

Environmental Water Quality BAE 452/552

Session 5 The Oxygen Problem

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Where are we?

Receiving Water Impacts:

- Physical, chemical, biological characteristics of water
- The oxygen problem ←
- Eutrophication
- Water quality criteria/standards
- Water quality monitoring

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Dissolved Oxygen in Natural Waters

The problem:

- Oxygen regime affected by waste discharges due to spring runoff from manure laden fields, high concentrations of biodegradable organics, combined sewer overflows (CSO)
- Secondary effects include nutrient enrichment and a sediment oxygen demand

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Dissolved Oxygen Standard

Oxygen content is most important for protecting fish and aquatic biota. Level of protection is classified into three groups:

- Prevention of fish-kills: < mg/L
- Active to specified degree: – mg/L
- Live, grow and reproduce: > mg/L

(these amounts vary for warm and cold water biota)

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Biochemical Oxygen Demand

- Content of biodegradable organics in waste discharges (from PS and NPS) is commonly expressed as the BOD.
- BOD reflects the Oxygen used to decompose organic materials into CO₂, H₂O, minerals, and organic nonbiodegradable residues.

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BOD₅ vs BOD_u

- Most waste is fully consumed after 20 – 30 days depending on nutrients available and temperature: Ultimate BOD (BOD_u)
- Standard methods often refer to the BOD after 5 days (BOD₅) as it was invented in London where the flow time to the open seas was never more than 5 days. (average temperature also was set long-term summer conditions: 18.3 °C)

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Oxygen Sinks

- Deoxygenation of biodegradable organics
- Sediment oxygen demand (SOD)
- Nitrification (ammonium to nitrate)
- Respiration (algae, plants)

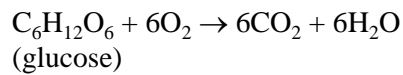
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Oxygen Sources

- Atmospheric re-aeration
- Photosynthesis (chlorophyll-containing organisms convert CO₂ or alkalinity of water into organic matter)

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Decomposition Reaction



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Reaction Kinetics

- Law of mass action: rate is proportional to the concentration of the reactants.

$$\frac{dc_A}{dt} = -kf(c_A, c_B)$$

Rate Law

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Reaction Kinetics

- Rate of reaction is proportional to product of a temperature-dependent constant k, and a function of the concentration of reactants f(c_A, c_B), determined experimentally

$$\frac{dc_A}{dt} = -kf(c_A, c_B)$$

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Reaction Kinetics

$$\frac{dc_A}{dt} = -kc_A^a c_B^b$$

- Powers in concentration function are called the 'reaction order' (often an integer)

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Reaction Kinetics

- Single reactant where n = 'order'

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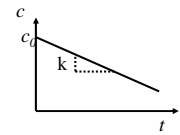
0th, 1st, and 2nd-order Reactions

- 0th order:

$$\frac{dc}{dt} = -k$$

k has units of
 $\text{M L}^{-3} \text{T}^{-1}$

If $c = c_0$ at $t = 0$:



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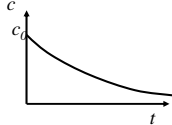
0th, 1st, and 2nd-order Reactions

- 1st order:

$$\frac{dc}{dt} = -kc$$

k has units of
 T^{-1}

If $c = c_0$ at $t = 0$:



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0th, 1st, and 2nd-order Reactions

- 2nd order:

$$\frac{dc}{dt} = -kc^2$$

k has units of
 $\text{L}^3 \text{M}^{-1} \text{T}^{-1}$

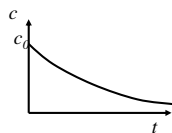
If $c = c_0$ at $t = 0$:

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0th, 1st, and 2nd-order Reactions

- In terms of $c(t)$:

$$c = c_0 \frac{1}{1 + kc_0 t}$$



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Differential Method

$$\frac{dc}{dt} = -kc^n$$

- Log transform:

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Stoichiometry

- How much of a reactant or product is consumed or created?
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Moles to grams conversion

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Stoichiometry

- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
- If a beaker contains 100 g m^{-3} as glucose or $100 \text{ g-glucose m}^{-3}$, how many moles of glucose:

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Stoichiometry

	Number of moles		Mass of one mole	
6 x C =	6	x	12 g	= 72 g
12 x H =	12	x	1 g	= 12 g
6 x O =	6	x	16 g	= 96 g
			Gram-molecular weight	= 180 g

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Stoichiometry

- Molar concentration:
 $100 \text{ g-glucose/m}^3$ (1 mole/180 g-glucose) =
 0.556 mole/m^3

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Stoichiometry

How many grams of carbon?

- Use of stoichiometric ratio of carbon to glucose:

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Stoichiometry

- How much O_2 consumed per 40 gC m^{-3} ?

r_{oc} = mass of oxygen consumed per carbon decomposed

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Temperature Effects

- Reaction rates are temperature dependent (about double for a rise of 10°C).
- Temperature dependence is described by the Arrhenius equation:

$$k(T_a) = Ae^{\frac{-E}{RT_a}}$$

where
 A = a pre-exponential factor
 E = activity energy (J mole⁻¹)
 R = the gas constant (8.314 J mole⁻¹K⁻¹)
 T_a = absolute temperature (K)

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Temperature Effects

- If we define the following constant:

$$\theta \equiv e^{\frac{E}{RT_1 T_2}}$$

- Then we can compare reaction rate constants at different temperatures (in °C):

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Temperature Effects

- In water quality, many reactions are reported at 20 °C:

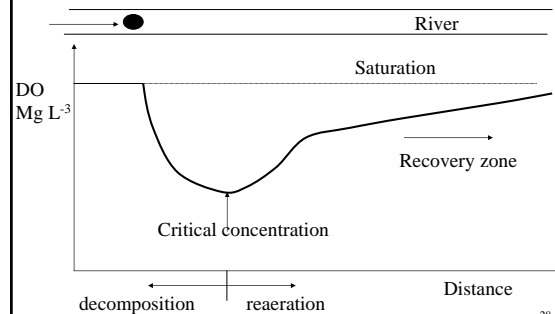
$$k(T) = k(20)\theta^{T-20}$$

θ values:

- 1.024 for oxygen reaeration
- 1.047 for BOD decomposition
- 1.066 for phytoplankton growth
- 1.08 for sediment oxygen demand

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Dissolved Oxygen Sag



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Experiment: closed bottle

- Strength of waste in discharge. Let's look at respiration/decomposition of life/death cycle in a closed-batch experiment:
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
respiration
- Place sugar and bacteria in bottle with initial O₂ content o₀, then close off

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Experiment: closed bottle

- Decomposition following 1st order reaction:

$$V \frac{dg}{dt} = -k_1 Vg \quad \begin{array}{l} g = \text{glucose conc. (mg-glucose L}^{-1}\text{)} \\ k_1 = \text{decomposition rate (d}^{-1}\text{)} \end{array}$$

- If the initial level of glucose is g₀, this equation can be solved for:

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Experiment: closed bottle

- Mass balance for O₂:

$$V \frac{do}{dt} = -r_{og} k_1 V g$$

$o = \text{oxygen conc. (mg-O L}^{-1}\text{)}$
 $r_{og} = \text{stoichiometric ratio}$
 $\text{O/glucose (mgO mg-glucose}^{-1}\text{)}$
 $k_1 = \text{decomposition rate (d}^{-1}\text{)}$

- Substituting the expression for g, and o₀:

$$o = o_0 - r_{og} g_0 (1 - e^{-k_1 t})$$

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Experiment: closed bottle

$$o = o_0 - r_{og} g_0 (1 - e^{-k_1 t})$$

- So, the concentration o in the bottle will reduce exponentially and asymptotically from an initial concentration o₀

$$o \rightarrow o_0 - r_{og} g_0$$

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BOD

- Waste discharge is more than glucose. So, the same bottle experiment with waste was adopted measuring how much oxygen was consumed: the BOD.
- A new variable, L (mgO L⁻¹), represents the amount of oxidizable organic matter remaining in the bottle expressed as oxygen equivalents.

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BOD

- Mass balance for L:

$$V \frac{dL}{dt} = -k_1 VL$$

- If the initial level is L₀, we obtain:

$$L = L_0 e^{-k_1 t}$$

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BOD

- Oxygen consumed: BOD = L₀ - L, or

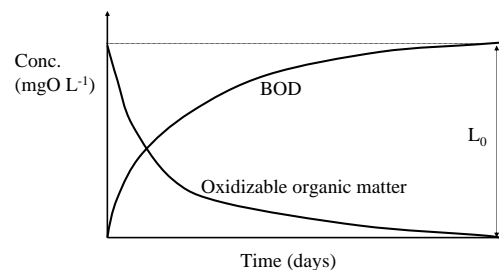
$$\text{BOD} = L_0 (1 - e^{-k_1 t})$$

where BOD is expressed as mgO L⁻¹

- L₀ can be the initial concentration of oxidizable organic matter, or ultimate BOD (BOD_u)

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BOD



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BOD

- Mass balance for O₂:

$$V \frac{do}{dt} = -k_1 V L_0 e^{-k_1 t}$$

- If original oxygen concentration is o₀:

$$o = o_0 - L_0(1 - e^{-k_1 t})$$

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BOD

$$o = o_0 - L_0(1 - e^{-k_1 t})$$

- So, the concentration o in the bottle will reduce exponentially and asymptotically from an initial concentration o₀

$$o \rightarrow o_0 - L_0$$

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BOD_u and BOD₅

$$BOD_t = BOD_u(1 - e^{-k_1 t})$$

- So, if the BOD₅ of a waste discharge is 250 mg L⁻¹, and k₁ is 0.46 d⁻¹:

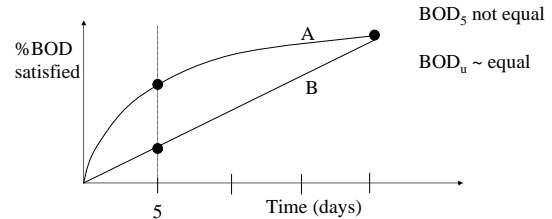
$$250 = BOD_u(1 - e^{-0.46 \times 5})$$

$$BOD_u = 250 / (1 - e^{-0.46 \times 5}) = 277.8 \text{ mg L}^{-1}$$

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BOD_u and BOD₅

- Without the k-value, BOD₅ not very useful:



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BOD_u and BOD₅

If BOD is measured daily, use Thomas method to find k and BOD_u:

$$\left(\frac{t}{BOD_t}\right)^{1/3} = (kBOD_u)^{1/3} + \left[\frac{k^{2/3}}{5.98(BOD_u)^{1/3}}\right]t$$

- Equation has form y = a + b x, so if plotted, should become a straight line where:

$$k = 5.98 (b/a), \text{ and } BOD_u = 1/(ka^3)$$

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BOD Model for a Stream

- Apply BOD equation to point source:

$$\frac{\partial L}{\partial t} = -U \frac{\partial L}{\partial x} - k_r L$$

k_r is total removal rate (d⁻¹), which is composed of both decomposition and settling:

$$k_r = k_d + k_s \text{ (note that } k_d = k_1 \text{ used before)}$$

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BOD Model for a Stream

$$k_s = \frac{v_s}{H}$$

where

v_s = BOD settling velocity (m d⁻¹)

H = water depth (m)

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BOD Model for a Stream

$$\frac{\partial L}{\partial t} = -U \frac{\partial L}{\partial x} - k_r L$$

L = amount of oxidizable organic matter (mgO L⁻¹)

k_r = total removal rate (d⁻¹)

U = mean velocity in the stream (Q = UA) (m d⁻¹)

T = time (d)

x = distance (m)

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BOD Model for a Stream

Assuming steady-state:

$$0 = -U \frac{dL}{dx} - k_r L$$

If we again use an initial concentration, L_0 , at the point of entry (assuming complete mixing):

$$L = L_0 e^{-\frac{k_r}{U} x}$$

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BOD Model for a Stream

L_0 can be calculated using a flow-weighted average of loading (w) and BOD discharge (r):

$$L_0 = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r}$$

where

Q = discharge (m³ d⁻¹)

L = oxidizable organic matter (mgO L⁻¹)

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BOD Model for a Stream

$$L = L_0 e^{-\frac{k_r}{U} x}$$

We can also determine the removal rate:

$$\ln(L) = \ln(L_0) - \frac{k_r}{U} x$$

A plot of ln(L) versus (x/U), travel time, should yield a straight line with a slope k_r

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Experiment: open bottle

- Mass balance for BOD and dissolved O₂:

$$V \frac{dL}{dt} = -k_d VL$$

$$V \frac{do}{dt} = -k_d VL + k_a V(o_s - o)$$

where k_a is reaeration rate (d⁻¹), o_s = saturation oxygen concentration (mgO L⁻³)

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Experiment: open bottle

- Reaeration constant is dependent on water velocity and depth (O'Connor-Dobbins formula):

$$k_a = 3.93 \frac{U^{0.5}}{H^{1.5}}$$

where

U = mean water velocity (m/s)

H = mean water depth (m)

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Experiment: open bottle

- We define the oxygen deficit D: $D = o_s - o$, and:

$$\frac{dD}{dt} = -\frac{do}{dt}$$

$$V \frac{dD}{dt} = k_d VL - k_a VD$$

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Experiment: open bottle

- If $L = L_0$ and $D = 0$, at $t = 0$:

$$L = L_0 e^{-k_d t}$$

$$D = \frac{k_d L_0}{k_a - k_d} (e^{-k_d t} - e^{-k_a t})$$

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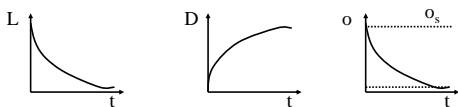
Experiment: closed & open bottle

- While in both the closed and open bottle, oxygen decreases, the difference is that in the open bottle, reaeration replenishes oxygen.

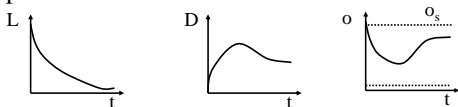
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Experiment: closed & open bottle

Closed bottle:



Open bottle:



BOD

Deficit

DO

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Oxygen Sag for Stream: PS

- For Point Source in a Stream at Steady State
- Mass balance:

$$0 = -U \frac{dL}{dx} - k_r L$$

and

$$0 = -U \frac{dD}{dx} + k_d L - k_a D$$

Remember that $k_r = k_d + k_s$!

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Oxygen Sag for Stream: PS

- If $L = L_0$ and $D = D_0$, at $x = 0$:

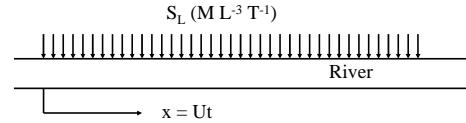
$$L = L_0 e^{-\frac{k_r}{U}x} \quad \text{Eqn. (A)}$$

$$D = D_0 e^{-\frac{k_a}{U}x} + \frac{k_d L_0}{k_a - k_r} \left(e^{-\frac{k_r}{U}x} - e^{-\frac{k_a}{U}x} \right)$$

↓ Reaeration
 ↓ BOD

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Oxygen Sag: Non-point Source



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Oxygen Sag: Non-point Source

- For Non-point Source in a Stream at Steady State:
- BOD mass balance for a no-flow source (0th order):

$$0 = -\frac{dL}{dx} - k_r L + S_L$$

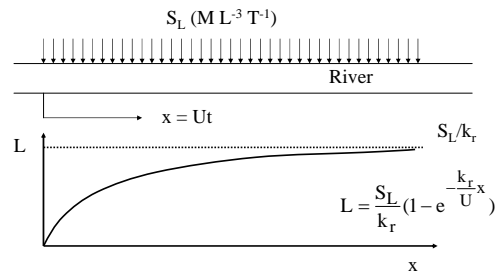
where S_L is the rate of the BOD distributed source ($\text{g m}^{-3} \text{d}^{-1}$)

For $D = 0$, at $x = 0$:

$$L = \frac{S_L}{k_r} \left(1 - e^{-\frac{k_r}{U}x} \right)$$

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Oxygen Sag: Non-point Source



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Oxygen Sag: Non-point Source

- For Non-point Source in a Stream at Steady State:
- Mass balance oxygen deficit for a no-flow source:

$$0 = -\frac{dD}{dx} - k_a D + k_d L$$

$$0 = -\frac{dD}{dx} - k_a D + \frac{k_d}{k_r} S_L \left(1 - e^{-\frac{k_r}{U}x} \right)$$

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Oxygen Sag: Non-point Source

- If $D = 0$, at $x = 0$: Eqn (B)

$$D = \frac{k_d S_L}{k_r k_a} \left(1 - e^{-\frac{k_a}{U}x} \right) - \frac{k_d S_L}{k_r (k_a - k_r)} \left(e^{-\frac{k_r}{U}x} - e^{-\frac{k_a}{U}x} \right)$$

'reaeration' term
BOD term

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Oxygen Sag: Non-point Source

Effects of plant and sediment oxygen demand:

$$0 = -\frac{dD}{dx} - k_a D - P + R + \frac{S_B}{H}$$

where

P and R = volumetric rates of plant photosynthesis and respiration ($\text{g m}^{-3} \text{d}^{-1}$)

S_B = areal rate of sediment O_2 demand ($\text{g m}^{-2} \text{d}^{-1}$)

H = mean water depth (m)

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Oxygen Sag: Non-point Source

For $D = 0$, at $x = 0$:

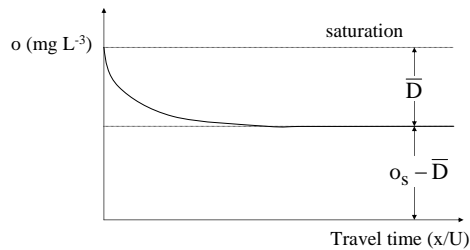
Eqn (C)

$$\bar{D} = \frac{-P + R + S_B/H}{k_a} \left(1 - e^{-\frac{k_a x}{U}}\right)$$

Thus, the deficit increases in a step-response fashion and asymptotically approaches a steady-state level \bar{D} , where the net deficit gain is balanced by reaeration losses.

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Oxygen Sag: Non-point Source



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Total Oxygen Sag

- The sum of point source and nonpoint source contributions makes up the total oxygen deficit:
- Eqn (A) + Eqn (B) + Eqn (C)
- This approach is also known as Streeter-Phelps (Thomann and Mueller, 1987)

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