Short answer & multiple choice (3 pts each):

1. What are two names given to the process through which mixing occurs between regions of high and low concentration?
   ```
   _ _ _ Dispersion
   _ _ _ Diffusion
   ```

2. When expressed in equivalent units (e.g., m/d), which process is generally faster?
   a. Particle settling;
   b. Diffusion across the sediment-water interface;
   c. Mixing across the summer thermocline;
   d. All are equally fast;
   e. None of the above

3. What is another name for the first-order Runge-Kutta numerical technique?
   ```
   _____ Crude Euler
   ```

4. What numerical technique is the “industry standard” for solving ordinary differential equations?
   ```
   4th Order Runge-Kutta
   ```

5. The Gauss-Seidel method is a numerical method used for:
   a. solving ordinary differential equations
   b. solving multiple partial differential equations
   c. solving multiple linear equations
   d. none of the above

6. A rule of thumb for selecting an appropriate time step to use with a Runge-Kutta numerical technique is that one should use:
   a. the longest time step that does not cause any further change in results;
   b. the shortest time step that does not cause any further change in results;
   c. a time step equal to the characteristic time;
   d. a time step equal to \( \frac{2}{\lambda} \) where \( \lambda \) is the eigenvalue.
   e. none of the above

7. In solving for the steady state conditions in three lakes in series where lake 1 is the upstream lake, lake 3 is furthest downstream, and lake 2 is in between, the easiest order in which to solve the three equations “by hand” is:
   a. 3 then 2 then 1
   b. 2 then 1 then 3
   c. 1 then 3 then 2
   d. 1 then 2 then 3
   e. It does not matter
   f. None of the above

   (1/21)
8. What is the major meteorological variable controlling the rate of exchange of a volatile substance between a lake and the overlying air?

**WIND SPEED**

9. Vertical mixing in lakes is slowest in:
   a. the summer epilimnion
   b. the summer thermocline
   c. the summer hypolimnion
   d. the unstratified water column in fall

10. The next two questions ask you to draw two lines on the lower of the two paired graphs. The upper graph depicts a historical change in loading for an arbitrary substance. On the lower graph, you are to draw two approximate trajectories for the concentration of the substance. One line should be for a lake with an eigenvalue of 1 yr\(^{-1}\) and the second line for a lake with an eigenvalue of 0.25 yr\(^{-1}\). I am looking for approximate shapes, so do not try to be overly exact in your calculation of points to put on the graphs. (3 pts each)
11a. Dollar Bay is a small embayment that connects with Portage Lake. Consider the dispersive exchange of chloride between the bay and the lake. The advective flow of water through the bay entrance is negligible. The chloride loading to the bay is 10 kg/yr. The concentration of chloride in the bay is consistently 0.2 g/m$^3$ higher than in Portage Lake. Given the dimensions below, calculate the value of $K_x$, the horizontal dispersion coefficient (m$^2$/yr) that exists at the bay entrance. (10 pts)

Bay surface area: 7.8x10$^3$ m$^2$
Bay mean depth: 4 m
Dimensions of Bay entrance: 10 m (width) x 2 m (depth)
Horizontal distance over which concentration gradient is observed: 20 m

**SOLUTION:**

$$V \frac{dC}{dt} = W + \frac{K_x}{\Delta x} (C_{Lake} - C_{Bay}) A_{cross-section}$$

$$K_x = \frac{-W \cdot \Delta x}{A_{cross-section} (C_{Lake} - C_{Bay})}$$

$$K_x = \frac{10^4 \frac{g}{yr} \cdot 20m}{20m^2 \left(-0.2 \frac{g}{m^3}\right)} = 5 \times 10^4 \frac{m^2}{yr}$$

(10/16)
b) Convert the dispersion coefficient \( (K_x) \) into a dispersion velocity \( (m/d) \). (5 pts)

**SOLUTION:**

\[
v_x = \frac{K_x}{\Delta x} = \frac{5 \times 10^4 \frac{m^2}{yr}}{20m} \cdot \frac{365 \frac{d}{yr}}{20m} = 6.85 \frac{m}{d}
\]

c) Calculate the magnitude of the dispersive flow \( (K_x', m^3/d) \). (5 pts)

**SOLUTION:**

\[
K_x' = v_x \cdot A_{cross-section} = 6.85 \frac{m}{d} \cdot 20m^2 = 137 \frac{m^3}{d}
\]

12. Consider Atrazine in the epilimnion of Lake Superior. The major processes affecting concentrations are shown in the figure below. \( P \) is the loading from wet deposition (precipitation) to the lake surface. (30 pts)
a. Write an equation for the gas exchange flux (mass transfer, not chemical reaction). State the units of this flux. (6 pts)

SOLUTION: \[ V \frac{dC}{dt} = v_{aw} (C* - C) A = v_{aw} \left( \frac{C_a}{K_H} - C_w \right) A \]

The flux is in units of mass per time.

b. Write an expression for the settling flux. Be sure to define and give units for any symbols that you use. State the units of this flux. (6 pts)

SOLUTION: \[ V \frac{dC}{dt} = v_s C \cdot A \]

Flux is in units of mass/time. \( V \) is volume (m\(^3\)), \( C \) is concentration (mg/m\(^3\)), \( t \) is time (d), \( v_s \) is settling velocity (m/d), \( A \) is area (m\(^2\)).

c. Write an expression for biodegradation of atrazine. Be sure to define and give units for any symbols that you use. State the units of the flux. (6 pts)

SOLUTION: \[ V \frac{dC}{dt} = kCV \]

Flux is in units of mass/time. \( V \) is volume (m\(^3\)), \( C \) is concentration (mg/m\(^3\)), \( t \) is time (d), \( k \) is biodegradation rate constant (1/d),

d. The rate of atrazine inputs to Lake Superior has been increasing in a linear fashion over the past 20 years. What is the equation (give equation number or write out the equation) for the expected trajectory of atrazine concentration in the lake? (3 pts)

ANSWER: Equation #19 best answers the question

e. If the use of atrazine were to be banned, what equation (#) or series of equations could be used to predict the concentration of atrazine in Lake Erie over time? (3 pts)

ANSWER: This question could be answered either with any of the numerical integrator equations (14, 16, 17, 18) or with the analytical solution for lake 4 in a lakes-in-series model (eqn #27)
13. The next several questions will revolve around polybrominated biphenyl diethers (PBDEs) in the Great Lakes. PBDE were widely used as flame retardants from the late 1970s through the present. They have not been widely studied in the environment yet, but are considered an “emerging chemical” of concern. These compounds are very hydrophobic which means that they sorb readily to particles and also tend to bioaccumulate in organisms. Concentrations in Great Lakes fish have been increasing over the past several years. Refer to the diagram below to answer the following questions.

![Diagram of PBDE processes]

a. Identify all (list the number next to the arrow) of the processes that could be described with the rate law for reversible reactions. (3 pts)

**ANSWER:** Processes #1, #7, #8, #9, #12 all are reversible reactions. (3/3)
b. Would increasing the amount of dissolved organic carbon (DOC) in the lake increase, decrease or not change the eigenvalue for PBDEs in a lake? Explain your answer. (7 pts)

**ANSWER:** Increasing the DOC concentration in a lake would **DECREASE** the eigenvalue for PBDEs causing higher concentrations of PBDEs in the lake and longer times for lake response. Increased DOC concentration would cause more PBDEs to bind with DOC; the bound PBDEs would not settle or volatilize from the lake. Because settling and volatilization are the fastest removal mechanisms, removal of PBDEs would be retarded, the residence time would be increased, and concentrations would increase.

c. (7 pts) An expression for the diffusive flux out of the sediments might be:

\[
J \left( \frac{g}{m^2 \cdot yr} \right) = \frac{D_{\text{eff}}}{\Delta z} \left( C_{\text{pw}} - f_{\text{dissolved}} C \right)
\]

**What is the characteristic time for diffusion** (year) if the value for \( D_{\text{eff}} \) is 5.6x10\(^{-6}\) cm\(^2\)/sec, \( \Delta z \) is 2 mm, \( f_{\text{dissolved}} \) is 5%, the mean depth of the lake is 150 m, and the lake surface area is 8.2x10\(^{10}\) m\(^2\)?

**SOLUTION:**

\[
k = \frac{D_{\text{eff}} \cdot f_{\text{diss}}} {\Delta z \cdot H} = \frac{5.6 \times 10^{-6} \text{ cm}^2 \cdot s^{-1} \cdot 0.05} {0.2 \text{ cm} \cdot 150 \text{ m} \cdot 100 \text{ cm/m}} = 9.33 \times 10^{-11} \text{ s}^{-1}
\]

\[
\tau = \frac{s}{k} \cdot \frac{\text{yr}} {3600 \cdot 24 \cdot 365 \text{s}} = 340 \text{ yr}
\]
d. BONUS (7 pts) We discussed in class the equilibrium partitioning between dissolved and particulate (sorbed) phases. Colloidal organic matter acts as a third phase to which contaminants bind. The total PBDE concentration has three components:
\[ C_T = C_{\text{dissolved}} + C_{\text{particulate}} + C_{\text{DOM-bound}} \]
The partitioning between dissolved- and DOM-bound phases may be described with an equilibrium coefficient:
\[ K_{\text{DOM}} = \frac{C_{\text{DOM-bound}} \left( \frac{\text{gPBDE}}{\text{gDOC}} \right)}{C_{\text{dissolved}} \left( \frac{\text{gPBDE}}{m^3} \right)} \]
The mass of PBDEs in the DOM-bound phase would be
\[ \text{mass(g)} = C_{\text{DOM-bound}} \left( \frac{\text{gPBDE}}{\text{gDOC}} \right) \cdot C_{\text{DOM}} \left( \frac{\text{gDOC}}{m^3} \right) \]

Write an expression for the fraction of PBDEs in the DOM-bound phase using the following symbols:
- \( C_{\text{DOM-bound}} \) (gPBDE/gDOC)
- \( C_{\text{DOM}} \) (gDOC/m³)
- \( K_{\text{DOM}} \) (m³/gDOC)
- \( K_D \) (m³/g particles)
- \( C_{\text{SS}} \) (g suspended solids/m³)
- \( C_{\text{part}} \) (gPBDE/g suspended solids)
- \( C_{\text{dis}} \) (gPBDE/m³)

**SOLUTION:**
\[ C_T = C_{\text{dis}} + C_{\text{part}} C_{\text{SS}} + C_{\text{DOM-bound}} C_{\text{DOM}} \]
\[ f_{\text{DOM}} = \frac{C_{\text{DOM-bound}} C_{\text{DOM}}}{C_T} \]
\[ C_{\text{DOM-bound}} = K_{\text{DOM}} C_{\text{dis}} \]
\[ C_{\text{part}} = K_D C_{\text{dis}} \]
\[ f_{\text{DOM}} = \frac{K_{\text{DOM}} C_{\text{dis}} C_{\text{DOM}}}{C_{\text{dis}} + C_{\text{SS}} K_D C_{\text{dis}} + K_{\text{DOM}} C_{\text{dis}} C_{\text{DOM}}} \]
\[ f_{\text{DOM}} = \frac{K_{\text{DOM}} C_{\text{DOM}}}{1 + C_{\text{SS}} K_D + K_{\text{DOM}} C_{\text{DOM}}} \]
EQUATIONS

1. \( a = Q + kV + vA = W/C \)

2. \( f_{\text{part.}} = \frac{K_D \cdot C_{ss}}{1 + K_D \cdot C_{ss}} \)

3. \( \beta = \frac{C}{C_{in}} = \frac{Q}{a} = \frac{Q}{Q + kV + vA} \)

4. \( \text{rate} = V_m \frac{C}{C + K_m} \)

5. \( \tau = \frac{\text{total \cdot mass \cdot in \cdot system}}{\text{total \cdot flux \cdot through \cdot system}} \)

6. \( \lambda = \frac{Q}{V} + k + \frac{v_A}{H} \)

7. \( C_1 = C_{1f} e^{-\lambda_f t} + C_{1s} e^{-\lambda_s t} \)

8. \( \lambda_{f,s} = 0.5 \left( [\alpha_{11} + \alpha_{22}] \pm \sqrt{(\alpha_{11} + \alpha_{22})^2 - 4(\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})} \right) \)

9. \( C_{1f,1s}^{1/2} = \frac{\pm(\lambda_f - \alpha_{22})C_{10} - \alpha_{12}C_{20}}{\lambda_f - \lambda_s} \)

10. \( C_{2f,2s}^{1/2} = \frac{\pm(\lambda_f - \alpha_{11})C_{20} - \alpha_{21}C_{10}}{\lambda_f - \lambda_s} \)

11. \( C_2 = C_{20} e^{-\lambda_{22} t} + \frac{W_2}{\lambda_{22} V_2} \left( 1 - e^{-\lambda_{22} t} \right) + \frac{\lambda_{21} C_{10}}{\lambda_{22} - \lambda_{11}} \left[ e^{-\lambda_{11} t} - e^{-\lambda_{22} t} \right] \)

12. \( C = C_0 e^{-\lambda t} + \frac{W}{\lambda V} \left( 1 - e^{-\lambda t} \right) \)

13. \( \text{if } \cdot u < 5.5, \text{then } \alpha = 0.5 \)

14. \( \text{if } \cdot u > 5.5, \text{then } \alpha = 2 \)

15. \( \left( \frac{dC}{dt} \right)_t = \frac{W'}{V} - \lambda C_{t-1} \)

16. \( C_{t+1} = C_t + \left( \frac{dC}{dt} \right)_t \cdot \Delta t \)

17. \( \left( \frac{dC}{dt} \right)_t = \frac{1}{6} \cdot \left[ \left( \frac{W'}{V} - \lambda C_{t-1} \right) + 2 \left( \frac{W'}{V} - \lambda \left( C_{t-1} + \frac{W'}{V} - \lambda C_{t-1} \cdot \Delta t \right) \right) \right] \)

\[ \left( \frac{dC}{dt} \right)_t = \frac{1}{6} \cdot \left[ \left( \frac{W'}{V} - \lambda C_{t-1} \right) + 2 \left( \frac{W'}{V} - \lambda \left( C_{t-1} + \frac{W'}{V} - \lambda C_{t-1} \cdot \Delta t \right) \right) \right] \cdot \Delta t \]
19. \[ C = C_0 e^{-\lambda t} + \frac{\beta}{\lambda^* V} (\lambda t - 1 + e^{-\lambda t}) \] where \[ W = W_0 + \beta t \]

20. \[ C = C_0 e^{-\lambda t} + \frac{W_0}{V (\lambda + b)} (e^{bt} - e^{-\lambda t}) \] where \[ W = W_0 e^{bt} \]

21. \[ \text{rate} = k(C-C^*) \]

22. \[ \nu^{H^2,D}_{a} \left( \frac{m}{\text{hr}} \right) = 7.2 \cdot u_{10m} \left( \frac{m}{s} \right) + 10.8 \]

23. \[ \frac{k}{k_2} = \Theta_{T_2-T_1} \]

24. \[ Q_{10} = \theta^{10} = \frac{k_{7+10}}{k_7} \]

25. \[ f_{\text{part.}} = \frac{K_D \cdot C_{SS}}{1 + K_D \cdot C_{SS}} \]

26. \[ k = A \exp \left( \frac{-E_A}{RT} \right) \]

27. \[ C_4 = C_4 e^{-\lambda_{4u}t} + \frac{\lambda_{43}}{\lambda_{44} - \lambda_{33}} C_{30} \left( e^{-\lambda_{3u}t} - e^{-\lambda_{4u}t} \right) + \frac{\lambda_{43} \lambda_{32}}{\lambda_{33} - \lambda_{22}} C_{20} \left( e^{-\lambda_{32}t} - e^{-\lambda_{44}t} - e^{-\lambda_{3u}t} - e^{-\lambda_{4u}t} \right) + \frac{\lambda_{43} \lambda_{31}}{\lambda_{33} - \lambda_{11}} C_{10} \left( e^{-\lambda_{31}t} - e^{-\lambda_{44}t} - e^{-\lambda_{3u}t} - e^{-\lambda_{4u}t} \right) \]