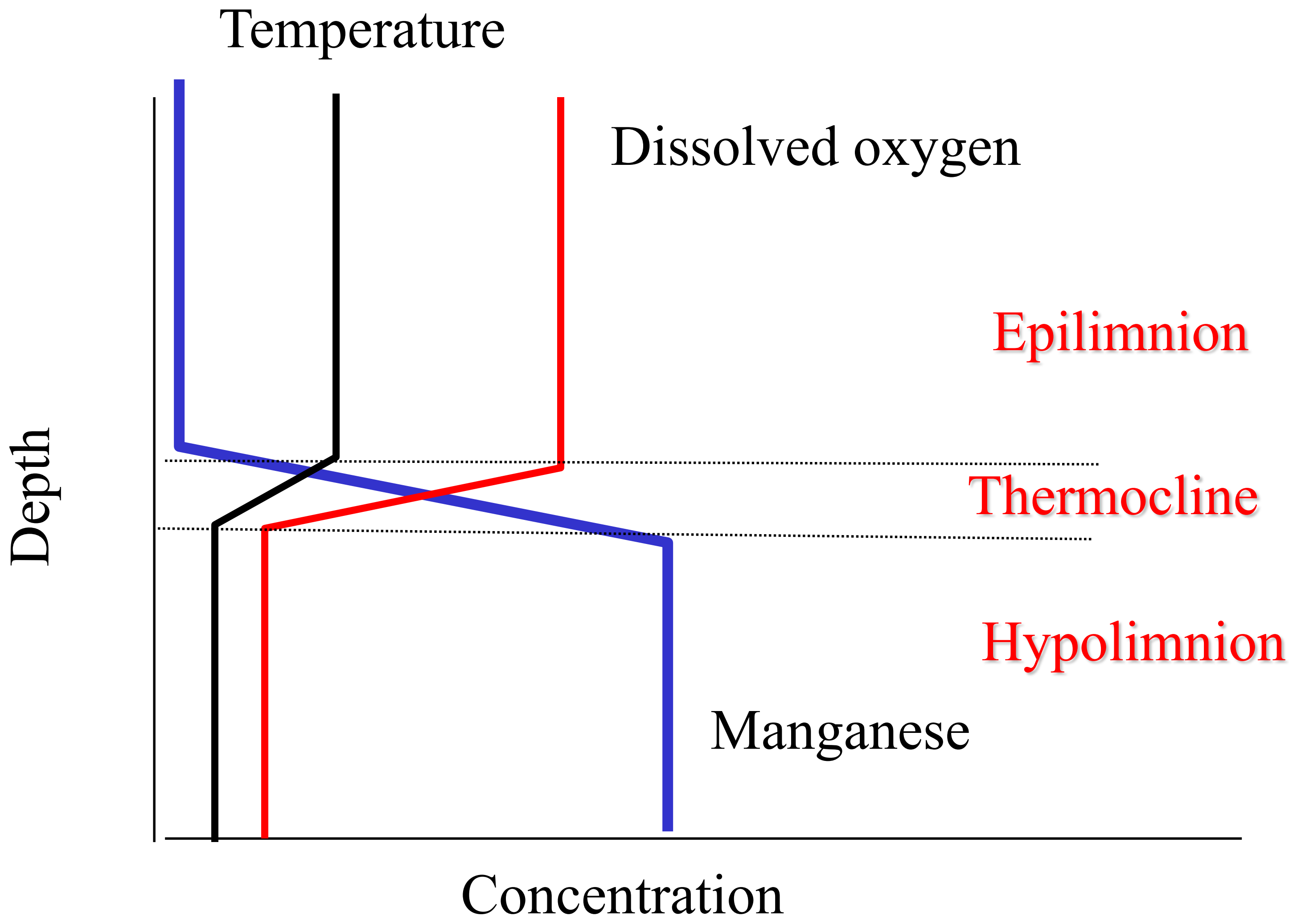
Dimictic Lakes



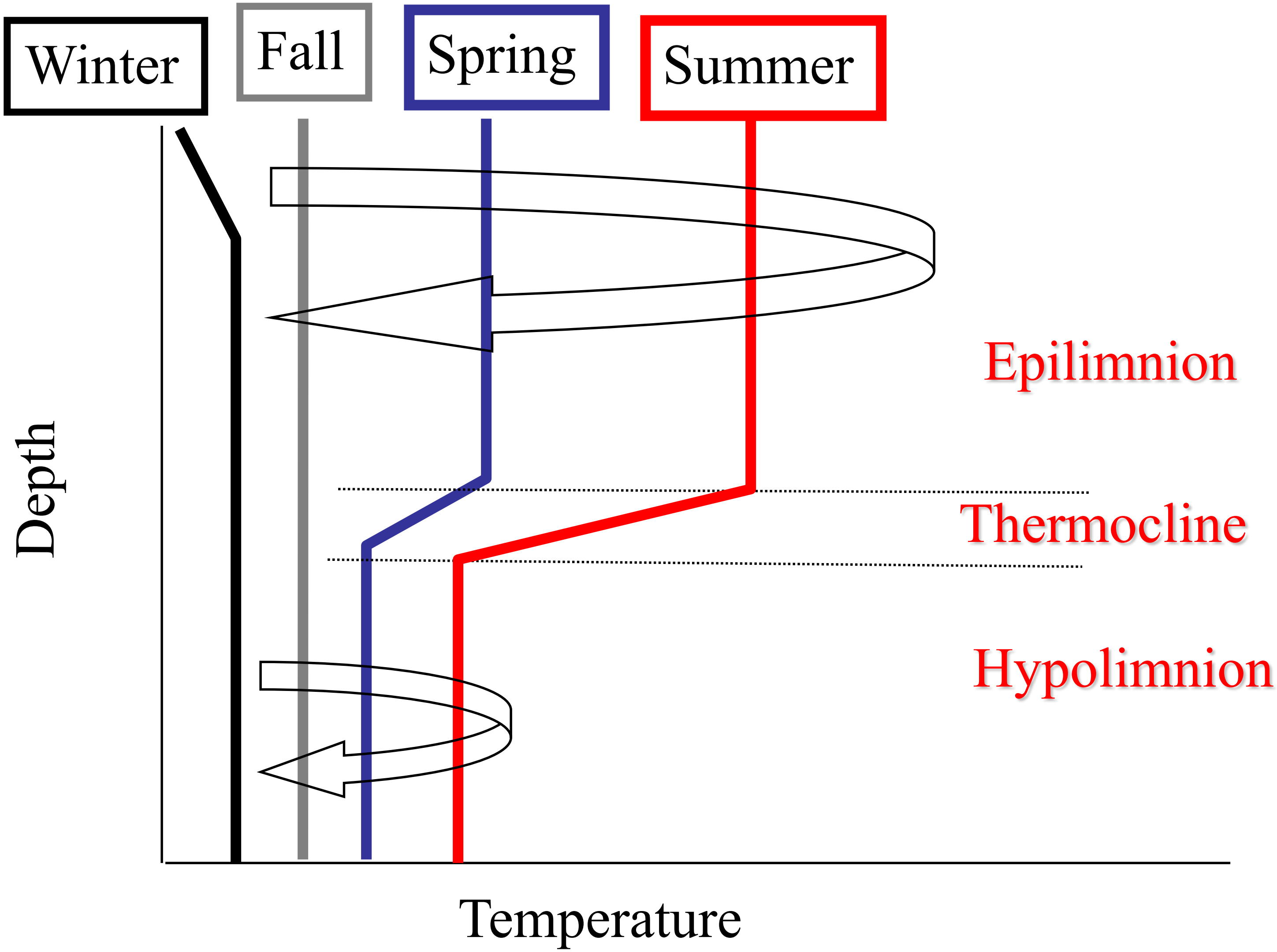
Temperature & Density



WQ Profiles in Stratified Lakes



Temp. Profiles in Stratified Lakes



- To next lecture