

## FINAL EXAM

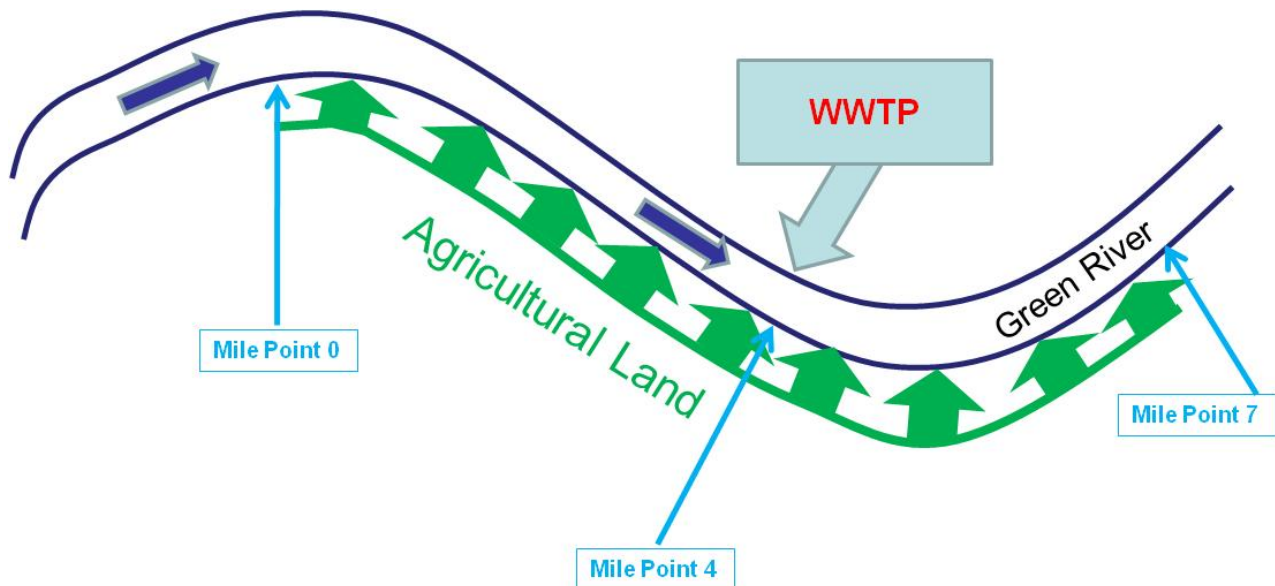
Closed book, 2 sheets of notes allowed.

Answer 2 of the following 3 questions. Please state any additional assumptions you made, and show all work.

1. (50%) The Snake River emerges from pristine headwaters and runs through an agricultural region. Four miles into this agricultural region is a municipal wastewater discharge (from the city of Lackawana). The BOD of the headwaters is 3 mg/L, and the dissolved oxygen is 8.2 mg/L (saturation is 9.1 mg/L for 20°C). Starting at mile point zero, there is a significant non-point agricultural runoff of BOD amounting to 35 kg/mile/day. At mile point 4 is the Lackawana WWTP outfall. Here a fully nitrified WW flow of 5 cfs is discharged with a CBOD of 30 mg/L and a DO of 6 mg/L. Immediately past this outfall is 3 more miles of agricultural land.

- A) Calculate the dissolved oxygen concentration immediately above the WWTP outfall (i.e. at MP 3.99999)**  
**B) Calculate the dissolved oxygen concentration immediately below the WWTP outfall (i.e. at MP 4.000001)**  
**C) Calculate the dissolved oxygen concentration at the end of the agricultural land (i.e. at MP 7)**

Assume complete mixing across the stream in cross section. Assume also a temperature of 20°C, a flow of 40 cfs from the headwaters and no incremental flow downstream except for flow from the WWTP. You may also assume an SOD downstream of the WWTP outfall of 1.5 g/m<sup>2</sup>/d.



Additional Information:

$$U = 0.200 \text{ ft/sec} = 3.27 \text{ miles/day}$$

$$DO_{\text{sat}} \text{ or } C_s = 9.1 \text{ mg/L (at } 20^\circ\text{C)}$$

$$\text{BOD deoxygenation rate (} k_N = k_d) = 0.8 \text{ day}^{-1} \text{ (at } 20^\circ\text{C)}$$

$$\text{CBOD settling rate (} k_s) = 0.080 \text{ day}^{-1} \text{ (at } 20^\circ\text{C)}$$

$$T = 20^\circ\text{C}$$

$$H = 6 \text{ ft} = 1.83 \text{ m}$$

$$\text{for } k_N \text{ and } k_d, \theta = 1.047$$

$$\text{for reareation, } \theta = 1.024$$

**A) Calculate the dissolved oxygen concentration immediately above the WWTP outfall (i.e. at MP 3.999999)**

Now the general form of the extended Streeter-Phelps equation is:

$$D = D_o e^{-k_a t} + \frac{k_d L_o}{k_a - k_r} (e^{-k_r t} - e^{-k_a t}) + \frac{k_d L_{NO}}{k_a - k_n} (e^{-k_n t} - e^{-k_a t}) + \frac{R - P + (S'_B/H)}{k_a} (1 - e^{-k_a t}) + \frac{k_d S_d}{k_r k_a} (1 - e^{-k_a t}) - \frac{k_d S_d}{k_r (k_a - k_r)} (e^{-k_r t} - e^{-k_a t}) + \frac{k_n S_{Nd}}{k_n k_a} (1 - e^{-k_a t}) - \frac{k_{nd} S_{Nd}}{k_n (k_a - k_n)} (e^{-k_n t} - e^{-k_a t})$$

And in this case without any NBOD or algal activity, this reduces to:

$$D = D_o e^{-k_a t} + \frac{k_d L_o}{k_a - k_r} (e^{-k_r t} - e^{-k_a t}) + \frac{(S'_B/H)}{k_a} (1 - e^{-k_a t}) + \frac{k_d S_d}{k_r k_a} (1 - e^{-k_a t}) - \frac{k_d S_d}{k_r (k_a - k_r)} (e^{-k_r t} - e^{-k_a t})$$

We are given the following:

$$k_d = 0.8 \text{ d}^{-1} \text{ @ } 20^\circ\text{C}$$

$$k_s = 0.08 \text{ d}^{-1} \text{ @ } 20^\circ\text{C}$$

$$H = 6 \text{ ft} = 1.83 \text{ m}$$

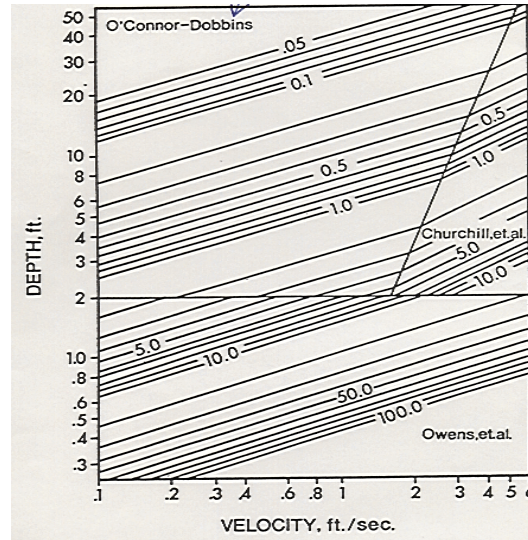
$$C_s = 9.1 \text{ mg/L}$$

$$U = 3.27 \text{ miles/day}$$

And since our design temperature is  $20^\circ\text{C}$ , there is no need for any temperature corrections

Now, begins the determination of the missing parameters

Reareation Constant:. Based on depth and velocity, it is appropriate to use the O'Connor Dobbins formula.



$$k_a = 12.9 \frac{(0.2)^{0.5}}{(6)^{1.5}} = 0.393d^{-1}$$

$$D = D_o e^{-0.393d^{-1}t} + \frac{k_d L_o}{0.393d^{-1} - k_r} (e^{-k_r t} - e^{-0.393d^{-1}t}) + \frac{(S'_B/H)}{0.393d^{-1}} (1 - e^{-0.393d^{-1}t}) + \frac{k_d S_d}{k_r 0.393d^{-1}} (1 - e^{-0.393d^{-1}t}) - \frac{k_d S_d}{k_r (0.393d^{-1} - k_r)} (e^{-k_r t} - e^{-0.393d^{-1}t})$$

And we might as well insert the given parameters too at this point

$$D = D_o e^{-0.393d^{-1}t} + \frac{0.8d^{-1}L_o}{0.393d^{-1} - k_r} (e^{-k_r t} - e^{-0.393d^{-1}t}) + \frac{(S'_B/1.83m)}{0.393d^{-1}} (1 - e^{-0.393d^{-1}t}) + \frac{0.8d^{-1}S_d}{k_r 0.393d^{-1}} (1 - e^{-0.393d^{-1}t}) - \frac{0.8d^{-1}S_d}{k_r (0.393d^{-1} - k_r)} (e^{-k_r t} - e^{-0.393d^{-1}t})$$

And now the overall CBOD loss rate is the sum of the deoxygenation rate and the settling rate, so:

$$k_r = k_d + k_s = 0.8 d^{-1} + 0.08 d^{-1} = \mathbf{0.88 d^{-1}} \quad @ 20^\circ\text{C}$$

The time of travel is equal to  $x/U$  or

$$t = x/U = 4 \text{ miles} / 3.27 \text{ miles/d} = \mathbf{1.222 d}$$

The areal non-point loading term is calculated from:

Cross sectional area ( $A_{cs} = Q/U = 40 \text{ cfs} / 3.27 \text{ mi/d}$ )

$$A_{cs} = \frac{40 \text{ ft}^3 \text{ s}^{-1}}{0.2 \text{ ft s}^{-1}} \left( \frac{m}{3.2808 \text{ ft}} \right)^2 = 18.58 \text{ m}^2$$

Now  $S_d$  is:

$$S_d = \frac{S}{A_{cs}} = \frac{35 \frac{Kg}{mi-d}}{18.58m^2} \left( \frac{mi}{5280ft} \right) \left( \frac{3.2808ft}{m} \right) \frac{1000g}{Kg} = \mathbf{1.1704 \frac{mg}{L-d}}$$

$$\begin{aligned} D = D_o e^{-0.393d^{-1}1.222d} + \frac{0.8d^{-1}L_o}{0.393d^{-1} - 0.88d^{-1}} (e^{-0.88d^{-1}1.222d} - e^{-0.393d^{-1}1.222d}) \\ + \frac{(S'_B/1.83m)}{0.393d^{-1}} (1 - e^{-0.393d^{-1}1.222d}) + \frac{0.8d^{-1}1.17 \frac{mg}{L-d}}{0.88d^{-1}0.393d^{-1}} (1 - e^{-0.393d^{-1}1.222d}) \\ - \frac{0.8d^{-1}1.17 \frac{mg}{L-d}}{0.88d^{-1}(0.393d^{-1} - 0.88d^{-1})} (e^{-0.88d^{-1}1.222d} - e^{-0.393d^{-1}1.222d}) \end{aligned}$$

Now all we need are the initial values for DO deficit and CBOD to solve. These are normally obtained from simple mass balances at the head of the reach, but since there was no upstream point source, these values are simple the upstream values as cited in the problem statement.

$$\begin{aligned} L_o = L_u = 3 \text{ mg/L} \quad (\text{note, I'm assuming that all CBOD values provided are "ultimate"}) \\ C_o = C_u = 8.2 \text{ mg/L} \end{aligned}$$

And therefore the deficit is:

$$D_o = C_s - C_o = 9.1 \text{ mg/L} - 8.2 \text{ mg/L} = 0.9 \text{ mg/L}$$

Now substituting in:

$$\begin{aligned} D = 0.9 \frac{mg}{L} e^{-0.393d^{-1}1.222d} + \frac{0.8d^{-1}3 \frac{mg}{L}}{0.393d^{-1} - 0.88d^{-1}} (e^{-0.88d^{-1}1.222d} - e^{-0.393d^{-1}1.222d}) \\ + \frac{(S'_B/1.83m)}{0.393d^{-1}} (1 - e^{-0.393d^{-1}1.222d}) + \frac{0.8d^{-1}1.17 \frac{mg}{L-d}}{0.88d^{-1}0.393d^{-1}} (1 - e^{-0.393d^{-1}1.222d}) \\ - \frac{0.8d^{-1}1.17 \frac{mg}{L-d}}{0.88d^{-1}(0.393d^{-1} - 0.88d^{-1})} (e^{-0.88d^{-1}1.222d} - e^{-0.393d^{-1}1.222d}) \end{aligned}$$

And recognizing that we don't have any SOD in this upstream region:

$$\begin{aligned} D = 0.9 \frac{mg}{L} e^{-0.393d^{-1}1.222d} + \frac{0.8d^{-1}3 \frac{mg}{L}}{0.393d^{-1} - 0.88d^{-1}} (e^{-0.88d^{-1}1.222d} - e^{-0.393d^{-1}1.222d}) \\ + \frac{0.8d^{-1}1.17 \frac{mg}{L-d}}{0.88d^{-1}0.393d^{-1}} (1 - e^{-0.393d^{-1}1.222d}) \\ - \frac{0.8d^{-1}1.17 \frac{mg}{L-d}}{0.88d^{-1}(0.393d^{-1} - 0.88d^{-1})} (e^{-0.88d^{-1}1.222d} - e^{-0.393d^{-1}1.222d}) \\ D = 0.557 \frac{mg}{L} + 1.368 \frac{mg}{L} + 1.033 \frac{mg}{L} - 0.606 \frac{mg}{L} = 2.35 \frac{mg}{L} \end{aligned}$$

$$\mathbf{C = C_s - D = 6.75 \text{ mg/L}}$$

**B) Calculate the dissolved oxygen concentration immediately below the WWTP outfall (i.e. at MP 4.000001)**

To calculate this value, we simply need a mass balance around the mixing point at the WWTP outfall.

$$C = \frac{Q_u C_u + Q_{ww} C_{ww}}{Q_u + Q_{ww}} = \frac{40 \frac{ft^3}{s} 6.7486 \frac{mg}{L} + 5 \frac{ft^3}{s} 6.0 \frac{mg}{L}}{40 \frac{ft^3}{s} + 5 \frac{ft^3}{s}} = 6.6654 \frac{mg}{L}$$

So:

$$C = 6.67 \text{ mg/L}$$

**C) Calculate the dissolved oxygen concentration at the end of the agricultural land (i.e. at MP 7)**

Now we use the same equations as in part “A”, but this time with new initial values and a non-zero SOD.

SOD: Recall that  $S'_B$  is given as  $1.5 \text{ g/m}^2/\text{d}$

And the initial deficit is simply from the saturation value and the answer in part B

$$D_o = C_s - C_o = 9.1 \text{ mg/L} - 6.665 \text{ mg/L} = 2.435 \text{ mg/L}$$

And finally, the initial CBOD is from a similar mass balance, but we first have to calculate the BOD at the end of the first reach. This is done with the BOD model including non-point sources:

$$L = L_o e^{-k_r t} + \frac{S_d}{k_r} (1 - e^{-k_r t})$$

$$L = 3 \frac{mg}{L} e^{-0.88 d^{-1} 1.222 d} + \frac{1.17 \frac{mg}{L-d}}{0.88 d^{-1}} (1 - e^{-0.88 d^{-1} 1.222 d}) = 1.0233 \frac{mg}{L} + 0.8763 \frac{mg}{L} = 1.90 \frac{mg}{L}$$

And the mass balance is:

$$L = \frac{Q_u L_u + Q_{ww} L_{ww}}{Q_u + Q_{ww}} = \frac{40 \frac{ft^3}{s} 1.90 \frac{mg}{L} + 5 \frac{ft^3}{s} 30 \frac{mg}{L}}{40 \frac{ft^3}{s} + 5 \frac{ft^3}{s}} = 5.022 \frac{mg}{L}$$

Finally the new time of travel is:

$$t = x/U = 3 \text{ miles} / 3.27 \text{ miles/d} = 0.9166 \text{ d}$$

So now we can plug these values into the Streeter-Phelps equation:

$$D = 2.435 \frac{mg}{L} e^{-0.393d^{-1} \cdot 0.9166d} + \frac{0.8d^{-1} 5.022 \frac{mg}{L}}{0.393d^{-1} - 0.88d^{-1}} (e^{-0.88d^{-1} \cdot 0.9166d} - e^{-0.393d^{-1} \cdot 0.9166d})$$

$$+ \frac{(1.5 \frac{g}{m^2-d} / 1.83m)}{0.393d^{-1}} (1 - e^{-0.393d^{-1} \cdot 0.9166d})$$

$$+ \frac{0.8d^{-1} 1.17 \frac{mg}{L-d}}{0.88d^{-1} - 0.393d^{-1}} (1 - e^{-0.393d^{-1} \cdot 0.9166d})$$

$$- \frac{0.8d^{-1} 1.17 \frac{mg}{L-d}}{0.88d^{-1} (0.393d^{-1} - 0.88d^{-1})} (e^{-0.88d^{-1} \cdot 0.9166d} - e^{-0.393d^{-1} \cdot 0.9166d})$$

$$D = 1.70 \frac{mg}{L} + 2.07 \frac{mg}{L} + 0.631 \frac{mg}{L} + 0.73 \frac{mg}{L} - 0.49 \frac{mg}{L} = 4.64 \frac{mg}{L}$$

$$C = C_s - D = 4.46 \text{ mg/L}$$

2. (50%) The Mill river parallels an interstate highway. Methyl t-Butyl Ether (MtBE), a constituent of gasoline, enters the river through runoff from the pavement (see table of MtBE properties from previous problem). This runoff enters the river at two points via storm overflows. These are located 33.2 Km and 15.8 Km upstream of the river's eventual discharge into the Monongahopla river. Assume that these two are the only significant sources of MtBE and that they can be represented by a characteristic incremental drainage area (750 ha for the most upstream discharge, and 1550 ha for the other). You may also assume an MtBE export coefficient for these drainage areas of 10 g/ha/yr.

- A. What is the expected concentration of MtBE at the end of the Mill River (i.e., confluence with the Monongahopla) under average flow conditions?**  
**B. What percentage of MtBE loss is due to volatilization?**

Assume that particulate forms of this compound biodegrade at 0.02 d<sup>-1</sup> as opposed to 0.001 d<sup>-1</sup> for the dissolved form. (universal gas constant, R=8.206x10<sup>-5</sup> atm m<sup>3</sup>/°K mole).

Characteristics of Mill River

Characteristic	Value
Mean Width	20 m
Average Flow	50,000 m <sup>3</sup> /day
Mean Depth	1 m
Mean Wind Speed	2.5 m/sec
Solids Settling Rate	0.2 m/d
Solids Burial Rate	0.000027 m/d
Sediment:Water Diffusive Exchange Rate	0.01 m/d
Water Column Suspended Solids	2.2 mg/L
Mixed Sediments Suspended Solids	12,000 mg/L
Thickness of Mixed Sediments	0.2 meters

Fraction of Organic Carbon in Solids	0.2
Density of Suspended Solids	1.55 g/mL

*Selected Physical and Chemical Properties of MtBE*

Property	Value	Special Conditions	Reference
Molecular Weight	88.15		
Melting Point	-109°C		Weast, 2000
Boiling Point	55.2°C		Weast, 2000
Density	0.7405 g/mL	20°C	Weast, 2000
Aqueous Solubility	4-5%	20°C	Gilbert & Calabrese, 1992
Log K <sub>ow</sub>	1.05		Gilbert & Calabrese, 1992
Vapor Pressure	2.45x10 <sup>+2</sup> mm Hg	20°C	Merck, 2000
Henry's Law Constant	5.87x10 <sup>-4</sup> atm-m <sup>3</sup> /mol		HSDB, 1994
Log K <sub>oc</sub>	2.7		Davidson et al., 1980
Diffusivity in Water	4 x 10 <sup>-6</sup> cm <sup>2</sup> /s		Estimated
Biodegradation Rate	0.001 d <sup>-1</sup>	Dissolved	Estimated
Photolysis Rate	0.0041 d <sup>-1</sup>		Estimated
Hydrolysis Rate	0.0071 d <sup>-1</sup>	25°C, neutral only	Estimated

**A. What is the expected concentration of MtBE at the end of the Mill River (i.e., confluence with the Monongahoopla) under average flow conditions?**

Properties of M tBE

M W =	88.15	
Log (Kow)=	1.05	
He=	0.000587	atm m <sup>3</sup> /m <sup>3</sup> ole
KB=	0.001	/d (diss)
KH=	0.0071	/d
KP=	0.0041	/d
D <sub>l</sub> =	0.000004	cm <sup>2</sup> /sec
W Q S=	10	ug/L
		0.02 /d (part)

Characteristics of Mill River

Q =	50000	cu meters/day	
H 1=	1	m =	3.280839895 ft
Mean Width	20	m	
U w=	2.5	m /sec	wind sp.
vs=	0.2	m /d	
vd= vb=	0.000027	m /d	(burial)
m 1=	2.2	mg/L	
m 2=	12000	mg/L	vu= (vr) 9.67E-06 m /d
H 2=	0.2	m	
Den=	1.55	g/m L	
foc=	0.2		
Tem p =	25	deg-C	
K f=vd	0.01	m /d	(diffusion)
Area =	20	m <sup>2</sup>	215.2782083 ft <sup>2</sup>
U =	2500	m /d =	0.09493171 ft/s watersp.

Loading Characteristics

runoff	First	Second	
Length	17.4	15.8	km
Ec=	10	10	g/ha/yr
DA=	750	1550	ha
W =DA *Ec=	7500	15500	g/yr
W =DA *Ec=	20.533881	42.43669	g/d
C o =	0.0004107	0.000849	mg/L



1. Determine Volatilization Rate

- Liquid Film Resistance (lake)
  - $K_L = 0.0017 * D^{1/4} * U_w = 1.7E-08 \text{ m/s} = 0.001469 \text{ m/d}$
- Liquid Film Resistance (river)
  - $K_a = 1.9 * U^{**0.5} / H^{**1.5} = 0.668833174 \text{ /d}$
  - $K_L = (32 / MW) ** 0.25 * K_a * H = 0.519158204 \text{ m/d}$
- Gas Film Resistance
  - $K_g = 168 * ((18 / MW) ** 0.25) * U_w = 282.3331265 \text{ m/d}$
- Dimensionless Henry's Law Const
  - $H_e = H_e / R T = 0.024004$
- Overall Volatilization Rate
  - $V_v = K_L * H_e / (H_e + R * (K_L / K_g)) = 0.482218657 \text{ m/d} = 5.58123E-06 \text{ m/s}$

2. Determination of Particulate/Dissolved Fractions

- Partition Coefficient
  - $K_d = 6.17 * 10^{-7} * f_{oc} * K_{ow} = 0.00000 \text{ L/mg} = 0.001385 \text{ L/g}$
- Porosity in Mixed Sediments
  - $\phi = 1 - (m_2 / \text{density}) = 0.992258$
- Porosity Corrected Partition Coeff for Mixed Sediments
  - $P_2 = P / \phi = 0.00 \text{ L/g}$
- Dissolved Fractions
  - $f_{d1} = 1 / (1 + P * m_1) = 0.999997$
  - $f_{d2} = 1 / (1 + P_2 * m_2) = 0.983531$
- Particulate Fractions
  - $f_{p1} = 1 - f_{d1} = 3.05E-06$
  - $f_{p2} = 1 - f_{d2} = 0.016469$

3. Determination of Water Column Decay Rate

- $k_{d1} = K_P + K_H + K_B (\text{diss}) = 0.0122 \text{ /day} = \text{photo} \quad \text{hydr} \quad \text{biodegr}$
- $k_{p1} = K_H + K_B (\text{part}) = 0.0271 \text{ /day} = 0.0041 \quad 0.0071 \quad 0.001$
- $k_{T1} = k_{d1} * f_{d1} + k_{p1} * f_{p1} = 0.012200045 \text{ /day}$

4. Determination of the Mixed Sediment Decay Rate

$$\begin{aligned} k_{d2} &= K_H + K_B \text{ (diss)} = 0.0081 \text{ /day} \\ k_{p2} &= K_H + K_B \text{ (part)} = 0.0271 \text{ /day} \\ k_{T2} &= k_{d2} \cdot f_{d2} + k_{p2} \cdot f_{p2} = 0.008412906 \text{ /day} \end{aligned}$$

5. Determine Sediment Feed Back Ratio

$$F_r' = 0.8520427 \quad F_r' = \frac{v_r + v_d F_{d2}}{v_r + v_b + v_d F_{d2} + k_2 H_2}$$

6. Determine Total Loss Velocity

$$\begin{aligned} v_T &= 0.4944213 \text{ m/d} = \begin{matrix} \text{internal} & \text{volatile} & \text{sediment} \\ 0.012200045 & 0.482217 & 4.08497E-06 \end{matrix} \\ v_T &= k_1 H_1 + v_v f_{d1} + (v_s f_{p1} + v_d f_{d1})(1 - F_r') \end{aligned}$$

7. Determine the Total Loss Rate

$$K_T = 0.4944213 \text{ /d} \quad K_T = \frac{v_T}{H_1}$$

8. Determine concentration of 1st reach

$$C = 1.315E-05 \text{ mg/L} \quad C_1 = C_{10} e^{-\frac{K_T x}{U}}$$

9. Determine concentration of 2nd reach

$$C = 3.788E-05 \text{ mg/L} \text{ answer to a} \quad C_1 = C_{10} e^{-\frac{K_T x}{U}}$$

**B. What percentage of MtBE loss is due to volatilization?**

10. Percent loss due to volatilization

$$v_v/v_T = 97.53\% \text{ answer to b}$$

3. (50%) On a separate sheet of paper, answer any five (5) of the following questions.

- A. Describe and contrast one mechanistic and one empirical approach to modeling THM precursors in surface waters.
- B. Explain what the light and dark bottle method measures and how it works

Important to mention that: Light bottles support photosynthesis, algal respiration and bacterial respiration (CBOD deox). Dark bottles support only the second and third. The third can be isolated by means of a classical BOD test.

- C. Describe the factors that determine gas transfer of toxics in rivers, and contrast this with the factors that determine gas transfer in lakes. In your description, relate micro-scale processes (molecules) to macro-scale (bulk water or air)
- D. Describe how you might model the impact of a seasonal load (e.g., canning operation) on two lakes in series when the direct loading is occurring to each lake.

Important to mention that: seasonal loadings are often well described by sinusoidal loads. Also it would be necessary to have separate loads and terms for each lake. The downstream lake would have a term for the impact of the load on the upstream lake.

- E. Describe the various steps involved in photolysis of toxics in surface waters. Include some discussion on how these steps are modeled.

Important to mention that:

There are at least 4 steps

- Light from the sun reaches the water surface (solar constant, reflectivity, cloud cover)
- Light penetrates the water to various depths (light extinction)
- Light is absorbed by the solute (absorptivity)
- Absorbed light energy will cause bond breakage (quantum yield)

Also there are direct and indirect or sensitized types of photolysis

- F. Discuss the ultimate fate of PCBs in the Great Lakes. Where do they end up, and why?

PCBs are poorly degraded aerobically. They adsorb to sediments, but they are even more susceptible to volatilization. Because of this tendency, they escape to the atmosphere and may re-condense in parts of the world that are especially cold with low Henry's law constants.

- G. Describe why sorption of many trace organic compounds has been found to be poorly described by conventional sorption models (simple hydrophobic partitioning) in surface waters.

Organic matter that coats particles is a complex mixture of compounds that cannot be uniformly and easily characterized. Some types of organic matter (especially black carbon) may be very strong adsorbents. Some particles are also affected and changed by the adsorption process (i.e., they do not simply act as partitioning agents, and do not conform to simple isotherm laws).

- H. Why does the Streeter-Phelps equation sometimes predict negative concentrations of dissolved oxygen, despite the fact that this is physically impossible? How can one correct this problem?

When the rate of DO consumption is high for a long period of time, the DO concentration can drop to zero. At that point it becomes anaerobic until which time the rate of deoxygenation drops below the rate of reaeration. However the streeter-phelps equation allows it to continue to drop into the negative range; something that doesn't actually occur in nature.