1. Basic Concepts and Mechanisms

Examples of Contaminant Transport

- effect of wastewater discharge to a river on downstream water quality
- effect of an incinerator on downwind air pollutant levels
- overall efficiency of a waste treatment technologies is influenced by the contaminant transport within the control facility
- performance of monitoring and measurement devices depends on the effective transport of contaminants from the sampling point to the detector

Physical Scale of Concern for Contaminant Transport

- Molecular dimension: transport of a contaminant into the pore of an adsorbent
- Global distance: transport of air and waterborne contaminants

Transport phenomena are subdivided into

1.1 Role of Simulation

Limitations:

However, still modeling and simulation is the most realistic and feasible approach to reach (1) quantitative answer, and (2) meaningful conclusions.

“All things are numbers” - Pythagoras (philosopher, mathematician)

1.2 Law of Conservation of Mass and Energy

- The most important laws of environmental modeling

In an environmental system without any reaction (e.g., no-interest bank account)

Amount of Accumulation = Amount of Input – Amount of Output

Rate of Accumulation = Rate of Input – Rate of Output

Assumptions

Completely mixed systems

where V = volume of a system [L^3];
C_{sys} = concentration of a contaminant in the system [M/ L^3];
T = elapsed time [T];
i = number of incoming paths of the contaminant into the system;
$Q_{in,i}$ = flowrate of the ith incoming path [L^3/T];
$C_{in,i}$ = concentration of the contaminant in the ith incoming path [M/ L^3];
j = number of outgoing paths of the contaminant from the system;
$Q_{out,j}$ = flowrate of the jth outgoing path [L^3/T]; and
$C_{out,j}$ = concentration of the contaminant in the jth outgoing path [M/ L^3];

If the volume of the system is constant,

At steady state the rate of accumulation is zero, i.e., $dC_{sys}/dt = 0$

If there is any sink or gain term (i.e., conversion or transformation) ?

Rate of Accumulation
= Rate of Input – Rate of Output +/- Rate of Transformation

where k = number of reactions that cause sink or gain of the contaminant; and
r_k = reaction rate of k^{th} reaction [M/L^3,T].

1.3 Contaminant Flux

- "Flux (symbol: J)" is a vector quantity, comprising both a magnitude and a direction

1.4 Advection

- Whenever a fluid is in motion, all contaminants in the fluid including both molecules and suspended particles are "advected" along with the fluid.

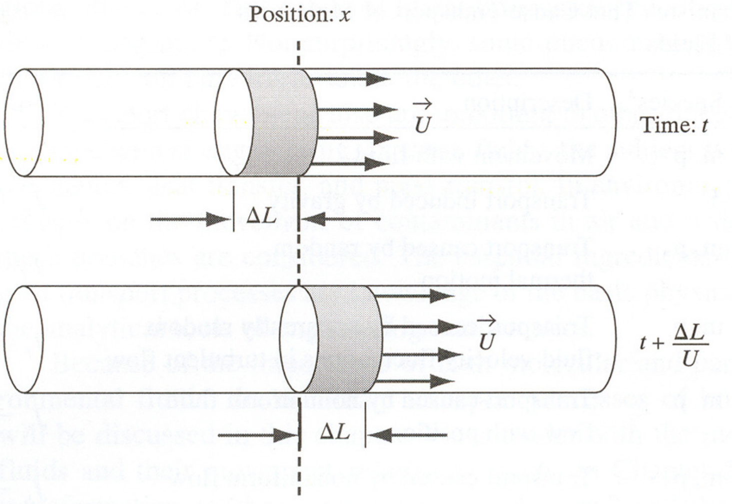

Figure 4.A.2 Advective flux of contaminant through a tube. The two pictures represent the same tube at two points in time, t and $t + \Delta t$, where $\Delta t = \Delta L / U$.

1.5 Molecular Diffusion (Brownian Motion)

- The botanist Robert Brown, who in 1827 reported observing, through a microscope, the wiggling motion of pollen grains suspended in water. The Brownian motion results from the random collisions of particles suspended in a fluid with surrounding molecules.
- Although the molecular-scale motion seems hopelessly disordered, the macroscopic effects are well understood and predictable. Qualitatively, the random motion of fluid molecules causes a net movement of species from high concentration region to low concentration one.
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1.5.1 Fick's Law

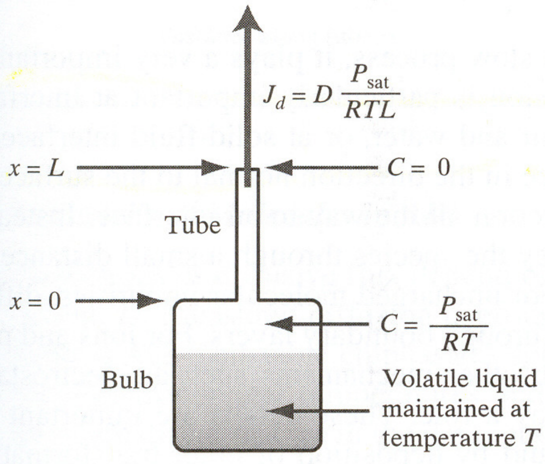


Figure 4.A.3 Apparatus for producing a controlled diffusive flux of a volatile species. P_{sat} is the saturation vapor pressure of the species at temperature T. Provided that the time scale for evaporation and condensation is much more rapid than the time scale for diffusion through the tube, a molar concentration P_{sat}/RT will be attained throughout the bulb. The vapor molecules will diffuse through the tube with a net diffusive flux J_d.

The escape rate of a volatile substance from the tube varies (1) in inverse proportion to the tube length, (2) in proportion to the cross-sectional area of the tube, and (3) in proportion to the partial pressure of the substance in the bulb.

where D = diffusion coefficient (or diffusivity)

as the distance Δx becomes infinitesimally small,

1.5.2 Significance of Diffusion

Diffusion is a slow transport process. Albert Einstein showed that characteristic distance a molecule (or a particle) will travel by diffusion in time t is given by

For example, a gas molecule with a diffusivity of 0.1 cm^2/sec is expected to move in 1 second a characteristic distance, $x = \sqrt{2 \times 0.1\mathrm{cm}^2/\mathrm{sec} \times 1\mathrm{sec}} = 0.45\mathrm{cm}$

Diffusion is particularly important at interfaces (or boundary layer) because there is no fluid advection at an interface in the direction normal to the surface.

Diffusivity of molecules in air (D_{air})

= 0.05 (Naphthalene) – 0.6 (Helium) cm^2/sec

Diffusivity of molecules in water (D_{water})

= 0.8 (Methanol) x 10^{-5} – 4.5 (Hydrogen) x 10^{-5} cm^2/sec

Example (Application of Diffusion)

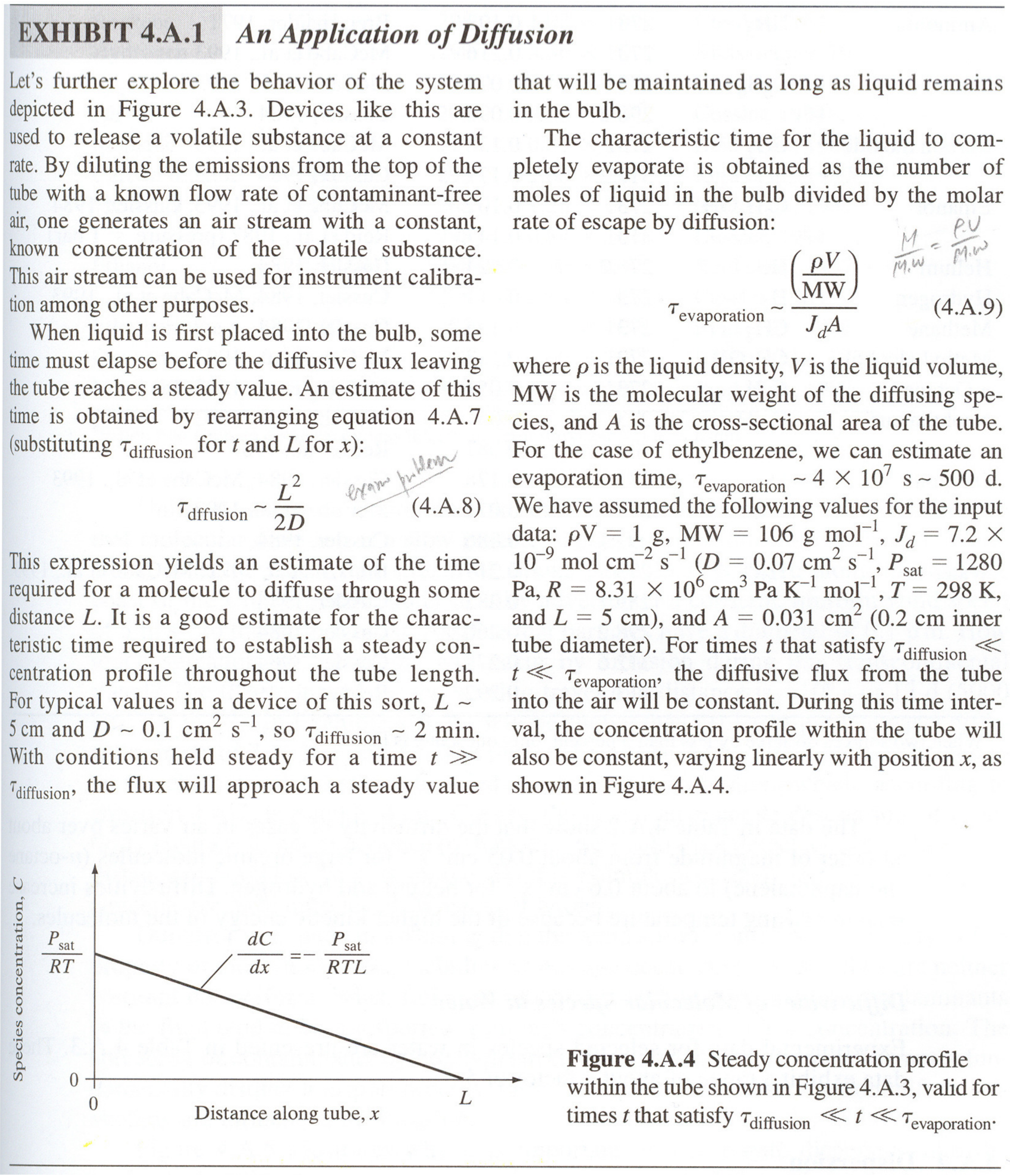


EXHIBIT 4.A.1 *An Application of Diffusion*

Let's further explore the behavior of the system depicted in Figure 4.A.3. Devices like this are used to release a volatile substance at a constant rate. By diluting the emissions from the top of the tube with a known flow rate of contaminant-free air, one generates an air stream with a constant, known concentration of the volatile substance. This air stream can be used for instrument calibration among other purposes.

When liquid is first placed into the bulb, some time must elapse before the diffusive flux leaving the tube reaches a steady value. An estimate of this time is obtained by rearranging equation 4.A.7 (substituting $\tau_{\text{diffusion}}$ for t and L for x):

$$\tau_{\text{diffusion}} \sim \frac{L^2}{2D} \qquad (4.A.8)$$

exam problem

This expression yields an estimate of the time required for a molecule to diffuse through some distance L. It is a good estimate for the characteristic time required to establish a steady concentration profile throughout the tube length. For typical values in a device of this sort, $L \sim 5$ cm and $D \sim 0.1$ cm^2 s^{-1}, so $\tau_{\text{diffusion}} \sim 2$ min. With conditions held steady for a time $t \gg \tau_{\text{diffusion}}$, the flux will approach a steady value that will be maintained as long as liquid remains in the bulb.

The characteristic time for the liquid to completely evaporate is obtained as the number of moles of liquid in the bulb divided by the molar rate of escape by diffusion:

$$\frac{M}{M.w} = \frac{\rho.V}{M.w}$$

$$\tau_{\text{evaporation}} \sim \frac{\left(\dfrac{\rho V}{\text{MW}}\right)}{J_d A} \qquad (4.A.9)$$

where ρ is the liquid density, V is the liquid volume, MW is the molecular weight of the diffusing species, and A is the cross-sectional area of the tube. For the case of ethylbenzene, we can estimate an evaporation time, $\tau_{\text{evaporation}} \sim 4 \times 10^7$ s $\sim$ 500 d. We have assumed the following values for the input data: $\rho V = 1$ g, MW $= 106$ g mol^{-1}, $J_d = 7.2 \times 10^{-9}$ mol cm^{-2} s^{-1} ($D = 0.07$ cm^2 s^{-1}, $P_{\text{sat}} = 1280$ Pa, $R = 8.31 \times 10^6$ cm^3 Pa K^{-1} mol^{-1}, $T = 298$ K, and $L = 5$ cm), and $A = 0.031$ cm^2 (0.2 cm inner tube diameter). For times t that satisfy $\tau_{\text{diffusion}} \ll t \ll \tau_{\text{evaporation}}$, the diffusive flux from the tube into the air will be constant. During this time interval, the concentration profile within the tube will also be constant, varying linearly with position x, as shown in Figure 4.A.4.

Figure 4.A.4 Steady concentration profile within the tube shown in Figure 4.A.3, valid for times t that satisfy $\tau_{\text{diffusion}} \ll t \ll \tau_{\text{evaporation}}$.

1.6 Dispersion

Dispersion is caused by nonuniform advection and influenced by diffusion.

For example, (1) air quality engineering, (2) the impact of wastewater discharges on rivers, lakes, or oceans, (3) movement of contaminants in groundwater, etc.

1.6.1 Shear-Flow Dispersion

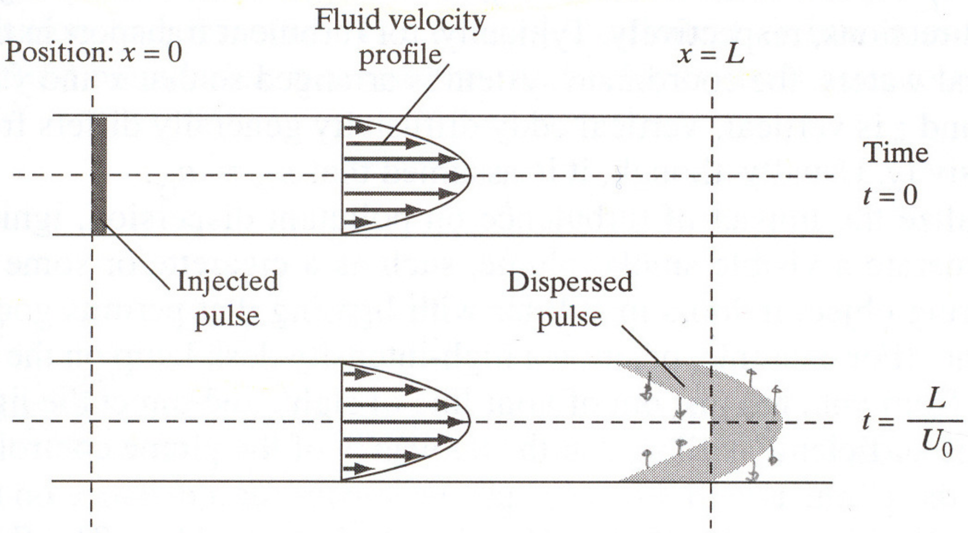


Figure 4.A.6 Schematic of a model problem illustrating the effects of shear-flow dispersion.

The velocity profile of the fluid flow is parabolic because of wall friction. Those molecules that lie close to the centerline of the tube are advected at a higher velocity than those near the wall.

However, the contaminant profile of a pulse input is not a parabolic line but a parabolic range. Contaminant molecules positioned near the leading edge of the pulse and near the center of the tube tend to diffuse toward the walls. Conversely, contaminant molecules located near the tailing edge of the pulse tend to diffuse toward the center.

In this case, the net effect of molecular diffusion is to slow the rate of dispersion.

Under laminar flow condition, the flux due to shear-flow dispersion is described by an equation analogous to Fick's law.

$$J_s = -\varepsilon_s \cdot \frac{dC}{dx}$$

where ε_s = shear-flow dispersivity

1.6.2 Turbulent Diffusion

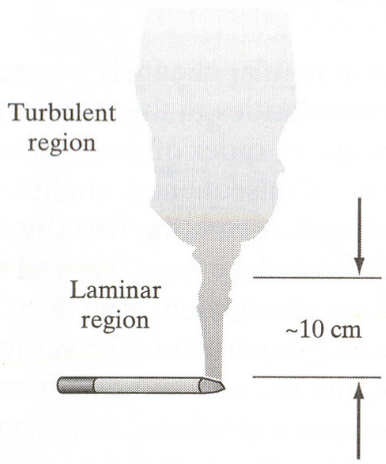


Figure 4.A.7 Schematic representation of time-averaged smoke plume rising from a smoldering cigarette in still air.

The flux due to turbulent dispersion is described by an equation analogous to Fick's law.

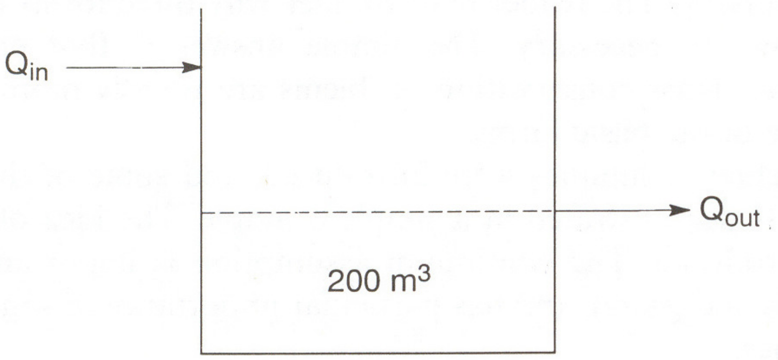
where ε_t, $\varepsilon_{t,x}$, $\varepsilon_{t,y}$, $\varepsilon_{t,z}$ = turbulent diffusion coefficients (or eddy diffusivities)

It is often assumed that $\varepsilon_{t,x} = \varepsilon_{t,y}$.

Turbulent diffusivities in rivers are one order magnitude smaller than shear-flow dispersion coefficient. In the atmosphere, turbulent diffusion is especially important in the vertical direction.

(Problem 1)

A 500-m^3 detention pond initially contains 200 m^3 of water. At the 200-m^3 level or below), there is no discharge from the pond, but discharge will begin for any level above 200 m^3.



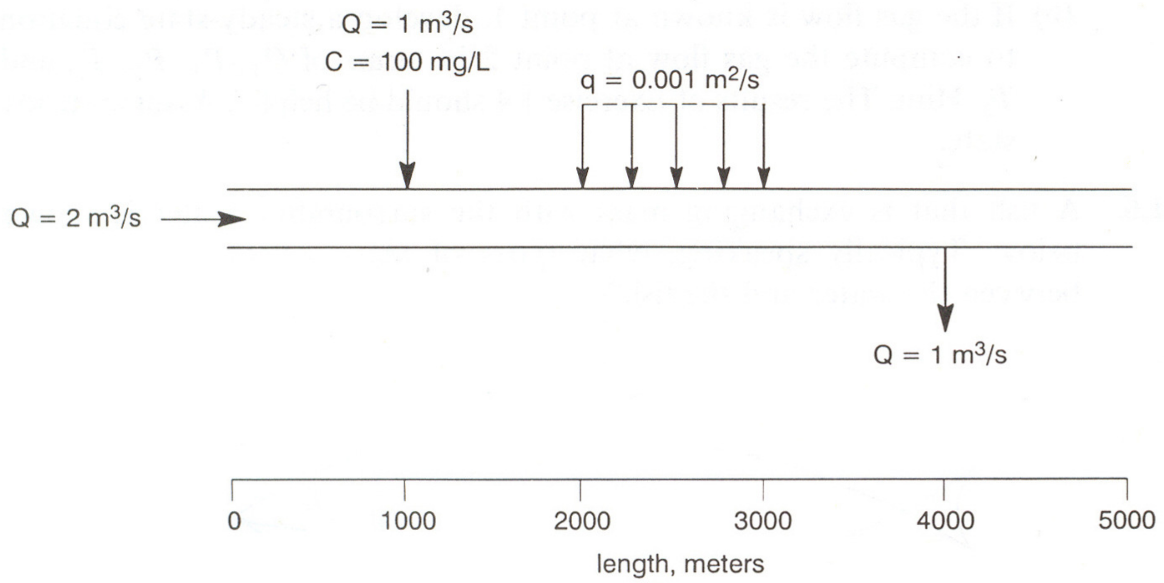
An input flow of 0.2 m^3/s begins, and at the same time, a valve controls the output flow according to the following expression:

$$Q_{out} = 0.001[V - 200]\left(\frac{m^3}{s}\right) \qquad \text{for } V > 200\,m^3$$

In the equation, V is the detention pond volume. Determine the pond volume over time, as well as the steady-state pond volume.

(Problem 2)

A 5000-m stretch of a certain river can be approximated for modeling purposes as:

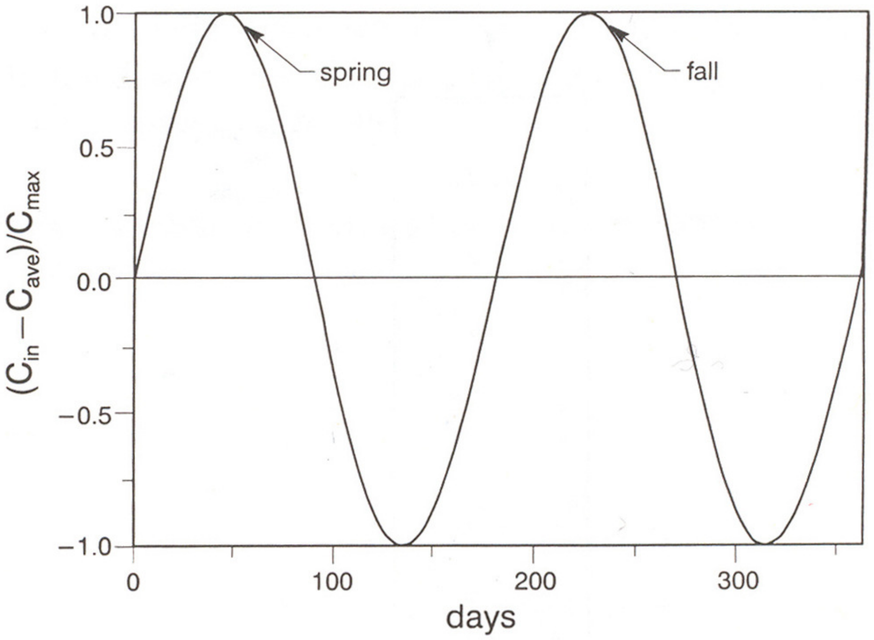


(At the 4,000m point, not the clean water but the contaminated water is pumped at the flow rate of 1 m^3/sec.)

In the figure, q is a distributed "nonpoint source" flow input given in units of $L^3/(L\text{-}T)$. As shown in the figure, at 1000 m, a flow enters the river with a contaminant concentration of 100 mg/L. This is a conservative contaminant, which means that it undergoes no reactions or degradation (e.g., NaCl). Plot the concentration of the contaminant along the 5000-m stretch of river. You may assume perfect mixing of the contaminant in the river cross section, but consider only transport downstream due to the average flow velocity.

(Problem 3)

A refractory organic compound (a compound not easily degraded biologically) enters a lake with a seasonally varying concentration profile which can be modeled as a sinusoidal function.



Exercise 1.10

The sinusoidal input can be described by the following function:

$$C_{in} = C_{ave} + C_{max}\sin(\omega_0 t)$$

where ω_0 is the frequency of the sinusoidal function:

$$\omega_0 = \frac{4\pi}{365}\frac{\text{rad}}{\text{day}}$$

(a) If there is no decay or other reaction of the compound in the lake (i.e., a conservative compound), use the systems approach (with the perfect mixing assumption) to show that the appropriate differential equation describing the system is

$$\frac{dC}{dt} + \frac{1}{\bar{t}}C = \frac{1}{\bar{t}}[C_{\text{ave}} + C_{\max}\sin(\omega_0 t)]$$

where $\bar{t}$ is the mean hydraulic detention time in the lake:

$$\bar{t} = \frac{V}{Q_{\text{in}}} = \frac{V}{Q_{\text{out}}}$$

(b) Show that for the initial condition $C = C_{\text{ave}}$ at $t = 0$, the solution to the differential equation given above is

$$C = C_{\text{ave}} + \frac{C_{\max}}{\frac{1}{\bar{t}} + \omega_0^2 \bar{t}}\left[\frac{1}{\bar{t}}\sin(\omega_0 t) - \omega_0 \cos(\omega_0 t) + \omega_0 e^{-t/\bar{t}}\right]$$

(c) For lake volume $V = 10^6\,\text{m}^3$ and $Q_{\text{in}} = Q_{\text{out}} = 0.35\,\text{m}^3/\text{s}$, plot the solution on the same figure with the input function shown above.

(d) For $t \rightarrow \infty$ and $1/\sqrt{t} \ggg w_0$, derive the expression of C. Next derive the expression of C for $t \rightarrow \infty$ and $1/\sqrt{t} \lll w_0$. Explain why these two solutions make sense (i.e., explain the effect of lake volume on the concentration of organic matter leaving the lake).