## 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 Green 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 Millstone).  The BOD of the headwaters is 1.8 mg/L, and the dissolved oxygen is 8.2 mg/L (saturation is 9.1 mg/L for $20^{o}$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 Millstone 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 3.999999)**
   **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 $20^{o}$C, a flow of 40 cfs from the headwaters and no incremental flow downstream except for flow from the Millstone WWTP.  Many years of discharge has resulted in a very high SOD immediately downstream of the WWTP outfall of 5 g/m$^2$/d for the first mile (i.e., up to MP 5).  After this, you can assume that it decreases to a fixed value of 0.5 g/m$^2$/d.
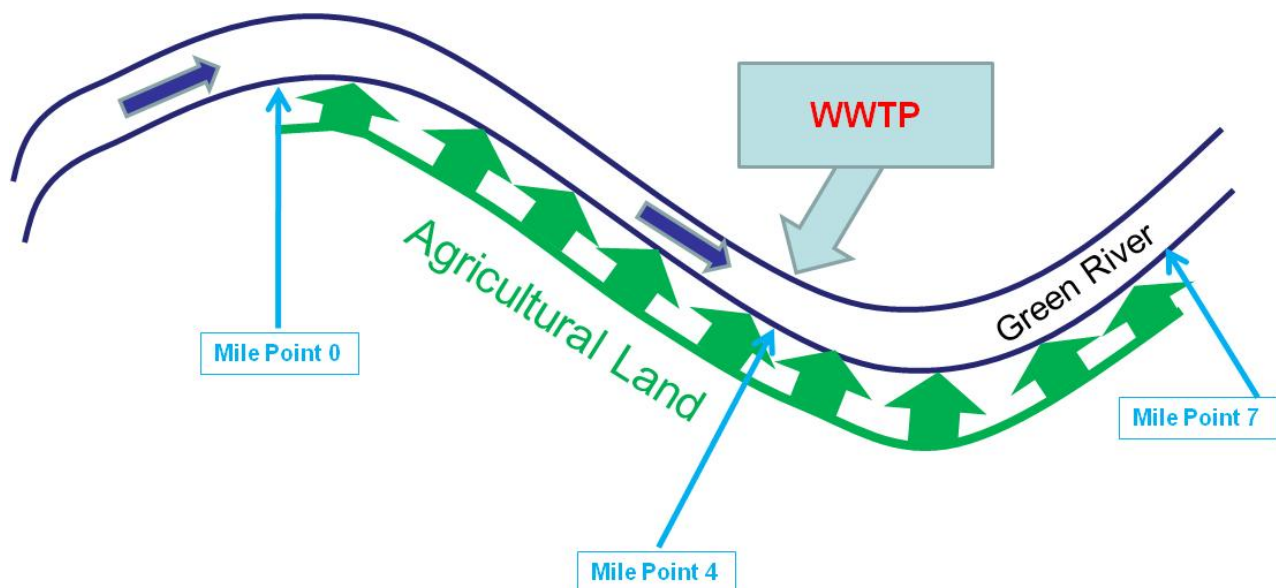
Additional Information:

| U = 0.200 ft/sec = 3.27 miles/day | T = 20$^{\circ}$C |
|---|---|
| DO$_{sat}$ or C$_S$ = 9.1 mg/L (at 20$^{\circ}$C) | H = 4 ft  = 1.22 m |
| BOD deoxygenation rate (k$_N$ = k$_d$) = 0.8 day$^{-1}$  (at 20$^{\circ}$C) | for k$_N$ and k$_d$, θ=1.047 |
| CBOD settling rate (k$_S$) = 0.080 day$^{-1}$      (at 20$^{\circ}$C) | for reareation, θ=1.024 |

### A) <u>Calculate the dissolved oxygen concentration immediately above the WWTP outfall (i.e. at MP 3.999999)</u>

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:

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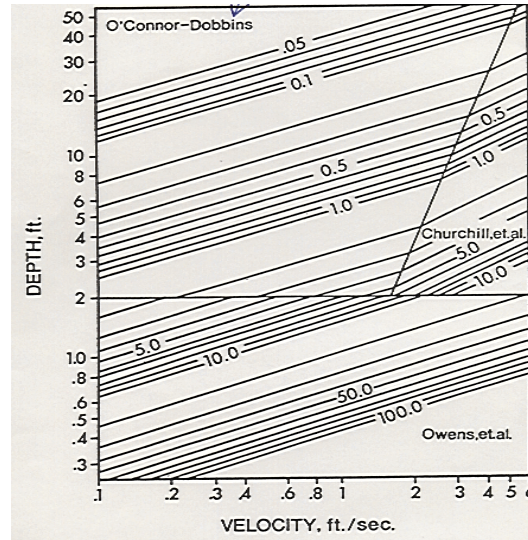$$- \frac{k_d S_d}{k_r(k_a - k_r)}(e^{-k_r t} - e^{-k_a t})$$

We are given the following:
    k$_d$ = 0.8 d$^{-1}$   @ 20°C
    k$_s$ = 0.08 d$^{-1}$   @ 20°C
    H = 6 ft = 1.83 m
    C$_s$ = 9.1 mg/L
    U = 3.27 miles/day

And since our design temperature is 20°C, there is no need for any temperature corrections

Now, begins the determination of the missing parameters

<u>Rearation Constant</u>:. Based on depth and velocity, it is appropriate to use the O'Connor Dobbins formula.

$$k_a = 12.9 \frac{(0.2)^{0.5}}{(4)^{1.5}} = 0.721 d^{-1}$$

$$D = D_o e^{-0.721d^{-1}t} + \frac{k_d L_o}{0.721d^{-1} - k_r}\left(e^{-k_r t} - e^{-0.721d^{-1}t}\right) + \frac{(S'_B/H)}{0.721d^{-1}}\left(1 - e^{-0.721d^{-1}t}\right)$$
$$+ \frac{k_d S_d}{k_r 0.721d^{-1}}\left(1 - e^{-0.721d^{-1}t}\right) - \frac{k_d S_d}{k_r(0.721d^{-1} - k_r)}\left(e^{-k_r t} - e^{-0.721d^{-1}t}\right)$$

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

$$D = D_o e^{-0.721d^{-1}t} + \frac{0.8d^{-1}L_o}{0.721d^{-1} - k_r}\left(e^{-k_r t} - e^{-0.721d^{-1}t}\right) + \frac{(S'_B/1.83m)}{0.721d^{-1}}\left(1 - e^{-0.721d^{-1}t}\right)$$
$$+ \frac{0.8d^{-1}S_d}{k_r 0.721d^{-1}}\left(1 - e^{-0.721d^{-1}t}\right) - \frac{0.8d^{-1}S_d}{k_r(0.721d^{-1} - k_r)}\left(e^{-k_r t} - e^{-0.721d^{-1}t}\right)$$

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

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

The <u>time of travel</u> is equal to x/U or

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

The <u>areal non-point loading</u> term is calculated from:

Cross sectional area (Acs = Q/U = 40 cfs / 3.27 mi/d)

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

Now $S_d$ is:

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

$$D = D_o e^{-0.721d^{-1}1.222d} + \frac{0.8d^{-1}L_o}{0.721d^{-1} - 0.88d^{-1}}\left(e^{-0.88d^{-1}1.222d} - e^{-0.721d^{-1}1.222d}\right)$$
$$+ \frac{(S_B'/1.83m)}{0.721d^{-1}}\left(1 - e^{-0.721d^{-1}1.222d}\right) + \frac{0.8d^{-1}1.17\frac{mg}{L-d}}{0.88d^{-1}0.721d^{-1}}\left(1 - e^{-0.721d^{-1}1.222d}\right)$$
$$- \frac{0.8d^{-1}1.17\frac{mg}{L-d}}{0.88d^{-1}(0.721d^{-1} - 0.88d^{-1})}\left(e^{-0.88d^{-1}1.222d} - e^{-0.721d^{-1}1.222d}\right)$$

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 souce, these values are simple the upstream values as cited in the problem statement.

$L_o = L_u = 1.8$ mg/L   (note, I'm assuming that all CBOD values provided are "ultimate")
$C_o = C_u = 8.2$ mg/L

And therefore the deficit is:

$D_o = C_s - C_o = 9.1$mg/L – 8.2 mg/L = 0.9 mg/L

Now substituting in:

$$D = 0.9\frac{mg}{L}e^{-0.721d^{-1}1.222d} + \frac{0.8d^{-1}1.8\frac{mg}{L}}{0.721d^{-1} - 0.88d^{-1}}\left(e^{-0.88d^{-1}1.222d} - e^{-0.721d^{-1}1.222d}\right)$$
$$+ \frac{(S_B'/1.83m)}{0.721d^{-1}}\left(1 - e^{-0.721d^{-1}1.222d}\right) + \frac{0.8d^{-1}1.17\frac{mg}{L-d}}{0.88d^{-1}0.721d^{-1}}\left(1 - e^{-0.721d^{-1}1.222d}\right)$$
$$- \frac{0.8d^{-1}1.17\frac{mg}{L-d}}{0.88d^{-1}(0.721d^{-1} - 0.88d^{-1})}\left(e^{-0.88d^{-1}1.222d} - e^{-0.721d^{-1}1.222d}\right)$$

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

$$D = 0.9\frac{mg}{L}e^{-0.721d^{-1}1.222d} + \frac{0.8d^{-1}1.8\frac{mg}{L}}{0.721d^{-1} - 0.88d^{-1}}\left(e^{-0.88d^{-1}1.222d} - e^{-0.721d^{-1}1.222d}\right)$$
$$+ \frac{0.8d^{-1}1.17\frac{mg}{L-d}}{0.88d^{-1}0.721d^{-1}}\left(1 - e^{-0.721d^{-1}1.222d}\right)$$
$$- \frac{0.8d^{-1}1.17\frac{mg}{L-d}}{0.88d^{-1}(0.721d^{-1} - 0.88d^{-1})}\left(e^{-0.88d^{-1}1.222d} - e^{-0.721d^{-1}1.222d}\right)$$

$$D = 0.3728\frac{mg}{L} + 0.6626\frac{mg}{L} + 0.8643\frac{mg}{L} - 0.4896\frac{mg}{L} = 1.41\frac{mg}{L}$$

$$C = C_s\text{-}D = 9.1\text{-}1.41 = 7.69 \text{ mg/L}$$

**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.

$$C = \frac{Q_u C_u + Q_{ww} C_{ww}}{Q_u + Q_{ww}} = \frac{40\frac{ft^3}{s}7.69\frac{mg}{L} + 5\frac{ft^3}{s}6.0\frac{mg}{L} +}{40\frac{ft^3}{s} + 5\frac{ft^3}{s}} = 7.502\frac{mg}{L}$$

So:

$$C = 7.50 \text{ mg/L}$$

**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. In addition, we must break this reach into two separate ones as the SOD is higher between MP 4 and 5 than it is between MP 5 and 7.

SOD: Recall that S'$_B$ is given as 5 g/m$^2$/d for the first mile downstream of the WWTP

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

$$D_o = C_s - C_o = 9.1\text{mg/L} - 7.50 \text{ mg/L} = 1.60 \text{ mg/L}$$

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:

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

$$L = 1.8\frac{mg}{L}e^{-0.88d^{-1}1.222d} + \frac{1.17\frac{mg}{L-d}}{0.88d^{-1}}(1 - e^{-0.88d^{-1}1.222d}) = 0.614\frac{mg}{L} + 0.8763\frac{mg}{L} = 1.49\frac{mg}{L}$$

And the mass balance is:

$$L = \frac{Q_u L_u + Q_{ww} L_{ww}}{Q_u + Q_{ww}} = \frac{40\frac{ft^3}{s}1.49\frac{mg}{L} + 5\frac{ft^3}{s}30\frac{mg}{L} +}{40\frac{ft^3}{s} + 5\frac{ft^3}{s}} = 4.658\frac{mg}{L}$$

Likewise for the deficit

$$D = \frac{Q_u D_u + Q_{ww} D_{ww}}{Q_u + Q_{ww}} = \frac{40\frac{ft^3}{s}1.41\frac{mg}{L} + 5\frac{ft^3}{s}3.1\frac{mg}{L} +}{40\frac{ft^3}{s} + 5\frac{ft^3}{s}} = 1.598\frac{mg}{L}$$

With the higher flow, and a fixed depth and velocity, we have a larger width and need to re-determine $S_d$ :

$$S_d = \frac{S}{A_{cs}} = \frac{35\frac{Kg}{mi-d}}{20.90m^2}\left(\frac{mi}{5280ft}\right)\left(\frac{3.2808ft}{m}\right)\frac{1000g}{Kg} = \mathbf{1.0404}\frac{mg}{L-d}$$

The new <u>time of travel</u> for the 1-mile reach with elevated SOD is:

t = x/U = 1 mile / 3.27 miles/d = **0.30555 d**

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

$$D = 1.598\frac{mg}{L}e^{-0.721d^{-1}0.3056d} + \frac{0.8d^{-1}5.022\frac{mg}{L}}{0.721d^{-1} - 0.88d^{-1}}\left(e^{-0.88d^{-1}0.3056d} - e^{-0.721d^{-1}0.3056d}\right)$$
$$+ \frac{\left(5\frac{g}{m^2-d}/1.22m\right)}{0.721d^{-1}}\left(1 - e^{-0.721d^{-1}0.3056d}\right)$$
$$+ \frac{0.8d^{-1}1.04\frac{mg}{L-d}}{0.88d^{-1}0.721d^{-1}}\left(1 - e^{-0.721d^{-1}0.3056d}\right)$$
$$- \frac{0.8d^{-1}1.04\frac{mg}{L-d}}{0.88d^{-1}(0.721d^{-1} - 0.88d^{-1})}\left(e^{-0.88d^{-1}0.3056d} - e^{-0.721d^{-1}0.3056d}\right)$$

$$D = 1.28\frac{mg}{L} + 0.89\frac{mg}{L} + 1.125\frac{mg}{L} + 0.26\frac{mg}{L} - 0.23\frac{mg}{L} = 3.33\frac{mg}{L}$$

**C = C$_s$-D = 9.1-3.33 = 5.77 mg/L**

Now recalculate initial conditions and do the same for the reach with the lower SOD

<u>SOD:</u> Recall that S'$_B$ is given as 0.5 g/m$^2$/d for the second and third mile downstream of the WWTP

The new <u>initial deficit</u> is simply from the answer above

D$_o$ = C$_s$ – C$_o$ = 9.1mg/L – 5.77 mg/L = 3.33 mg/L

And finally, the <u>initial CBOD</u> is the BOD at the end of the previous reach.  This is done with the BOD model including non-point sources:

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

$$L = 4.658\frac{mg}{L}e^{-0.88d^{-1}0.3056d} + \frac{1.04\frac{mg}{L-d}}{0.88d^{-1}}\left(1 - e^{-0.88d^{-1}0.3056d}\right) = 3.56\frac{mg}{L} + 0.28\frac{mg}{L} = 3.84\frac{mg}{L}$$

Note that there is no change in the $S_d$ value

$$S_d = \frac{S}{A_{cs}} = \frac{35\frac{Kg}{mi-d}}{20.90m^2}\left(\frac{mi}{5280ft}\right)\left(\frac{3.2808ft}{m}\right)\frac{1000g}{Kg} = \mathbf{1.0404\frac{mg}{L-d}}$$

The new <u>time of travel</u> for the 2-mile reach with lower SOD is:

$$t = x/U = 2 \text{ mile} / 3.27 \text{ miles/d} = \mathbf{0.6111\ d}$$

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

$$D = 1.598\frac{mg}{L}e^{-0.721d^{-1}0.6111d} + \frac{0.8d^{-1}3.84\frac{mg}{L}}{0.721d^{-1} - 0.88d^{-1}}\left(e^{-0.88d^{-1}0.6111d} - e^{-0.721d^{-1}0.6111d}\right)$$
$$+ \frac{\left(0.5\frac{g}{m^2-d}/1.22m\right)}{0.721d^{-1}}\left(1 - e^{-0.721d^{-1}0.6111d}\right)$$
$$+ \frac{0.8d^{-1}1.04\frac{mg}{L-d}}{0.88d^{-1}0.721d^{-1}}\left(1 - e^{-0.721d^{-1}0.6111d}\right)$$
$$- \frac{0.8d^{-1}1.04\frac{mg}{L-d}}{0.88d^{-1}(0.721d^{-1} - 0.88d^{-1})}\left(e^{-0.88d^{-1}0.6111d} - e^{-0.721d^{-1}0.6111d}\right)$$

$$D = 2.14\frac{mg}{L} + 1.15\frac{mg}{L} + 0.203\frac{mg}{L} + 0.47\frac{mg}{L} - 0.35\frac{mg}{L} = 3.61\frac{mg}{L}$$

**C = C$_s$-D = 9.1-3.61 = 5.49 mg/L**

2. (50%) It is now well established that 17α-ethynylestradiol (also known as EE2, the active ingredient in birth control pills) causes feminization of male fish even when present at very low levels. In a 2007 publication[1], Karen Kidd of the Canadian Freshwater Institute, Jim Lazorchak of the USEPA and their colleagues showed that exposure to 5 ng/L (5x10$^{-9}$g/L) of EE2 for 3 years resulted in the total collapse of the native fathead minnow population in an experimental lake. Other short term studies have shown impacts on fish physiology as low as 0.1 ng/L of EE2.

Minnow Lake located near and urban center in Massachusetts will be receiving treated effluent from a small wastewater treatment plant serving a new residential development. The developers are interested in low impact development (LID) so they decided discharge the wastewater locally. Applying a factor of safety of 50x to the Kidd et al. (2007) results and considering the short-term

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[1] PNAS, 104:21:8897-8901.

data, you decided that the EE2 concentration should not exceed 0.1 ng/L.  So your job is to **determine the % EE2 removal required of the new WWTP so that the steady state concentration of EE2 in the lake stays under 0.1 ng/L**.

Assume the lake is at a temperature of 20°C.  You should assume that most loading occurs due to direct discharge from the WWTP.  The average wastewater flow is 0.25 MGD (946 $m^3$/d) and the average raw wastewater concentration of EE2 is 100 ng/L.  You may also assume that particulate forms of this compound biodegrade aerobically at 0.02 $d^{-1}$ as opposed to 0.005 $d^{-1}$ for the dissolved form. (universal gas constant, R=8.206x$10^{-5}$ atm $m^3$/°K mole).  Assume that EE2 does not biodegrade anaerobically.

*Selected Physical and Chemical Properties of Ethynylestradiol*

| Property | Value | Special Conditions | Reference |
|---|---|---|---|
| Molecular Weight | 296.39 | | |
| Melting Point | 145°C | | |
| Aqueous Solubility | 19.1 mg/L | 20°C | Yalkowski, 1999 |
| Log $K_{ow}$ | 3.67 | | Hansch et al., 1995 |
| Diffusivity in Water | 4 x $10^{-6}$ $cm^2$/s | | Estimated |
| Henry's Law Constant | 1x$10^{-6}$ atm-$m^3$/mol | | Estimated |
| Biodegradation Rate | 0.005 $d^{-1}$ | Dissolved | Estimated from Cajthaml et al., 2009 |
| | 0.02 $d^{-1}$ | Particulate | |
| pKa | 10.4 | | Hurwitz & Liu, 1977 |
| Photolysis Rate | 0.166 $d^{-1}$ | | Estimated from Leech et al., 2009 |
| Hydrolysis Rate | 0.001 $d^{-1}$ | 20°C, neutral only | Estimated |

## Characteristics of Minnow Lake

| Characteristic | Value |
|---|---|
| Volume | 1,000,000 $m^3$ |
| Average Outflow | 20,000 $m^3$/day |
| Mean Depth | 3 m |
| Mean Wind Speed | 0.5 m/sec |
| Solids Settling Rate | 0.2 m/d |
| Solids Burial Rate | 0.000007 m/d |
| Sediment:Water Diffusive Exchange Rate | 0.001 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 |
| Drainage area | 2300 ha |

## 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?**

1. First determine the volatilization rate

Liquid film resistance for a lake

$$K_l = 0.0017 D_l U_w$$

$$K_l = 0.0017 \frac{s}{cm^2}\left(0.000004 \frac{cm^2}{s}\right) 0.5 \frac{m}{s} = 3.4 x 10^{-9} \frac{m}{s} = 0.000294 \frac{m}{d}$$

Next the gas film resistance:

$$K_g = 346(MW^{-0.25}) U_w = 346(296.39^{-0.25}) 0.5 \frac{m}{s} = 41.69 \frac{m}{d}$$

At this point, you can do it via 2 different equations
i. calculate a dimensionless Henry's Law Constant

$$H_e' = \frac{H_e}{RT} = \frac{10^{-1} \frac{atm-m^3}{mol}}{0.00008206 \frac{atm-m^3}{°K-mol}(273+20)°K} = 4.16 x 10^{-5}$$

And overall rate or velocity of volatilization:

$$v_v = \frac{K_l K_g H_e'}{K_l + K_g H_e'}$$

$$v_v = \frac{0.000294 \frac{m}{d} 41.69 \frac{m}{d} 4.16 x 10^{-5}}{0.000294 \frac{m}{d} + 41.69 \frac{m}{d} 4.16 x 10^{-5}} = \mathbf{0.0002512 \frac{m}{d}}$$

ii. or you can use the equation with the more conventional Henry's law constatant:

$$v_v = K_l \frac{H_e}{H_e + RT_a \left(K_l / K_g\right)}$$

But this gets you exactly the same answer


2. Next, the partition coefficient

$$K_d = 6.17 x 10^{-7} f_{oc} K_{ow}$$

$$K_d = 6.17 x 10^{-7} (0.2)(10^{3.67}) = \mathbf{5.77 x 10^{-4} \frac{L}{mg}}$$


3. Next, the fractions dissolved and particulate:     e.g.:   $F_d = \dfrac{1}{1 + K_d m}$

For the water column

$$F_{d1} = \frac{1}{1 + K_d m_1}$$

$$F_{d1} = \frac{1}{1 + 5.77 x 10^{-4} \frac{L}{mg} 2.2 \frac{mg}{L}} = \mathbf{0.99873}$$

$$F_{p1} = \frac{K_d m_1}{1 + K_d m_1}$$

$$F_{p1} = \frac{5.77 x 10^{-4} \frac{L}{mg} 2.2 \frac{mg}{L}}{1 + 5.77 x 10^{-4} \frac{L}{mg} 2.2 \frac{mg}{L}} = \mathbf{0.00127}$$

For the mixed sediments

   note that we can make a small porosity-based adjustment to the partition coefficient

$$F_{d2} = \frac{1}{1 + 5.82 x 10^{-4} \frac{L}{mg} 12,000 \frac{mg}{L}} = \mathbf{0.1253}$$

and

$$F_{p2} = \frac{5.82 x 10^{-4} \frac{L}{mg} 12,000 \frac{mg}{L}}{1 + 5.82 x 10^{-4} \frac{L}{mg} 12,000 \frac{mg}{L}} = \mathbf{0.8747}$$

4. Sediment resuspension rate is obstained by a mass balance on the mixed sediments:

$$v_r = \frac{v_s m_1 - v_b m_2}{m_2}$$

$$v_r = \frac{0.2 \frac{m}{d} 2.2 \frac{mg}{L} - 0.000007 \frac{m}{d} 12,000 \frac{mg}{L}}{\left(12,000 \frac{mg}{L}\right)} = \mathbf{2.97 x 10^{-5} \frac{m}{d}}$$

6. Next determine the overall decay rates:

   A. For the water column

The dissolved and particulate rates incorporate the sum of the biodegradation and hydrolysis rates, and the dissolved rate also includes photolysis

$$k_{d1} = k_{b-diss} + k_h + k_p = 0.005 d^{-1} + 0.001 d^{-1} + 0.166 d^{-1} = 0.172 d^{-1}$$

and

$$k_{p1} = k_{b-part} + k_h = 0.02 d^{-1} + 0.001 d^{-1} = 0.021 d^{-1}$$

And the overall rate is:

$$k_{T1} = k_{d1} f_{d1} + k_{p1} f_{p1} = 0.172 d^{-1} 0.99873 + 0.021 d^{-1} 0.00127 = \mathbf{0.1718 d^{-1}}$$

   B. Mixed sediments:

The dissolved are particulate rates are just the sum of the biodegradation and hydrolysis rates, as there is no photolysis in the mixed sediments

$$k_{d2} = k_{b-diss} + k_h = 0.005d^{-1} + 0.001d^{-1} = 0.006d^{-1}$$

and

$$k_{p2} = k_{b-part} + k_h = 0.02d^{-1} + 0.001d^{-1} = 0.021d^{-1}$$

And the overall rate is:

$$k_{T2} = k_{d2}f_{d2} + k_{p2}f_{p2} = 0.006d^{-1}0.1253 + 0.021d^{-1}0.8747 = \mathbf{0.0191d^{-1}}$$

7. The sediment feedback ratio is:

$$F_r' = \frac{v_r + v_d F_{d2}}{v_r + v_b + v_d F_{d2} + k_{T2}H_2}$$

$$F_r' = \frac{2.97x10^{-5}\frac{m}{d} + 0.001\frac{m}{d}0.1253}{2.97x10^{-5}\frac{m}{d} + 7x10^{-6}\frac{m}{d} + 0.001\frac{m}{d}0.1253 + 0.0191d^{-1}0.2m} = \mathbf{0.0389}$$

8. Now the total loss velocity is:

$$V_T = k_{T1}H_1 + v_v f_{d1} + (v_s f_{p1} + v_d f_{d1})(1 - F_r')$$

$$V_T = 0.1718d^{-1}3m + 8.37x10^{-5}d^{-1}0.99873$$
$$+ \left(8.35x10^{-5}\frac{m}{d}0.00127 + 0.001\frac{m}{d}0.99873\right)(1 - 0.0389)$$

$$V_T = \mathbf{0.517\frac{m}{d}}$$

9. Determine Total Loss Rate

$$K_T = \frac{V_T}{H_1} = \frac{0.517\frac{m}{d}}{3m} = \mathbf{0.172d^{-1}}$$

10. Determine Lambda

$$\lambda = \frac{Q}{V} + K_T = \frac{20,000\frac{m^3}{d}}{1,000,000m^3} + 0.172d^{-1} = \mathbf{0.192d^{-1}}$$

$$C_{T1} = \frac{W}{\lambda V}$$

11. Determine steady state value

$$C_{T1} = \frac{W}{\lambda V}$$

where

$$W = Qc_{in} = 946\frac{m^3}{d}\left(100\frac{ng}{L}\right)10^{-9}\frac{g}{ng}10^{+3}\frac{L}{m^3} = 0.0946\frac{g}{d}$$

So

$$C_{T1} = \frac{W}{\lambda V} = \frac{0.0946\frac{g}{d}}{0.192d^{-1}1,000,000m^3} = 4.92x10^{-7}\frac{g}{m^3} = \mathbf{0.492\frac{ng}{L}}$$

12. Determine percent removal required, give a standard of 0.1 ng/L.

$$\%removal = 100\%\frac{0.492\frac{ng}{L} - 0.1\frac{ng}{L}}{0.492\frac{ng}{L}} = \mathbf{79.7\%}$$

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.

A. Describe and contrast one mechanistic and one empirical approach to modeling nutrients in surface waters.
B. Describe three ways to assess algal photosynthetic production using in-situ methods (i.e., done in the water body of interest)
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 the various steps involved in photolysis of toxics in surface waters. Include some discussion on how these steps are modeled.
E. Discuss the role of the octanol-water partition coefficient and the Henry's law constant in determining the fate of contaminants in natural waters. Use a graph to help your description.
F. Explain how "Black Carbon" affects sorption in natural systems
G. 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?