Water Pollution-4
-Surface Water Quality

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Oxygen Depletion in Rivers

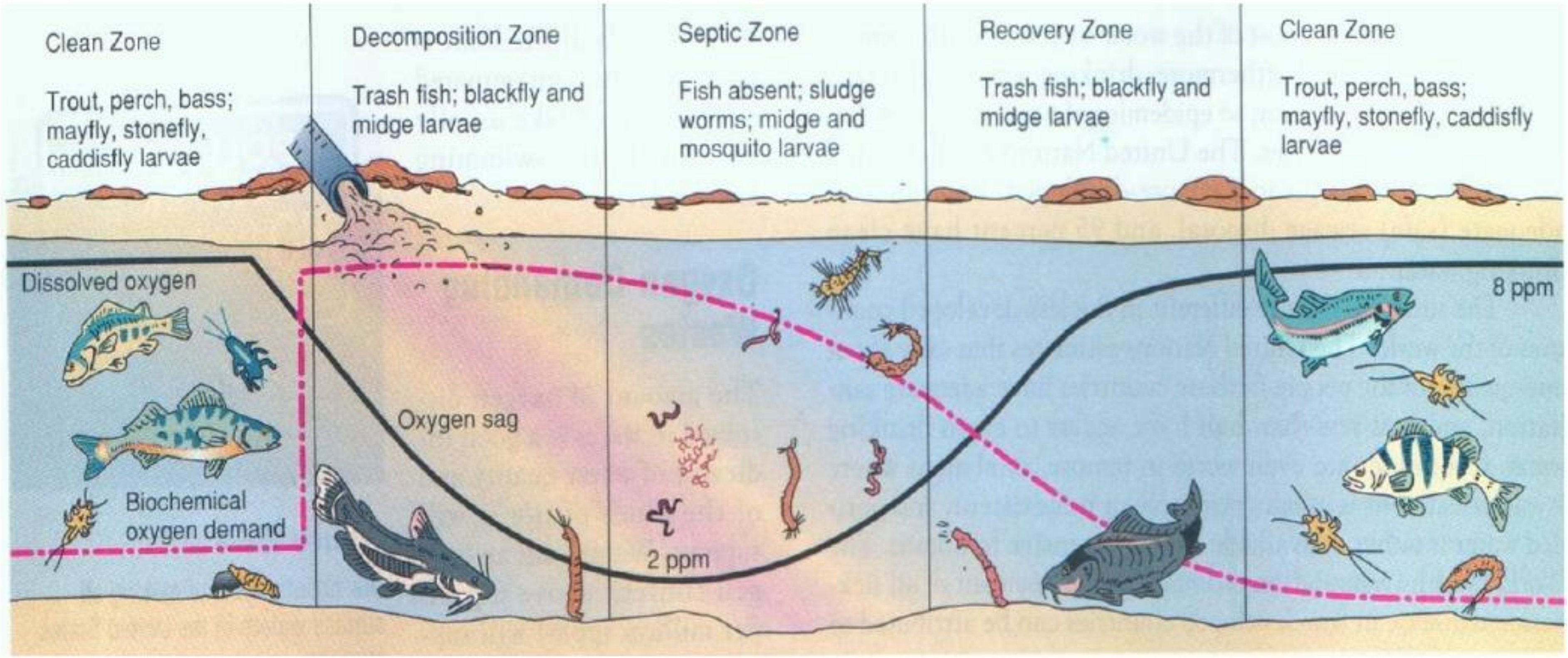
√ Oxygen Depletion in Rivers

- River health is directly related to DO concentration profile.
- The critical level for DO is ~3 mg/L.
- No fish will survive if DO < 1 mg/L.
- Lower DO: floating sludge, odors and fungal growth
- Factors Affecting DO profile:

Sources	Sinks
Atm. Reaeration	Discharge (BOD) respiration
Photosynthesis	Nitrification
Advection (confluence)	Benthal O_2 demand (sediments)

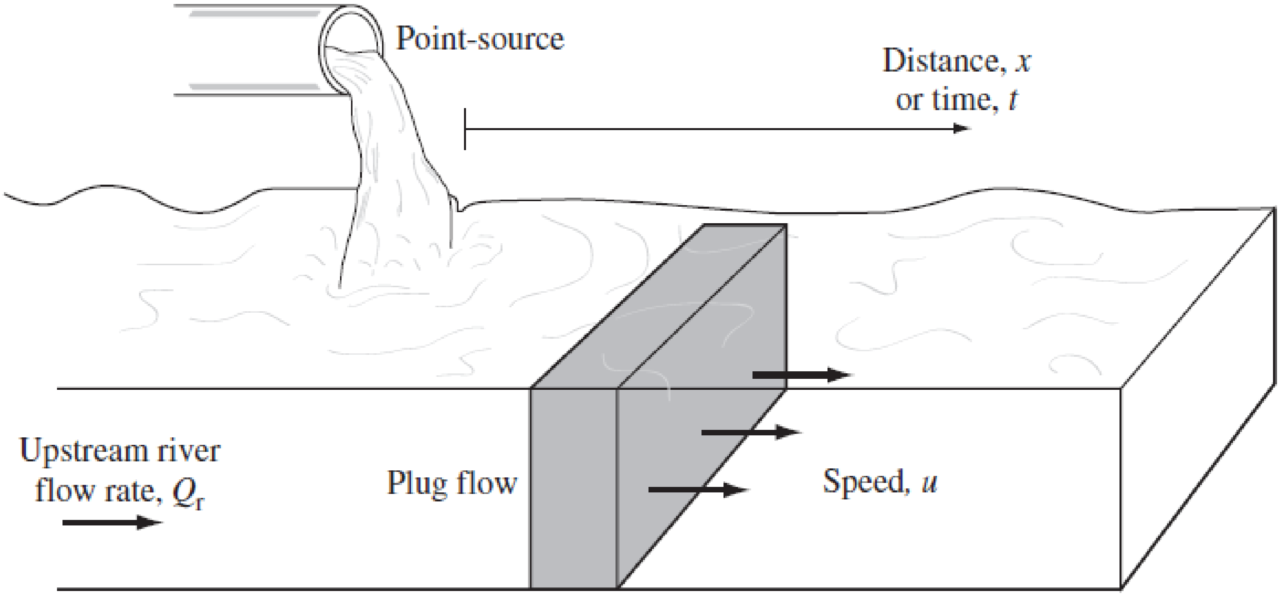
- Temperature also a factor (less DO at high T)

DO Sag Curve and Aquatic Wildlife



DO Model: Discharge and Mixing

√ Consider a waste discharge mixing with a stream flow



$$L_o = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r} = \text{BOD of mixed stream (x = 0)}$$

L_0 = ultimate BOD of the mixture of streamwater and wastewater (mg/L)
L_r = ultimate BOD of the river just upstream of the point of discharge (mg/L)
L_w = ultimate BOD of the wastewater (mg/L)
Q_r = volumetric flow rate of the river just upstream of the discharge point (m^3/s)
Q_w = volumetric flow rate of wastewater (m^3/s)

DO Model: Discharge and Mixing

- Initial DO deficit (D_0) in combined flow is the saturation value minus the actual DO.

Do not confuse DO with D_0

$$D_0 = DO_{sat} - \frac{Q_w(DO_w) + Q_r(DO_r)}{Q_w + Q_r}$$

D = dissolved oxygen deficit = $(DO_s - DO)$
DO_s = saturated value of dissolved oxygen
DO = actual dissolved oxygen at a given location downstream

DO Model: Deoxygenation

√ O_2 depletion is primarily due to heterotrophic respiration.

- Deoxygenation can occur rapidly and results in an oxygen deficit (relative to typical levels)

- Deoxygenation rate (proportional to BOD) = $k_d L_t$ = **$k_d L_0 \exp(-k_d t)$** = ***dD/dt***

Recall the BOD degradation rate

$$\frac{dL_t}{dt} = kL_t$$

$$L_t = L_o e^{-kt}$$

$$k = k_d$$

k_d = deoxygenation rate coefficient (≈ k)

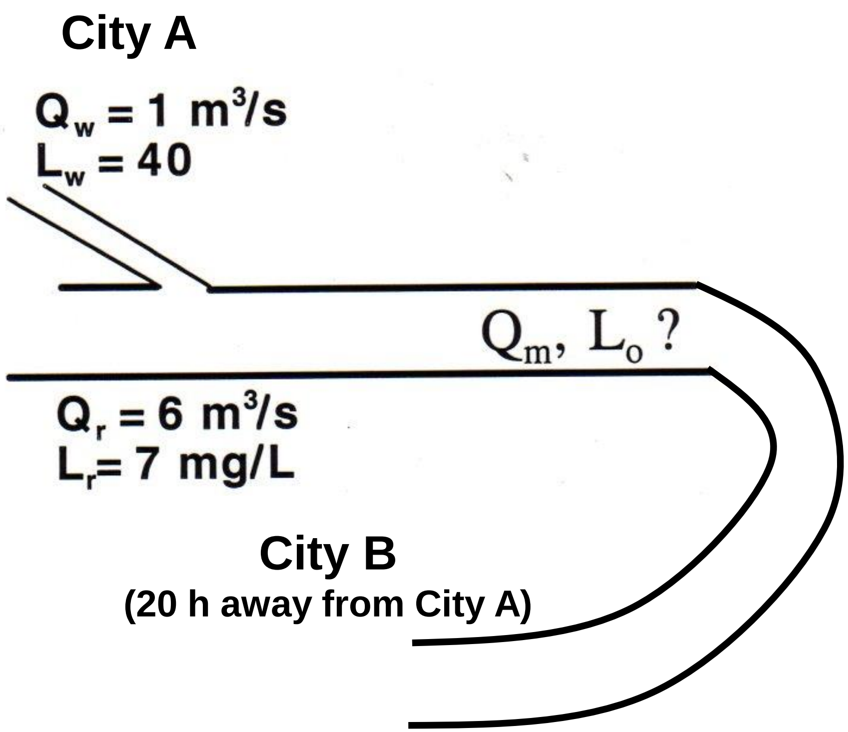
L_o = ultimate carbonaceous biochemical O_2 demand

Example

- River was characterized as BOD = 7 mg/L, flow = 6 m^3/s.

  Discharge into the river at City A: BOD = 40 mg/L, inflow = 1 m^3/s.

  What is the BOD just after discharge and at city B, 20 hours after discharge at City A? (k_d = 0.15 d^{-1})



DO Model: Reaeration

√ Primarily a function of gas exchange with atmosphere.

- Oxygen dissolves in water, and equilibrium (saturated) concentration follows Henry's law

- Assume that the rate of reaeration is proportional to the oxygen deficit (D)

D = saturated DO - actual DO = DO_s – DO

DO is f(T, atm, Cl^-)

$$\text{Rate of reaeration} = k_r D$$

k_r = reaeration constant (time^{-1})

Solubility of Oxygen in Water (mg/L) at 1 atm Pressure

	Chloride Concentration in Water (mg/L)			
Temperature (°C)	0	5,000	10,000	15,000
0	14.62	13.73	12.89	12.10
5	12.77	12.02	11.32	10.66
10	11.29	10.66	10.06	9.49
15	10.08	9.54	9.03	8.54
20	9.09	8.62	8.17	7.75
25	8.26	7.85	7.46	7.08
30	7.56	7.19	6.85	6.51

Source: Thomann and Mueller, 1987.

DO Model: Reaeration

- Reaeration rate = $\boldsymbol{k_r}$**D**

  - Where k_r = reaeration coefficient (depends on mixing and flow rate)

$$k_r = \frac{3.9\sqrt{u}}{H^{3/2}}$$

k_r – reaeration rate (1/day)
u – average stream velocity (m/s)
H – average stream depth (m)

0.1 to 0.23/day for small pounds

0.69 to 1.5/day for swift streams

- Generally slower than DO consumption (i.e., deoxygenation) when the BOD is high (e.g., near the discharge point).

DO Model: Deoxygenation & Reaeration

√ The combination of the deoxygenation and reaeration rates represent the O_2 behavior.

- Assumptions

  - Mixing occurs across the river cross-section y and z

  - No mixing in *x* direction (no dispersion in flow direction)

  - Point source, plug flow conditions:
    Solution to plug flow is the first order expression

Streeter–Phelps Oxygen Sag Equation

- Rate of increase of oxygen deficit = rate of deoxygenation – rate of reaeration

$$\frac{dD}{dt} = k_d L_o e^{-k_d t} - k_r D$$

- Solution:

$$D = \frac{k_d L_o}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_o\, e^{-k_r t}$$

D_o : initial DO deficit of river-sewage mixture

Streeter–Phelps Equation

- Quantify Deficit (in dissolved oxygen) progressing downstream (in terms of time or distance)

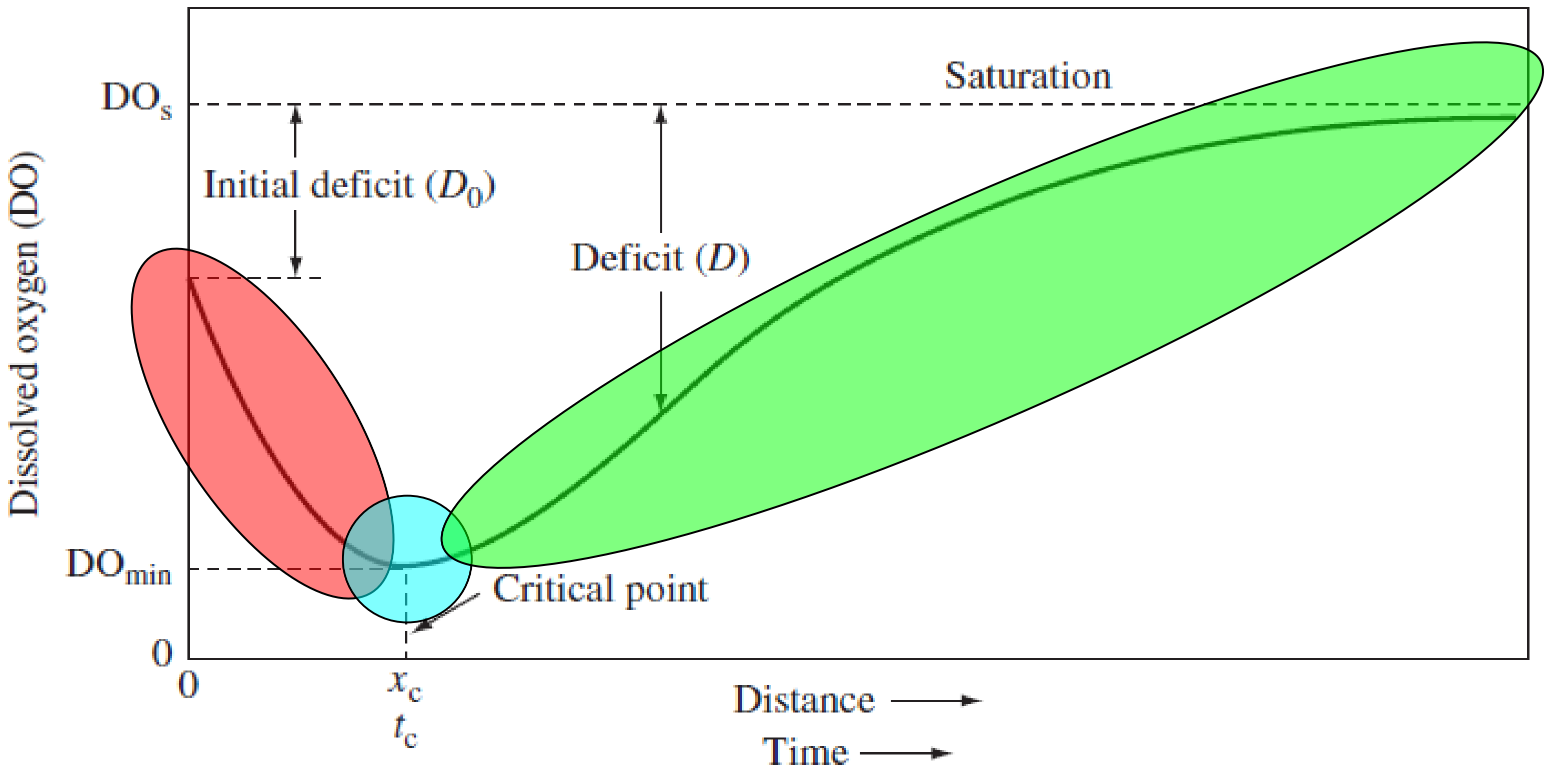
- Distance is easier to conceptualize and can be easily substituted

Distance = (velocity) x (time)

x* = *u* x *t

$$D = \frac{k_d L_0}{k_r - k_d}\left(e^{-k_d x/u} - e^{-k_r x/u}\right) + D_o\, e^{-k_r x/u}$$

Streeter–Phelps Equation



Deoxygenation > reaeration

Deoxygenation = reaeration

Deoxygenation < reaeration

Streeter–Phelps Equation

- Deoxygenation > reaeration at the beginning

$$\frac{dD}{dt} = k_d L_o e^{-kt} - k_r D$$

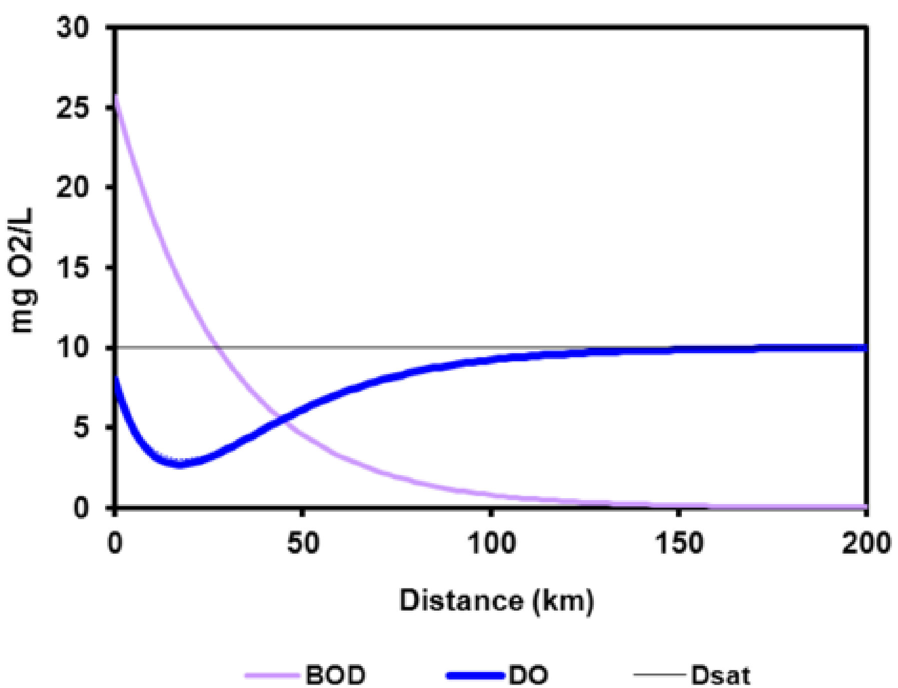
- At some point the rates are equal – this is when DO is a minimum (determined by setting dD/dt = 0)

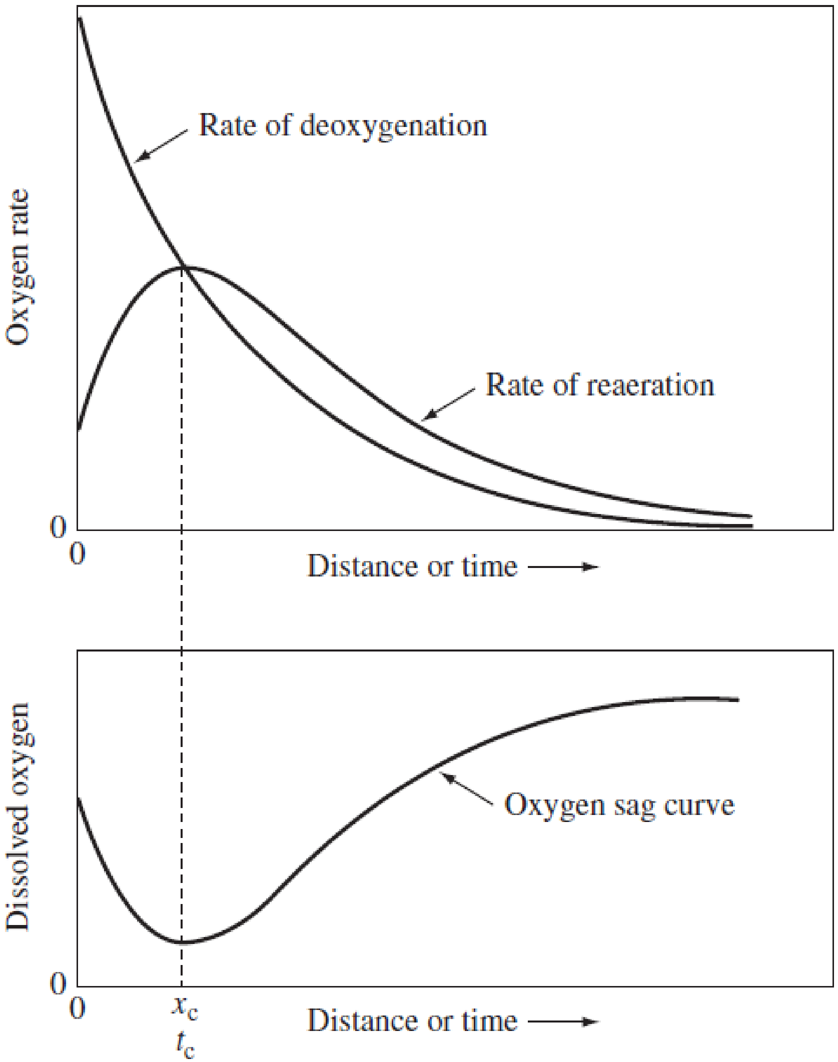
Critical point,

$$t_c = \frac{1}{k_r - k_d} \ln\left(\frac{k_r}{k_d}\left[1 - \frac{D_o(k_r - k_d)}{k_d L_o}\right]\right)$$

- Later, deoxygenation rate decreases (with BOD) and reaeration becomes faster.

DO Sag Curve and BOD Profile





Example

- Where will the critical point occur if

  L_o= BOD of river/sewage mix = 10.9 mg/L

  DO at mix. point = 7.6 mg/L

  u = 0.3 m/s, depth = 3.0 m

  T = 20 °C, k_d = 0.2 /day

$$t_c = \frac{1}{k_r - k_d} \ln\left(\frac{k_r}{k_d}\left[1 - \frac{D_o(k_r - k_d)}{k_d L_o}\right]\right)$$

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Source: Thomann and Mueller, 1987.

Example (Solution)

First, we need to find k_r and D_o

For k_r use the O'Connor-Dobbins empirical formula

$$k_r = \frac{3.9\sqrt{u}}{H^{3/2}} = \frac{3.9\ \mathrm{u}^{1/2}}{\mathrm{H}^{3/2}} =$$

To find the critical point

$$t_c = \frac{1}{k_r - k_d} \ln\left(\frac{k_r}{k_d} \left[1 - \frac{D_o \left(k_r - k_d \right)}{k_d L_o} \right] \right)$$

$$=$$

with the given flow rate and stream size

x = u t

Example

- What will be the minimum DO in this river? Could find the minimum DO value

t_c = 2.67 days

Using the oxygen sag equation with this value of t,
we find that the maximum oxygen deficit is 3.1 mg/L.

$$D = \frac{k_d L_o}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_o\, e^{-k_r t}$$

If the deficit is 3.1 mg/L and DO saturation is 9.1 mg/L

DO_{min} = 9.1 – 3.1 = 6.0 mg/L

Remarks

- The model can be used to determine the assimilative capacity of rivers, or to set permits for sewage discharge.
  - If the proposed discharge results in DO that is too low, allowed sewage is should be reduced (lower BOD concentration and/or inflow rate).

- Temperature effects are important - in hot weather the DO_{sat} is lower and respiration is faster.

- More complex models consider photosynthesis and diurnal variations (sine functions). Other factors such as benthal DO demand by sludge and nitrification can also be considered.

(http://en.wikipedia.org/wiki/Streeter-Phelps_equation#Expanded_model)

Water Quality of Lakes & Reservoirs

- Lakes and Reservoirs require special attention because they are not moving or flowing (no easy flushing) so inputs and oxygenations process have different effects

- **Oligotrophic**
  - A new body of water (young lake)
  - "little nutrients"

- **Eutrophic**
  - "well fed"
  - Phytoplankton grow and die (drop to the bottom)
  - Organic matter decays, using up oxygen
  - Silt and organic matter accumulate at bottom
    - → lake becomes more shallow and warms up
    - → also becomes murky
    - → eventually becomes a marsh or a bog

- **Eutrophication:** natural aging process takes thousands of years.

How Do Humans Affect Eutrophication?

- Generation of:
  - municipal wastewater
  - industrial wastes
  - agricultural runoff

- Accelerated eutrophication due to human activities
  = **<u>cultural eutrophication</u>**

All these inputs stimulate algae growth

How Do Humans Affect Eutrophication

√ **Result of eutrophication:**

- Algae blooms
  - Odor & taste problems
  - Algal toxins (e.g., microcystin)
  - DO consumed with algal decay
- Low dissolved oxygen may drive out fish
- Anaerobic conditions – odor (H_2S), dissolution of heavy metals
  pH drop due to fatty acids

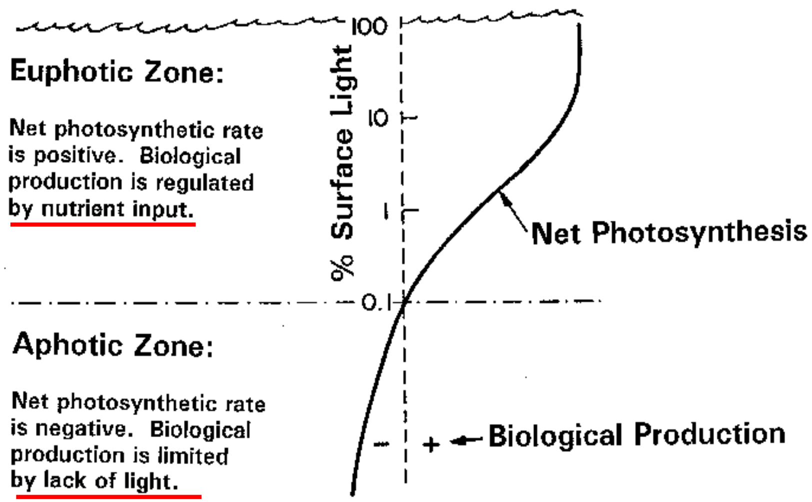
Eutrophication Factors

√ **Sunlight**

- Sunlight affects photosynthesis (algae need light).
- Oligotrophic lakes (e.g.,. Lake Tahoe)
  - Clear and photosynthesis occurs down to 100 m +
- Eutrophic lakes
  - Murky and photosynthesis may be limited to upper layer.
- Layers based on photosynthesis activity
  - **Euphotic Zone:**

    O_2 input by photosynthesis
    > O_2 removed by respiration
  - **Aphotic Zone:**

    little light (little photosynthesis, mainly benthic activity)



Eutrophication Factors

√ **Nutrient**

- Many nutrients are important to life
  - C, N, P, S, Ca, Mg, K, Se, Pb, Zn, Cu….
  - To control algae growth we can control nutrient levels, but which one(s)?

    phosphorus (P) or nitrogen (N)

- *Liebig's Law of the Minimum –*
  - Total biomass of any organism is determined by the nutrient present in the lowest concentration relative to the organism's stoichiometric requirement (which is determined by the organism's elemental composition)

Eutrophication Factors

√ **Nutrient**

- If you determine which is the limiting nutrient and make it scarcer, the algae population will be reduced.

- Eutrophic lakes have primarily blue-green algae (cyanobacteria), which can get N from the atmosphere
  - Need to focus on limiting P

    0.01 mg/L-P "acceptable"

    0.02 mg/L-P "excessive" → cause algal blooms

- Very deep lakes
  - Less recirculation of P, tend to be oligotrophic.

Eutrophication Factors

√ **Nutrient**

- Consider empirical elemental composition of algae:
  - $C_{106}H_{263}O_{110}N_{16}P$
- N/P = 16 × (14 g/mol) / 1 × (31 g/mol) = 7.2
  - For every 7.2 g of N utilized, 1 g of P is used
- Rule of thumb:

  N/P > 10 → P is limiting

  N/P < 5 → N is limiting
- No algae blooms will occur if:
  - P < 0.015 mg/L
  - N < 0.3 mg/L

Eutrophication Factors

√ **Phosphorus**

- For well mixed lakes at steady state, small S, and $Q_{in} = Q_{out}$, sink term is mainly due to settling

<u>**Rate of P addition = Rate of P removal**</u>

$$QC_{in} + S = QC + v_S AC$$

$$C = \frac{QC_{in} + S}{Q + v_s A}$$

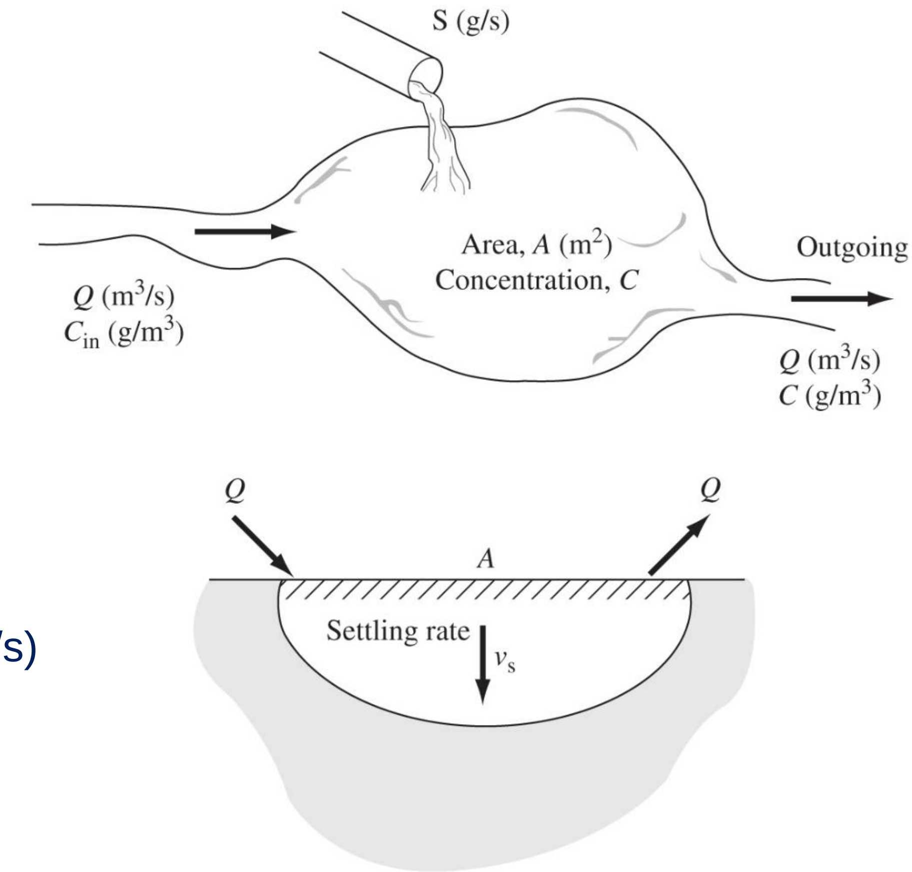


Figure: 05-19

S = rate of P addition from all point-source(s) (g/s)
Q = inflow/outflow rate from lake (m^3/s)
V_s = P settling rate (m/s)
A = surface area of lake (m^2)
C = concentration of phosphorus (g/m^3)

Eutrophication Factors

√ **Temperature**

- **Temperature affects water density.**
  – Water has a maximum density at 4 degrees C
- Density ↓ for T < 4℃
- Density ↓ for T > 4℃

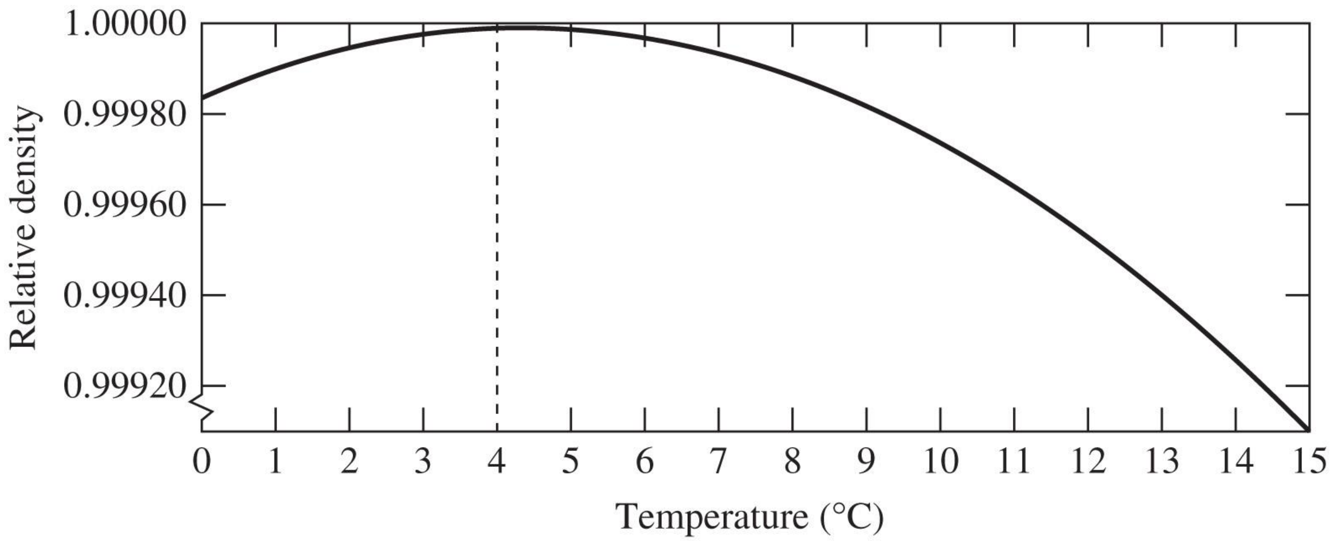


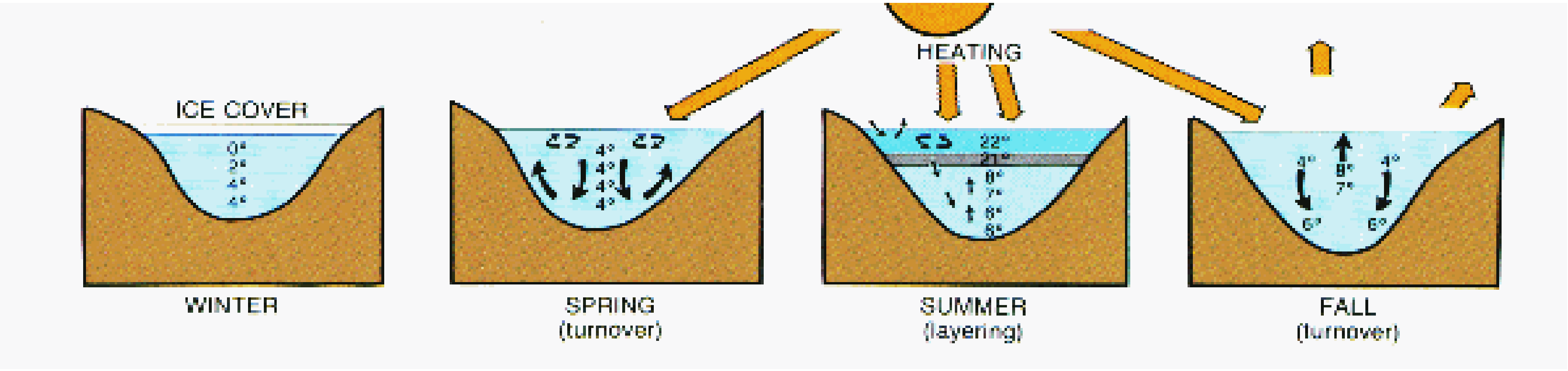
Figure: 05-20

Thermal Stratification

- In the summer:
  - Water is warmed by the sun > 4℃
  - Top layer warms up, becomes less dense than bottom layer

    → Top warmer layer stays at the top of the lake
- In the winter:
  - Top water is colder than 4℃
  - As top layer cools, it becomes less dense than bottom layer

    → Top layer (ice) stays at top of the lake
- In both extremes, there is little vertical mixing due to temperature related density differences – this is known as thermal stratification



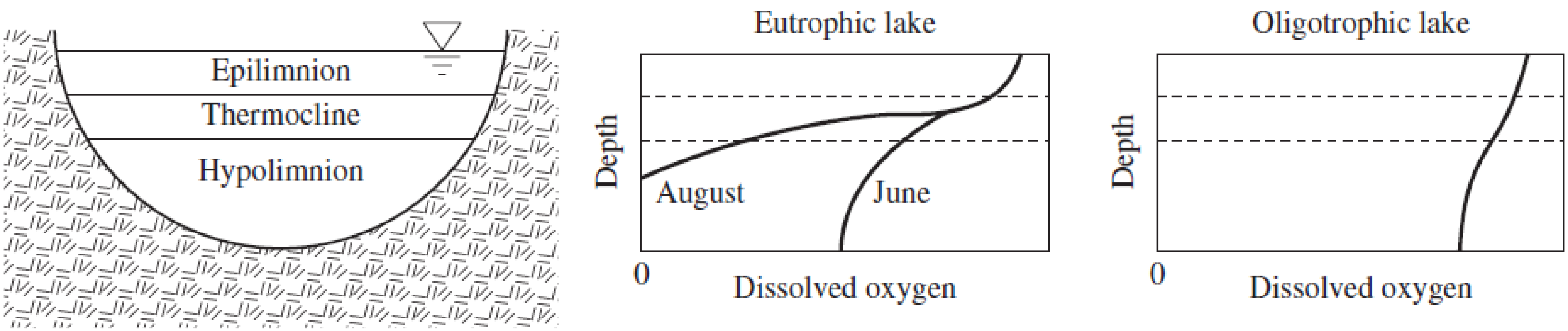
Thermal Stratification

- To get from summer temperature profile to the winter temperature profile (and vice versa), top layer must pass through a point when the temperature is 4℃ (denser, sinks and displaces bottom layer water which rises)

- This allows for periodic mixing (and nutrient recycling) in climates where it gets cold enough to freeze and/or warm enough to thaw.

- Due to thermal stratification, the warm and cold parts of the lake act independently

Thermal Stratification



- ***Epilimnion*** – (usually) upper warmer layer, uniform T, mixing is affected by waves and wind
- ***Hypolimnion*** – cold, lower layer
- Transition happens in the *thermocline/metalimnion*

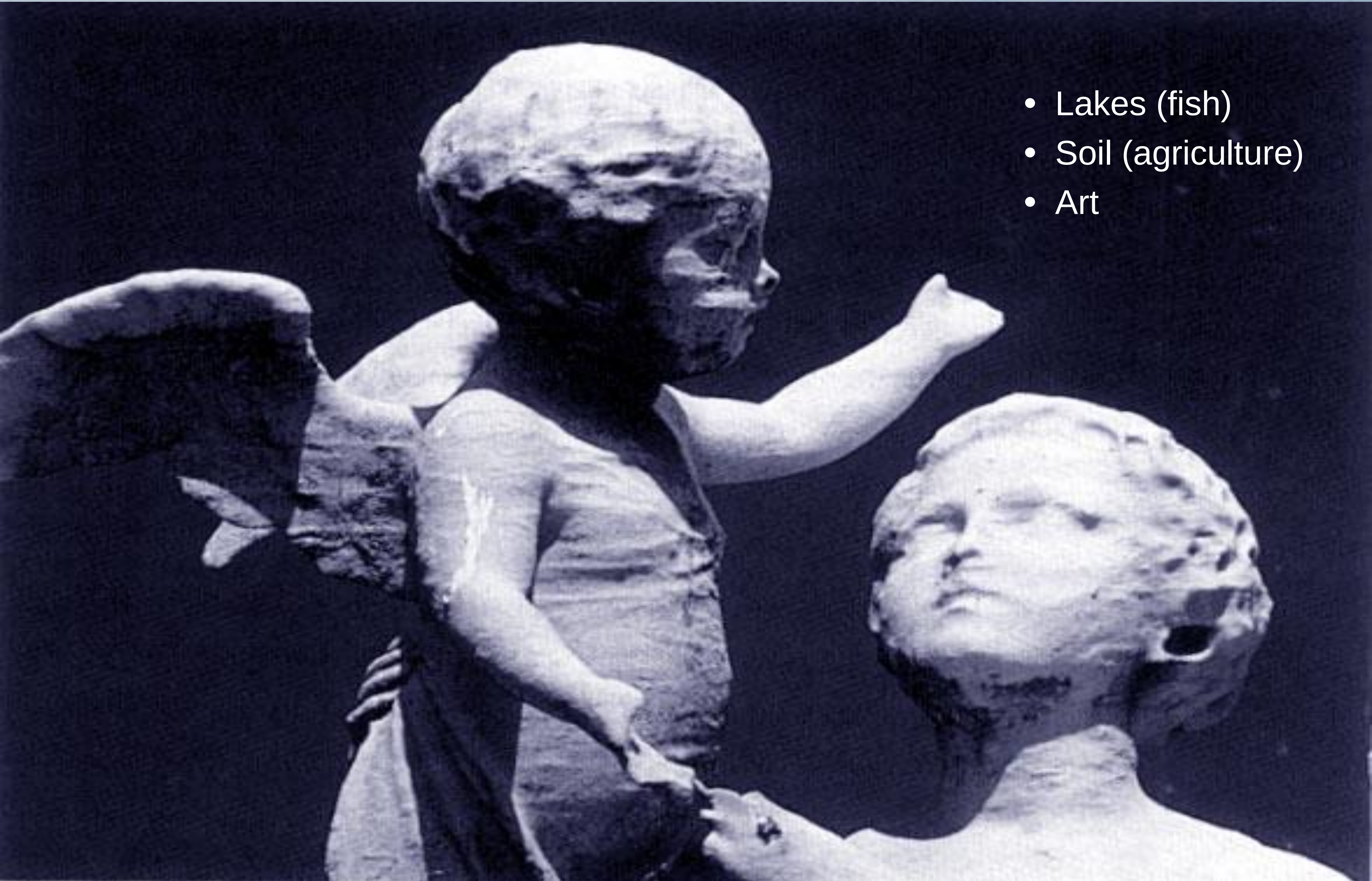
√ How does this stratification affect DO?

- For both eutrophic and oligotrophic lakes, warm upper layer (epilimnion) can get oxygen from reaeration and photosynthesis
- In the hypolimnion, DO only from photosynthesis, this may happen in a oligotrophic lake but unlikely in a eutrophic (turbid) lake

Acidification

- Rainwater in equilibrium with CO_2 has a pH of 5.5
- Northeastern US rain can have a pH < 4
- California fogs have pH around 3
- Low pH values primarily due to S and N oxide emissions (generate sulfuric and nitric acid)
- The term acid deposition includes both acid rain and the deposition of acid gases and particles
- Acid deposition effects
  - Materials : attacks marble, limestone as well as metals
  - Terrestrial ecosystems : stresses plants, hinders growth
  - Aquatic ecosystems : fish & aquatic life

Acid Rain



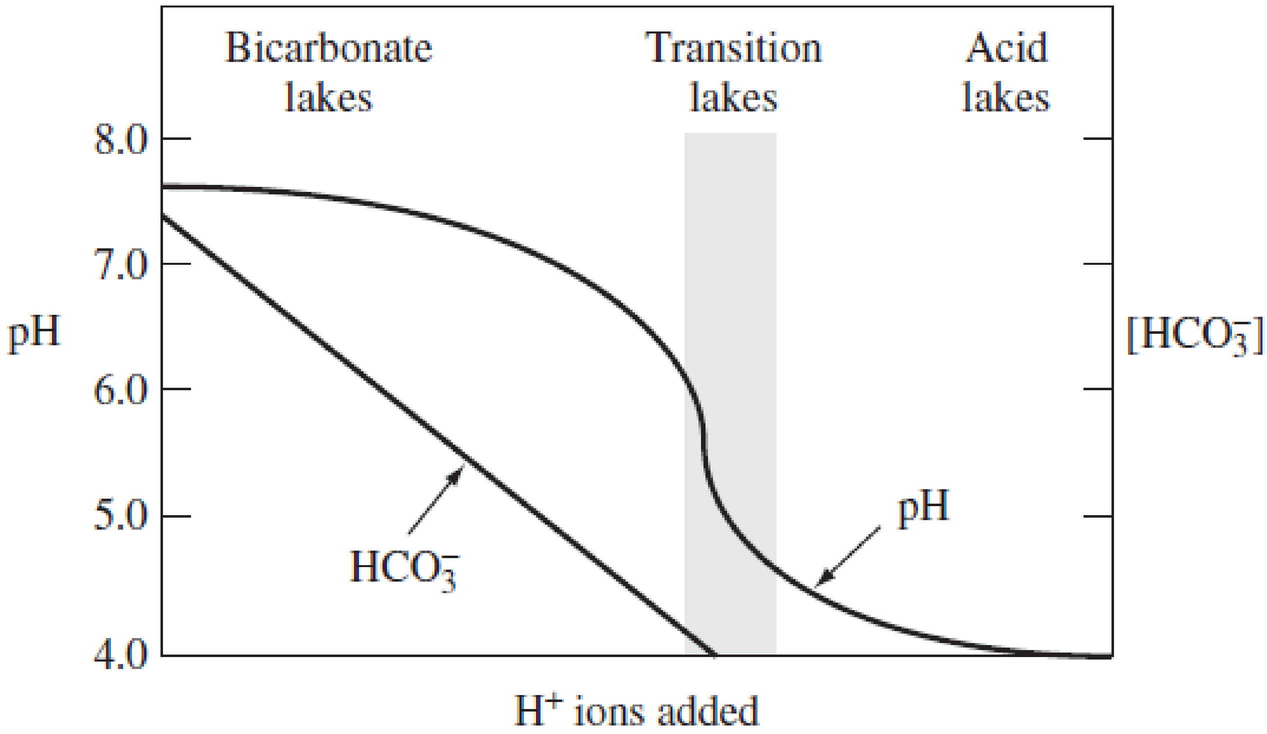
- Lakes (fish)
- Soil (agriculture)
- Art

Acid Rain and Lakes

- If the pH of a lake falls below 5.5, aquatic life becomes stressed.
- Few species will survive in a pH below 5.
- Some lakes have natural buffers or chemicals to neutralize the H^+
- Carbonates are important buffers: $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
- As H^+ is added to the aquatic system, carbonic acid is formed and pH does not change if there is an infinite source of bicarbonate (buffering).
- There is a documented correlation between the pH and the fish population
  - Bicarbonate lakes are well populated.
  - Many acidic lakes are barren.

Acid Rain and Lakes

- Bicarbonate buffering strongly resists acidification until pH drops below 6.3. As more H^+ ions are added, pH decreases rapidly after the point.



Acid Rain and Lakes

- What determines the bicarbonate concentration and vulnerability to acidification?
  - Soils, size of water body, vegetation and geography

- Soils are important because they are the source of limestone for buffering; lakes with calcareous soils (lots of limestone) are well neutralized

- Soils of nearby land are also important
  - If soils are thin and impermeable, the runoff will enter the water body with little contact between the precipitation and natural buffers

- Local vegetation can also affect acidification
  - Deciduous trees (loose leaves annually) tend to decrease acidity
  - Conifers (pine trees) tend to increase it

Acid Rain and Lakes

- Acidification also has effects on **heavy metal mobility.**
  - Metals dissolve as the pH drops

    e.g., Gibbsite

    $Al(OH)_3 + 3\,H^+ \leftrightarrow Al^{3+} + 3H_2O$

- Aluminum is toxic to fish, and even if the pH doesn't kill them the aluminum could.
  - Air pollution control is mitigating acid rain