

Chapter 4

Physical Processes

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In this chapter, the reader will learn about the physical processes that are important in the movement of pollutants through the environment and in processes used to control and treat pollutant emissions. The chapter begins with a study of the use of material and energy balances. These tools are fundamental to environmental engineering and form the basis for reactor design. An understanding of mass and energy balances is essential to the solution of a greater number of environmental engineering and science problems.

The chapter continues with a discussion of the processes of advection and dispersion, which are responsible for the transport of pollutants through the environment. Transport of pollutants through the movement of wind and water currents (i.e., advection) is the mechanism by which pollutants can move great distances through the environment. On a smaller scale, however, molecular diffusion (i.e., random motion) is often more important than advection. On larger scales, turbulent dispersion can also be significant. For example, the movement of air pollutants on global scales can sometimes be best described as a process of turbulent dispersion.

The final section of this chapter extends this description of transport processes with a look at the movement of particles in fluids, and, in a reversal of that problem, the movement of a fluid through soil. The speed of particle settling and the velocity of groundwater flow is governed by the interplay of forces acting on the particle or the groundwater.

4.1 MASS BALANCES

The law of conservation of mass states that mass can neither be produced nor destroyed. Conservation of mass and conservation of energy (covered in Section 4.2) provide the basis for two tools that are used routinely in environmental engineering and science: the mass balance and the energy balance.

This principle of conservation of mass means that if the amount of a chemical somewhere (for example, in a lake) increases, then that increase cannot be the result of some "magical" formation. The chemical must have been either carried into the lake from elsewhere or produced via chemical or biological reaction from other compounds that were already in the lake. Similarly, if reactions produced the mass increase of this chemical, they must also have caused a corresponding decrease in the mass of some other compound(s).

Thus, conservation of mass provides a basis for compiling a budget of the mass of the chemical. In the case of a lake, this budget keeps track of the amounts of chemical entering the lake, the amount leaving the lake, and the amount formed or destroyed by chemical reaction. This budget can be balanced over a given time period, similarly to the way a checkbook is balanced. Equation 4-1 describes the mass balance:

$$\begin{aligned} (\text{Mass at time } t + \Delta t) = & (\text{mass at time } t) \\ & + \left(\begin{array}{l} \text{mass that entered} \\ \text{from } t \text{ to } t + \Delta t \end{array} \right) - \left(\begin{array}{l} \text{mass that exited} \\ \text{from } t \text{ to } t + \Delta t \end{array} \right) \quad (4-1) \\ & + \left(\begin{array}{l} \text{net mass of chemical produced} \\ \text{from other compounds by} \\ \text{reactions between } t \text{ and } t + \Delta t \end{array} \right) \end{aligned}$$

Each term of Equation 4-1 has units of mass. This form of balance is most useful when there is a clear beginning and end to the balance period (Δt), so that the change in mass over the balance period can be determined. For example, when balancing a checkbook, a balance period of one month is often used.

In environmental problems, however, it is usually more convenient to work with values of *mass flux*—the *rate* at which mass enters or leaves a system. To develop an equation in terms of mass flux, the mass-balance equation is divided by Δt to produce an equation with units of mass per unit time. Dividing Equation 4-1 by Δt and moving the first term on the right (mass at time t) to the left-hand side yields the following equation:

$$\begin{aligned} \frac{(\text{Mass at time } t + \Delta t) - (\text{mass at time } t)}{\Delta t} = & \frac{\left(\begin{array}{l} \text{mass entering from} \\ t \text{ to } t + \Delta t \end{array} \right) - \left(\begin{array}{l} \text{mass exiting from } t \\ \text{to } t + \Delta t \end{array} \right)}{\Delta t} + \frac{\left(\begin{array}{l} \text{net chemical} \\ \text{production} \\ \text{between } t \text{ and} \\ t + \Delta t \end{array} \right)}{\Delta t} \quad (4-2) \end{aligned}$$

Note that each term in Equation 4-2 has units of mass time⁻¹. The left-hand side of Equation 4-2 is equal to $\Delta m/\Delta t$. In the limit as $\Delta t \rightarrow 0$, the left-hand side becomes dm/dt , the rate of change of chemical mass in the lake. As $\Delta t \rightarrow 0$, the first two terms on the right side of Equation 4-2 become the rate at which mass

enters the lake (the mass flux into the lake) and the rate at which mass exits the lake (the mass flux out of the lake). The last term of Equation 4-2 is the *net rate* of chemical production or loss.

The symbol \dot{m} is used to refer to a mass flux with units of (mass time⁻¹). Making this substitution, the equation for mass balances is then

$$\begin{aligned} \left(\begin{array}{l} \text{mass} \\ \text{accumulation} \\ \text{rate} \end{array} \right) &= (\text{mass flux in}) - (\text{mass flux out}) + \left(\begin{array}{l} \text{net rate of} \\ \text{chemical} \\ \text{production} \end{array} \right) \\ \text{or } \frac{dm}{dt} &= \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{reaction}} \quad (4-3) \end{aligned}$$

Equation 4-3 is the governing equation for mass balances used throughout environmental engineering and science.

4.1.1 The Control Volume

A mass balance is only meaningful in terms of a specific region of space, which has boundaries across which the terms \dot{m}_{in} and \dot{m}_{out} are determined. This region is called the *control volume*. In the previous section, we used a lake as our control volume, and included mass fluxes into and out of the lake. Theoretically, any volume of any shape and location can be used as a control volume. Realistically, however, certain control volumes are more useful than others. *The most important attribute of a control volume is that it have boundaries over which \dot{m}_{in} and \dot{m}_{out} can be calculated.*

4.1.2 Terms of the Mass-Balance Equation for a CMFR

A well-mixed tank is an analog for many control volumes used in environmental situations. For example, in the lake example it might be reasonable to assume that the chemicals discharged into the lake are mixed throughout the entire lake. The term *completely mixed flow reactor* (CMFR) is used for such a system. (Other terms, most commonly continuously stirred tank reactor (CSTR), are also used for such systems.) A schematic diagram of a CMFR is shown in Figure 4-1, and two examples of CMFRs are depicted in Figure 4-2. The next sections describe each term in a mass balance of a hypothetical compound within the CMFR in Figure 4-1.

4.1.2.1 Mass Accumulation Rate, dm/dt

The rate of change of mass within the control volume, dm/dt , is referred to as the mass accumulation rate. To directly measure the mass accumulation rate, one would have to determine the total mass within the control volume of the compound for which the mass balance is being conducted. This would usually not be easy, and it is not usually necessary. If the control volume is well mixed, then the

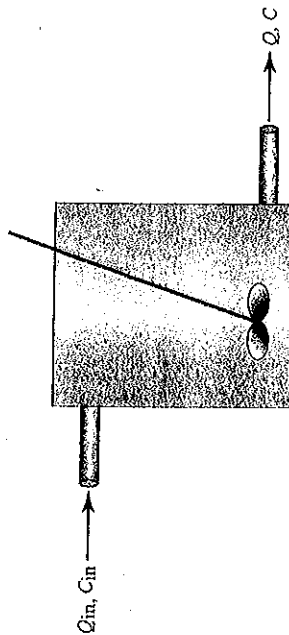


Figure 4-1. Schematic diagram of a Completely Mixed Flow Reactor (CMFR). The stir bar is used as a symbol to indicate that the CMFR is well mixed.

concentration of the compound is the same throughout the control volume, and the mass in the control volume is equal to the product of that concentration, C , and the volume, V . (To ensure that $C \times V$ has units of [mass time⁻¹], C must be expressed in [mass volume⁻¹] units.) Expressing mass as $C \times V$, the mass accumulation rate is equal to

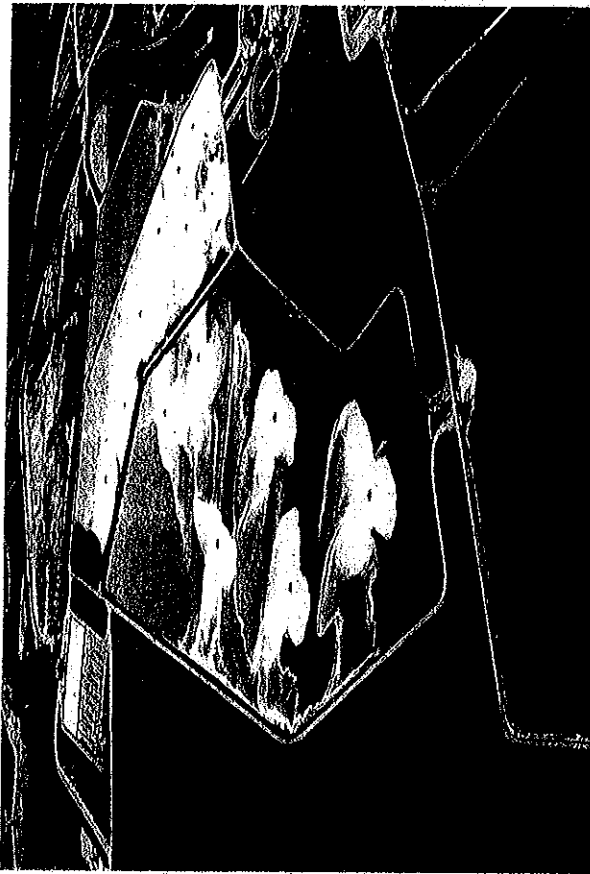
$$\frac{dm}{dt} = \frac{d(VC)}{dt} \quad (4-4)$$

In most cases (and in all cases in this text), the volume is constant and can be moved outside the derivative, resulting in

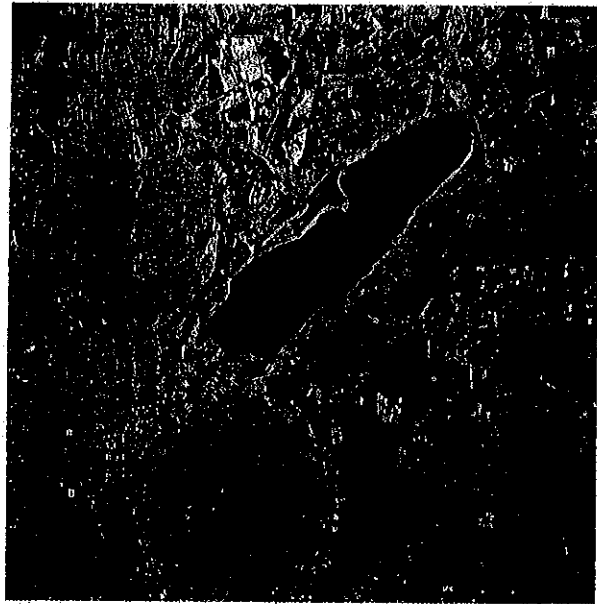
$$\frac{dm}{dt} = V \frac{dC}{dt} \quad (4-5)$$

In any mass-balance situation, once a sufficient amount of time has passed conditions will approach *steady state*, meaning that conditions no longer change with time. In *steady-state* conditions, the concentration, and hence the mass, within the control volume remains constant. In this case, $dm/dt = 0$. If, however, insufficient time has passed since a flow, inlet concentration, reaction term, or other problem condition has changed, the mass in the control volume will vary with time, and the mass balance will be *non-steady state*.

How much time must pass before steady state is reached depends on the conditions of the problem. To see why, consider the approach to steady state of the amount of water in two large, initially empty sinks. In the first sink, the faucet is opened halfway, and the drain is opened slightly. Initially, the mass of water in the sink increases over time, since the faucet flow exceeds the flow rate out of the drain. Conditions are changing, so this is a non-steady-state situation. However, as the water level in the sink rises, the flow rate out of the drain will increase, and eventually the drain flow will equal the faucet flow. At this point, the water level will cease rising, and the situation will have reached steady state. If this experiment is then repeated with a second sink, but this time with the drain opened fully, the drain flow will increase more rapidly, and will equal the faucet



(a)



(b)

Figure 4-2. Examples of Completely Mixed Flow Reactors (CMFRs) in an engineered and a natural system. (a) Aerated wastewater lagoons use biological degradation to treat wastewater. The lagoons are generally earthen basins with a large surface area (up to several acres) and depth of 5 to 15 feet. With these conditions and a round or square layout, the lagoons usually attain completely mixed conditions. (Tom Hollyman/Photo Researchers.) (b) Onondaga Lake, located in Syracuse, New York, is an alkaline lake with a surface area of 11.7 km² and a mean depth of 12 m. Two tributaries account for 75% of the annual flow into the lake, and the local sewage treatment plant accounts for approximately 60% of the remainder. For many compounds, Onondaga Lake can be modeled as a CMFR. (Courtesy Martin Auer.)

flow while the water level in the sink is still low. In this case, then, steady state will be reached more rapidly. In general, the speed at which steady state is approached depends upon the magnitude of the mass flux terms, relative to the total mass in the control volume.

Determining whether a mass-balance problem is steady state or not is something of an art. However, if conditions of the problem have changed recently, then the problem is probably a non-steady state. On the other hand, if conditions have remained constant for a very long time, it is probably a steady-state problem. Treating a steady-state problem as non-steady state will always result in the correct answer, while treating a non-steady-state problem as steady state will not. (This does not mean that one should treat all problems as non-steady state, however. Non-steady-state solutions are generally more difficult, so it is advantageous to identify steady state whenever it is present.)

EXAMPLE 4.1 DETERMINING WHETHER A PROBLEM IS STEADY STATE

For each of the following mass-balance problems, determine whether a steady-state or non-steady-state mass balance would be appropriate.

- A mass balance on chloride (Cl^-) dissolved in a lake. Two rivers bring chloride into the lake, and one river removes chloride. No significant chemical reactions occur, as chloride is soluble and nonreactive. What is the annual average concentration of chloride in the lake?
- A degradation reaction within a well-mixed tank is used to destroy a pollutant. Inlet concentration and flow are held constant, and the system has been operating for several days. What is the pollutant concentration in the effluent, given the inlet flow and concentration and the first-order decay rate constant?
- The source of pollutant in problem (b) is removed, resulting in an instantaneous decline of the inlet concentration to zero. How long would it take until the outlet concentration reaches 10% of its initial value?

SOLUTION

- Over an annual period, river flows and concentrations can be assumed to be relatively constant. Since conditions are not changing, and since a single value independent of time is requested for chloride concentration, the problem is steady state.
- Again, conditions in the problem are constant and have remained so for a long time, so the problem is steady state. Note that the presence or absence of a chemical reaction does not provide any information on whether the problem is steady state or not.
- There are two clues that this problem is non-steady state. First, conditions have changed recently—the inlet concentration dropped to zero. Second,

the solution requires calculation of a time period, which means that conditions must be varying with time.

4.1.2.2 Mass Flux in, \dot{m}_{in}

Often, the volumetric flow rate, Q , of each input stream entering the control volume is known. In Figure 4-1, the pipe has a flow rate of Q_{in} , with corresponding chemical concentration of C_{in} . The mass flux into the CMFR is then given by

$$\dot{m}_{in} = Q_{in} \times C_{in} \quad (4-6)\text{F}$$

If it is not immediately clear how $Q \times C$ results in a mass flux, consider the units of each term:

$$\dot{m} = Q \times C$$

$$\left[\frac{\text{mass}}{\text{time}} \right] = \left[\frac{\text{volume}}{\text{time}} \right] \times \left[\frac{\text{mass}}{\text{volume}} \right]$$

(Note that the concentration must be expressed in [mass volume⁻¹] units.)

If the volumetric flow rate is not known, it may be calculated from other parameters. For example, if the fluid velocity v and the cross-sectional area A of the pipe are known, then $Q = v \times A$.

In some situations, mass may enter the control volume through direct emission into the volume. In this case, the emissions are frequently specified in mass flux units (mass time⁻¹), which can be used in a mass balance directly. For example, if a mass balance is performed on the air pollutant carbon monoxide (CO) in the atmosphere over a city, estimates of the total CO emissions (in units of tons day⁻¹) from cars and power plants in the city would be used.

Another way to describe the flux is in terms of a *flux density*, J , times the area through which the flux occurs. J has units of *mass area⁻¹ time⁻¹* and is discussed further when diffusion is covered in Section 4.3. This type of flux notation is most useful at interfaces where there is no fluid flow, such as the interface between the air and water at the surface of a lake.

Often, the mass flux in is composed of several terms. For example, a tank may have more than one inlet, or the air over a city may receive CO blowing from an upwind urban area in addition to its own emissions. In such cases, \dot{m}_{in} is the sum of all individual contributions to mass input fluxes.

4.1.2.3 Mass Flux out, \dot{m}_{out}

In most cases, there is only one effluent flow from a CMFR. In such cases, the mass flux out may be calculated just as \dot{m}_{in} was calculated in Equation 4-6:

$$\dot{m}_{out} = Q_{out} \times C_{out} \quad (4-7)$$

In the case of a well-mixed control volume, the concentration is constant throughout. Therefore, the concentration in flow exiting the control volume is referred to simply as C , the concentration in the control volume, and

$$\dot{m}_{\text{out}} = Q_{\text{out}} \times C \quad (4-8)\text{F}$$

4.1.2.4 Net Rate of Chemical Reaction, $\dot{m}_{\text{reaction}}$

The term $\dot{m}_{\text{reaction}}$ (\dot{m}_{rxn}) refers to the net rate of production of a compound from chemical or biological reactions. It has units of mass time⁻¹. Thus, if other compounds react to form the compound, \dot{m}_{rxn} will be greater than zero; if the compound reacts to form some other compound(s), resulting in a loss, \dot{m}_{rxn} will be negative.

Although the chemical reaction term in a mass balance has units of mass time⁻¹, chemical reaction rates are usually expressed in terms of concentration, not mass. To calculate \dot{m}_{rxn} , then, we multiply the rate of change of concentration by the CMFR volume to obtain the rate of change of mass within the control volume:

$$\dot{m}_{\text{rxn}} = V \times \left(\frac{dC}{dt} \right)_{\text{reaction only}} \quad (4-9)\text{F}$$

where the term $(dC/dt)_{\text{reaction only}}$ is obtained from the rate law for the reaction and is equal to the rate of change in concentration that would occur if the reaction took place in isolation, with no influent or effluent flows.

There are a number of possible forms for mass flux due to reaction. The most common include:

- 1. Conservative Compound.** Compounds with no chemical formation or loss within the control volume are termed *conservative*. Conservative compounds are not affected by chemical or biological reactions, and thus $(dC/dt)_{\text{reaction only}} = \dot{m}_{\text{reaction}} = 0$. The term *conservative* is used for these compounds because their mass is truly conserved: what goes in is equal to what goes out.
- 2. Zero-order Decay.** The rate of loss of the compound is constant. For a compound with zeroth-order decay, $(dC/dt)_{\text{reaction only}}$ equals $-k$ and \dot{m}_{rxn} equals $-Vk$. Zero-order reactions are discussed in Chapter 3 (Section 3.2).
- 3. First-order Decay.** The rate of loss of the compound is directly proportional to its concentration: $(dC/dt)_{\text{reaction only}}$ equals $-kC$. For such a compound, \dot{m}_{rxn} equals $-VkC$. First-order reactions are discussed in Chapter 3 (Section 3.2).
- 4. Production at a rate dependent on the concentrations of other compounds in the CMFR.** In this situation, the chemical is produced by reactions involving other compounds in the CMFR, and $(dC/dt)_{\text{reaction only}}$ is greater than zero.

4.1.2.5 Steps in Mass-Balance Problems

Solution of mass-balance problems involving CMFRs will generally be straightforward if the problem is done carefully. Most difficulties in solving mass-balance problems arise from uncertainty regarding the location of control volume boundaries or values of the individual terms in the mass balance. Therefore, it is suggested that the following steps be followed for each mass-balance problem.

1. Draw a schematic diagram of the situation, and identify the control volume and all influent and effluent flows. All mass flows that are known or are to be calculated must cross the control-volume boundaries, and it should be reasonable to assume that the control volume is well mixed.

2. Write the mass-balance equation in general form:

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}}$$

3. Determine whether the problem is steady state ($dm/dt = 0$) or non-steady state ($dm/dt = V dC/dt$).

4. Determine whether the compound being balanced is conservative ($\dot{m}_{\text{rxn}} = 0$) or nonconservative (\dot{m}_{rxn} must be determined based on the reaction kinetics and Equation 4-9).

5. Replace \dot{m}_{in} and \dot{m}_{out} with known or required values, as just described.

6. Finally, solve the problem. This will require solution of a differential equation in non-steady-state problems and solution of an algebraic equation in steady-state problems.

4.1.3 Reactor Analysis: The CMFR

Reactor analysis refers to the use of mass balances to analyze pollutant concentrations in a control volume that is either a chemical reactor or a natural system modeled as a chemical reactor. Ideal reactors can be divided into two types: CMFRs (Completely Mixed Flow Reactors) and PFRs (Plug Flow Reactors). CMFRs are used to model well-mixed environmental reservoirs. Plug Flow Reactors (PFRs) (described in Section 4.1.5 below) behave essentially like pipes, and are used to model situations such as downstream transport in a river, in which fluid is not mixed in the upstream-downstream direction.

This section presents several examples involving CMFRs in different combinations of steady-state or non-steady-state conditions and conservative or non-conservative compounds, as summarized in Table 4-1. Example 4.2 demonstrates the use of CMFR analysis to determine the concentration of a substance resulting from the mixing of two or more influent flows. Examples 4.3 through 4.5 refer to the tank depicted in Figure 4-1 and demonstrate steady-state and non-steady-state situations with and without first-order chemical decay. Calculations analogous to those in Examples 4.3, 4.4, and 4.5 can be used to determine the concentration of pollutants exiting a treatment reactor, the rate of increase of pollutant

Table 4-1. Summary of CMFR Examples

Example Number	Form of dm/dt	Form of $\dot{m}_{\text{reaction}}$
Example 4.2	Steady state	Conservative
Example 4.3	Steady state	First-order decay
Example 4.4	Non-steady state	First-order decay
Example 4.5	Non-steady state	Conservative

concentrations within a lake resulting from a new pollutant source, or the period required for pollutant levels to decay from a lake or reactor once a source is removed.

EXAMPLE 4.2. STEADY-STATE CMFR WITH CONSERVATIVE CHEMICAL: THE MIXING PROBLEM

A pipe from a municipal wastewater-treatment plant discharges $1.0 \text{ m}^3 \text{ s}^{-1}$ of poorly treated effluent containing 5.0 mg L^{-1} of phosphorus compounds (reported as mg P L^{-1}) into a river with an upstream flow rate of $25 \text{ m}^3 \text{ s}^{-1}$ and a background phosphorus concentration of $0.010 \text{ mg P L}^{-1}$ (see Figure 4-3). What is the resulting concentration of phosphorus (in mg L^{-1}) in the river just downstream of the plant outflow?

SOLUTION

To solve this problem, two mass balances will be applied to first determine the downstream volumetric flow rate (Q_d) and, second, determine the downstream phosphorus concentration (C_d). First a control volume must be selected. To en-

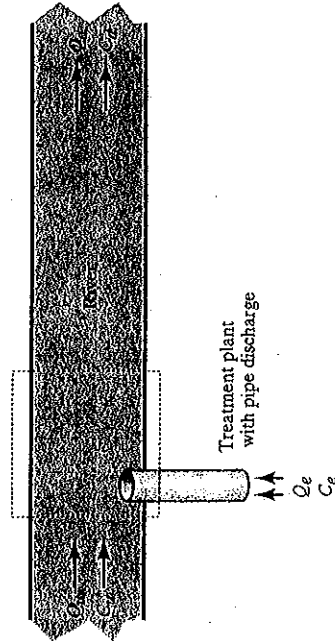


Figure 4-3. Mixing problem used in Example 4.2. The control volume is indicated by the area inside the dashed lines.

sure that the input and output fluxes cross the control volume boundaries, the control volume must cross the river upstream and downstream of the plant's outlet and must also cross the discharge pipe. The selected control volume is shown in Figure 4-3 as a dotted line. It is assumed to extend down river far enough that the discharged wastewater and the river water become well mixed before leaving the control volume. As long as that assumption is met, it makes no difference to the analysis how far downstream the control volume extends.

Before beginning the analysis, it should be determined whether this is a steady-state or non-steady-state problem, and whether the chemical reaction term will be nonzero. Because the problem statement does not refer to time at all, and it seems reasonable to assume that both the river and wastewater discharge have been flowing for some time and will continue to flow, this is a steady-state problem. In addition, this problem concerns the concentration resulting from rapid mixing of the river and effluent flows. Therefore, we can define our control volume to be small, and can safely assume that chemical or biological degradation is insignificant during the time spent in the control volume and thus treat this as a steady-state problem.

Step 1. Determine the downstream flow rate, Q_d . Q_d can be found by conducting a mass balance on the total river-water mass. In this case, the "concentration" of river water in (mass volume $^{-1}$) units is simply the density of the water, ρ :

$$\begin{aligned} \frac{dm}{dt} &= \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}} \\ &= \rho Q_{\text{in}} - \rho Q_{\text{out}} + 0 \end{aligned}$$

where the term $\dot{m}_{\text{reaction}}$ has been set to zero because the mass of water is conserved. Since this is a steady-state problem, $dm/dt = 0$. Therefore, as long as the density ρ is constant, $Q_{\text{in}} = Q_{\text{out}}$, or $(Q_u + Q_e) = 26 \text{ m}^3 \text{ s}^{-1} = Q_d$.

Step 2. Determine the phosphorus concentration downstream of the discharge pipe, C_d . C_d can be found by using the standard mass-balance equation with steady-state conditions and with no chemical formation or decay:

$$\begin{aligned} \frac{dm}{dt} &= \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}} \\ 0 &= (C_u Q_u + C_e Q_e) - C_d Q_d + 0 \end{aligned}$$

and

$$\begin{aligned} C_d &= \frac{C_u Q_u + C_e Q_e}{Q_d} \\ &= \frac{(0.010 \text{ mg L}^{-1})(25 \text{ m}^3 \text{ s}^{-1}) + (5.0 \text{ mg L}^{-1})(1.0 \text{ m}^3 \text{ s}^{-1})}{26 \text{ m}^3 \text{ s}^{-1}} \\ &= 0.20 \text{ mg L}^{-1} \end{aligned}$$

The CMFR shown in Figure 4-1 is used to treat an industrial waste product, using a reaction that destroys the pollutant according to first-order kinetics, with $k = 0.216 \text{ day}^{-1}$. The reactor volume is 500 m^3 , the volumetric flow rate of the single inlet and exit is $50 \text{ m}^3 \text{ day}^{-1}$, and the inlet pollutant concentration is 100 mg L^{-1} . What is the outlet concentration after treatment?

SOLUTION

An obvious control volume is the tank itself. The problem requests a single, constant outlet concentration, and all problem conditions are constant. Therefore, this is a steady-state problem ($dm/dt = 0$). The mass-balance equation with a first-order decay term ($[dC/dt]_{\text{reaction only}} = -kC$ and $\dot{m}_{\text{rxn}} = -VkC$) is

$$\begin{aligned} \frac{dm}{dt} &= \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}} \\ 0 &= QC_{\text{in}} - QC - VkC \end{aligned}$$

Solving for C , we find that

$$C = C_{\text{in}} \times \frac{Q}{Q + kV}$$

or

$$C = C_{\text{in}} \times \frac{1}{1 + kV/Q}$$

The numerical solution is

$$\begin{aligned} C &= 100 \text{ mg L}^{-1} \times \frac{50 \text{ m}^3 \text{ day}^{-1}}{50 \text{ m}^3 \text{ day}^{-1} + (0.216 \text{ day}^{-1})(500 \text{ m}^3)} \\ &= 32 \text{ mg L}^{-1} \end{aligned}$$

The manufacturing process that generates the waste in Example 4.3 has to be shut down, and, starting at $t = 0$, the concentration C_{in} entering the CMFR is set to 0. What is the outlet concentration as a function of time after the concentration

is set to 0? How long does it take the tank concentration to reach 10% of its initial, steady-state value?

SOLUTION

The tank is again the control volume. In this case, the problem is clearly non-steady-state, because conditions change as a function of time. The mass-balance equation is

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}}$$

$$V \frac{dC}{dt} = 0 - QC - kCV$$

and

$$\frac{dC}{dt} = -\left(\frac{Q}{V} + k\right)C$$

(a) To determine C as a function of time, the preceding differential equation must be solved. Rearranging and integrating

$$\int_{C_0}^C \frac{dC}{C} = \int_0^t -\left(\frac{Q}{V} + k\right) dt$$

Integration yields

$$\ln(C) - \ln(C_0) = -\left(\frac{Q}{V} + k\right)t$$

Because $(\ln(x) - \ln(y))$ is equal to $\ln(x/y)$,

$$\ln\left(\frac{C}{C_0}\right) = -\left(\frac{Q}{V} + k\right)t$$

which yields

$$\frac{C}{C_0} = e^{-(Q/V+k)t}$$

We can verify that this solution is reasonable by considering what happens at $t = 0$ and $t = \infty$. At $t = 0$, the exponential term is equal to 1 and $C = C_0$, as expected. As $t \rightarrow \infty$, the exponential term approaches zero, and concentration declines to zero, again as expected, since C_{in} is equal to zero.

We can now plug in values to determine the dependence of C on time. Example 4.3 provides Q and V . The initial concentration is equal to the concentration before C_{in} was set to zero, which was found to be 32 mg/L

in Example 4.3. Plugging in these values yields the outlet concentration as a function of time

$$\begin{aligned} C_t &= 32 \text{ mg L}^{-1} \times \exp \left[- \left(\frac{50 \text{ m}^3 \text{ day}^{-1}}{500 \text{ m}^3} + \frac{0.216}{\text{day}} \right) t \right] \\ &= 32 \text{ mg L}^{-1} \times \exp \left(- \frac{0.316}{\text{day}} t \right) \end{aligned}$$

This solution is plotted in Figure 4-4a.

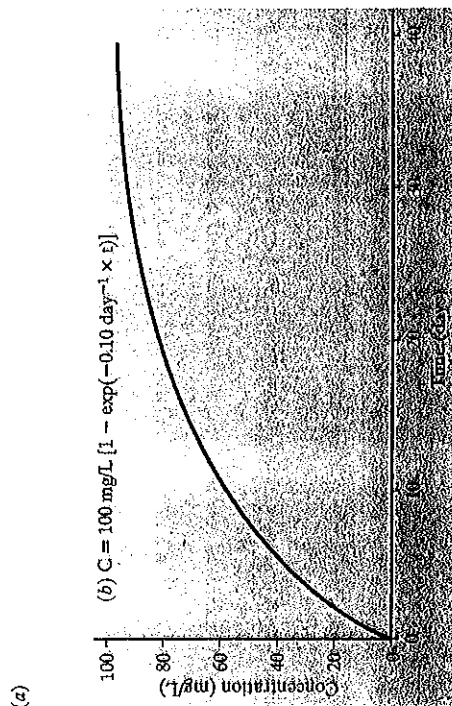
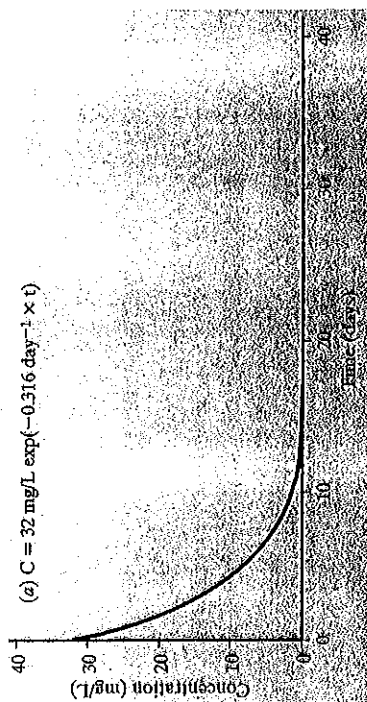


Figure 4.4. Concentration versus time profiles for the solutions to Examples 4.4 and 4.5. (a) First-order decay in concentration resulting from the removal of \dot{m}_{in} at time zero. The decay in concentration results from the sum of chemical reaction loss (\dot{m}_{rxn}) and the mass flux out term (\dot{m}_{out}). (b) Exponential approach to steady-state conditions when a reactor is started with initial concentration equal to zero. In the absence of a chemical reaction loss term, concentration in the reactor exponentially approaches the inlet concentration.

(b) How long will it take the concentration to reach 10% of its initial, steady-state value? That is, at what value of t is $C_t/C_0 = 0.10$? At the time when $C_t/C_0 = 0.10$,

$$\frac{C}{C_0} = 0.10 = \exp \left(- \frac{0.316}{\text{day}} t \right)$$

Taking the natural logarithm of both sides,

$$\ln(0.10) = -2.303 = - \frac{0.316}{\text{day}} t$$

or

$$t = 7.3 \text{ days}$$

EXAMPLE 4.5 NON-STeady-STATE CMFR CONSERVATIVE SUBSTANCE

The CMFR reactor depicted in Figure 4-1 is filled with clean water prior to being started. After start-up, a waste stream containing 100 mg L^{-1} of a conservative pollutant is added to the reactor at a flow rate of $50 \text{ m}^3 \text{ day}^{-1}$. The volume of the reactor is 500 m^3 . What is the concentration exiting the reactor as a function of time after it is started?

SOLUTION

Again, the tank will serve as a control volume. We are told that the pollutant is conservative, so $\dot{m}_{\text{rxn}} = 0$. The problem asks for concentration as a function of time, so the mass balance must be non-steady state. The mass balance equation is

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_{\text{rxn}}$$

$$V \frac{dC}{dt} = QC_{\text{in}} - QC + 0$$

and

$$\frac{dC}{dt} = - \left(\frac{Q}{V} \right) (C - C_{\text{in}})$$

Because of the extra term on the right (C_{in}), this equation cannot be immediately solved. However, with a change of variables we can transform the mass-balance equation into a simpler form that can be integrated directly, using the same method used in Example 4.4. Let $y = (C - C_{\text{in}})$. Then, $dy/dt =$

$dC/dt = d(C_{in}/dt)$. Since C_{in} is constant, $dC_{in}/dt = 0$, and thus $dy/dt = dC/dt$. Therefore, the last of the preceding equations is equivalent to

$$\frac{dy}{dt} = -\frac{Q}{V}y.$$

Rearranging and integrating,

$$\int_{y(0)}^{y(t)} \frac{dy}{y} = \int_0^t -\frac{Q}{V} dt$$

which yields

$$\ln\left(\frac{y(t)}{y(0)}\right) = -\frac{Q}{V}t$$

or

$$\frac{y(t)}{y(0)} = e^{-(Q/V)t}$$

Replacing y with $(C - C_{in})$, the following equation is obtained

$$\frac{C - C_{in}}{C_0 - C_{in}} = e^{-(Q/V)t}$$

Since clean water is present in the tank at start-up, $C_0 = 0$, and

$$\frac{C - C_{in}}{-C_{in}} = e^{-(Q/V)t}$$

Rearranging results in

$$C - C_{in} = -C_{in}e^{-(Q/V)t}$$

or

$$C = C_{in} \times (1 - e^{-(Q/V)t})$$

This is the solution to the question posed in the problem statement. Note what happens as $t \rightarrow \infty$: $e^{-(Q/V)t} \rightarrow 0$ and $C \rightarrow C_{in}$. This is not surprising, since this is a conservative substance. If the reactor is run for a long enough period, the concentration in the reactor will eventually reach the inlet concentration. This final equation (plotted in Figure 4-4b) provides C as a function of time, and can

be used to determine how long it would take for the concentrations to reach, say, 90% of the inlet value.

4.1.4 The Batch Reactor

A reactor that has no inlet or outlet flows is termed a *batch reactor*. A batch reactor is essentially just a tank in which a reaction is allowed to occur. After one batch is treated, the reactor is emptied and a second batch can be treated. Because there are no flows, $\dot{m}_{in} = 0$ and $\dot{m}_{out} = 0$. Therefore, the mass-balance equation reduces to

$$\frac{dm}{dt} = \dot{m}_{rxn} \quad (4-10)$$

or

$$V \frac{dC}{dt} = V \left(\frac{dC}{dt} \right)_{\text{reaction only}} \quad (4-11)$$

or

$$\frac{dC}{dt} = \left(\frac{dC}{dt} \right)_{\text{reaction only}} \quad (4-12)$$

Thus, in a batch reactor, the change in concentration with time is simply that resulting from chemical reaction alone. For example, for a first-order decay reaction, $r = -kC$ and thus

$$\frac{dC}{dt} = -kC \quad (4-13)$$

or

$$\frac{C_t}{C_0} = e^{-kt} \quad (4-14)$$

as discussed in Section 3.2.2.

4.1.5 The Plug-Flow Reactor

The *plug-flow reactor* (PFR) is used to model the chemical transformation of compounds as they are transported in systems resembling "pipes." The "pipe" may represent a river, a region between two mountain ranges through which air flows, or a variety of other engineered or natural conduits through which liquids

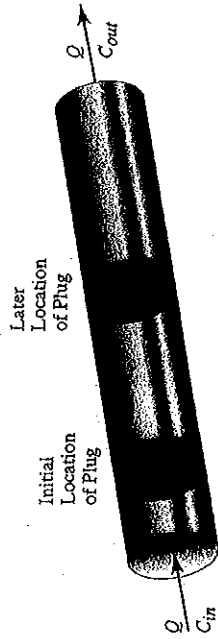


Figure 4-5. Schematic diagram of a plug-flow reactor.

or gases flow. Of course, it can even represent a pipe. A schematic diagram of a PFR is shown in Figure 4-5, and examples of PFRs in an engineered and a natural system are shown in Figure 4-6.

As fluid flows down the PFR, the fluid is mixed in the radial direction, but mixing does not occur in the axial direction. That is, each *plug* of fluid is considered a separate entity as it flows down the pipe. However, time passes as the plug of fluid moves downstream (or downwind). Therefore, there is an implicit time

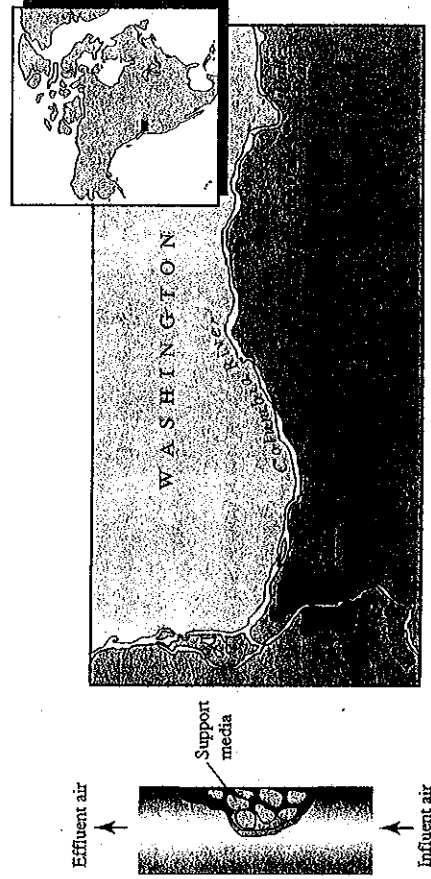


Figure 4-6. Examples of plug-flow reactors in an engineered and a natural system. (a) Packed-tower biofilters are used to remove organic compounds from wastewater and odorous air emissions, such as hydrogen sulfide (H_2S) from gas-phase emissions. Biofilters consist of a column packed with a support medium, such as rocks, plastic rings, or activated carbon, on which a biofilm is grown. Contaminated water or air is passed through the filter, and bacterial degradation results in the desired reduction of pollutant emissions. (b) The Columbia River flows 1,200 mi from its source in Canada into the Pacific Ocean. Prior to reaching the ocean, the Columbia River flows southward into the United States and forms the border between the states of Oregon and Washington. Shown is a stretch of the river near The Dalles, Washington, where the river once narrowed and spilled over a series of rapids, christened *les Dalles*, or the trough, by the voyageurs—early French explorers. A large dam has since been constructed near The Dalles. The section of the river downstream of the dam could be modeled as a plug-flow reactor.

dependence even in steady-state PFR problems. However, because the velocity of the fluid (v) in the PFR is constant, time and downstream distance (x) are interchangeable, and $t = x/v$. That is, it always takes an amount of time equal to x/v for a fluid plug to travel a distance x down the reactor. This observation can be used with the mass-balance formulations just given to determine how chemical concentrations vary during flow through a PFR.

To develop the equation governing concentration as a function of distance down a PFR, the evolution of concentration with time within a single fluid plug will be analyzed. The plug is assumed to be well mixed in the radial direction, but does not mix at all with the fluid ahead or behind it. As the plug flows downstream, chemical decay occurs, and concentration decreases. The mass balance for mass within this moving plug is then the same as that for a batch reactor:

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_{rxn} \quad (4-15)$$

$$V \frac{dC}{dt} = 0 - 0 + V \left(\frac{dC}{dt} \right)_{\text{reaction only}} \quad (4-16)$$

where \dot{m}_{in} and \dot{m}_{out} are set equal to zero because there is no mass exchange across the plug boundaries.

Equation 4-16 can be used to determine concentration as a function of flow time within the PFR for any reaction kinetics. In the case of first-order decay, $V(dC/dt)_{\text{reaction only}} = -VkC$, and

$$V \frac{dC}{dt} = -VkC \quad (4-17)$$

which results in

$$\frac{C_t}{C_0} = \exp(-kt) \quad (4-18)$$

It is generally desirable to express the concentration at the outlet of PFR in terms of the inlet concentration and PFR length or volume, rather than time spent in the PFR. In a PFR of length L , each plug travels for a period $\theta = L/v = L \times A/Q$, where A is the cross-sectional area of the PFR and Q is the flow rate. The product of length and cross-sectional area is simply the PFR volume, so Equation 4-18 is equivalent to

$$\frac{C_{out}}{C_{in}} = \exp - \frac{kV}{Q} \quad (4-19)$$

Note that Equation 4-19 has no time dependence. Although concentration within a given plug changes over time as that plug flows downstream, the concentration at a given fixed location within the PFR is constant with respect to time, since all plugs reaching that location have spent an identical period in the PFR.

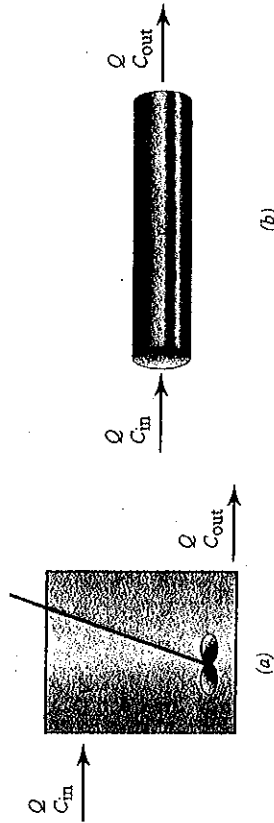


Figure 4-7. Completely mixed flow reactor (a) and plug-flow reactor (b) used to compare the two reactor types.

4.1.5.1 Comparison of the PFR to the CMFR

The ideal CMFR and the PFR are fundamentally different and thus behave differently. When a parcel of fluid enters the CMFR, it is immediately mixed throughout the entire volume of the CMFR. In contrast, each parcel of fluid entering the PFR remains separate during its passage through the reactor. These differences are highlighted using an example involving the continuous addition of a pollutant to each reactor, with destruction of the pollutant within the reactor according to first-order kinetics. The two reactors are depicted in Figure 4-7.

This example assumes that the incoming concentration (C_{in}), the flow rate (Q), and the first-order reaction rate constant (k) are known and are the same for both reactors. Then, two common problems are considered: (1) if the volume V is known (the same for both reactors), what is the resulting outlet concentration (C_{out}) exiting the CMFR and PFR? and (2) if an outlet concentration is specified,

Table 4-2. Comparison of CMFR and PFR Performance*

Example 1. Determine C_{out} , given C_{in} , V , Q , and k .†	
CMFR	PFR
$C_{out} = C_{in}/(1 + kV/Q)$	$C_{out} = C_{in} \exp(-kV/Q)$
$C_{out}/C_{in} = 0.50$	$C_{out}/C_{in} = 0.37$
Example 2. Determine V , given C_{in} , C_{out} , Q , and k .‡	
CMFR	PFR
$V = (C_{in}/C_{out} - 1) \times (Q/k)$	$V = -(Q/k) \ln(C_{out}/C_{in})$
$V = 1,900 L$	$V = 300 L$

*Example 1 compares the effluent concentration (C_{out}) for a PFR and CMFR of the same volume; Example 2 compares the volume required for each reactor type if a given percent removal is required.

† $V = 100 L$, $Q = 5.0 L s^{-1}$, $k = 0.05 s^{-1}$.

‡ $C_{out}/C_{in} = 0.5$, $Q = 5.0 L s^{-1}$, $k = 0.05 s^{-1}$.

what volume of reactor is required for the CMFR and for the PFR? Table 4-2 summarizes the results of this comparison and lists the input variables.

The results shown in Table 4-2 indicate that, for equal reactor volumes, the PFR is more efficient than the CMFR and, for equal outlet concentrations, a smaller PFR is required. Why is this? The answer has to do with the fundamental difference between the two reactors—fluid parcels entering the PFR travel downstream without mixing, while fluid parcels entering the CMFR are immediately mixed with the low-concentration fluid within the reactor. Since the rate of chemical reaction is proportional to concentration, the result is that the rate of chemical reaction within the CMFR is reduced, relative to that within the PFR.

This effect is illustrated in Figure 4-8. The mass flux due to reaction is equal to $(-VkC)$ in both reactors. However, in the PFR, concentration decreases exponentially as each plug passes through the PFR, as shown by the solid curve in Figure 4-8. The average mass flux due to reaction in the PFR is simply the average value of this curve—the value indicated by the dashed line in Figure 4-8. In

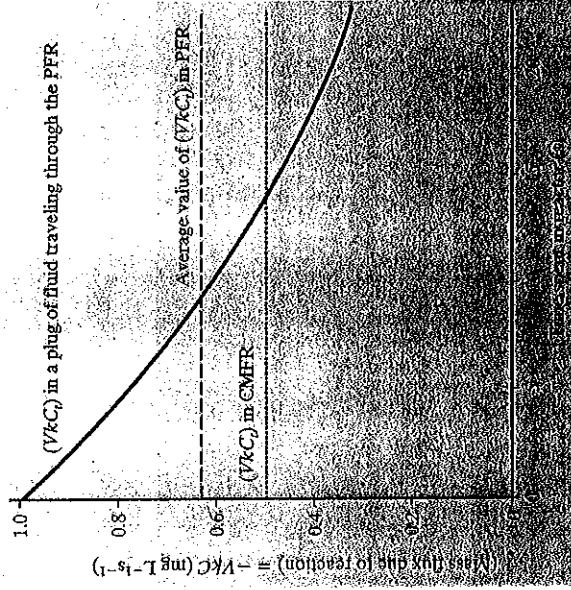


Figure 4-8. Origin of the higher destruction efficiency of a PFR under conditions of first-order decay. The rate of chemical destruction ($\dot{m}_{rxn} = -VkC$) is shown as a function of time spent in the reactor for a PFR (solid line) and CMFR (dotted line) for the conditions given in example 1 of Table 4-2. Since concentration changes as each plug passes through the PFR ($C = C_{in} \exp[-k\Delta t]$), the value of \dot{m}_{rxn} changes. The average rate of destruction in the PFR is shown by a dashed line. The rate of chemical destruction is constant throughout the well-mixed CMFR and is equal to $-VkC$. Since the high inlet concentration is diluted immediately upon entering the CMFR, the rate of reaction is lower than that throughout most of the PFR, and is lower than the average rate of reaction in the PFR.

contrast, dilution as the incoming fluid is mixed into the CMFR immediately reduces the influent concentration to that within the CMFR, resulting in a reduced rate of destruction, indicated by the dotted line in Figure 4-8.

4.1.5.1.1 Response to Inlet Spikes CMFRs and PFRs also differ in their response to spikes in the inlet concentration. In many pollution-control systems, inlet concentrations or flows are not constant. For example, flow into municipal wastewater-treatment plants varies dramatically over the course of each day. It is often necessary to ensure that a temporary increase in inlet concentration does not result in excessive outlet concentrations. This requires the use of CMFRs, as a result of the mixing that occurs within CMFRs but not within PFRs.

Consider the effect of a temporary doubling of the concentration entering a PFR and CMFR, each designed to reduce the influent concentration by the same amount, with the flow, first-order decay rate constant, and required degree of destruction equal to the values given in example 2 of Table 4-2.

The resulting changes in outlet concentration for the PFR and CMFR are shown in Figure 4-9. The concentration in fluid exiting the CMFR begins to rise

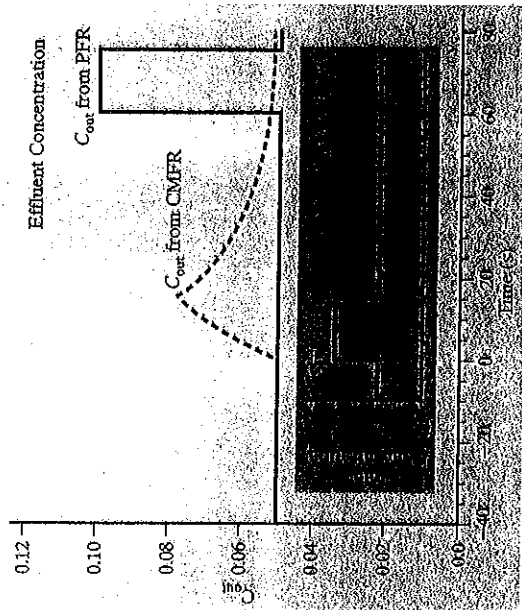


Figure 4-9. The response of a CMFR and PFR to a temporary increase in inlet concentration. The influent concentration, shown in the lower, inset figure, increases to 2.0 during the period $t = 0-15$ s. The resulting concentrations exiting the CMFR and PFR of example 2 of Table 4-2 are shown as a function of time before, during, and after the temporary doubling of inlet concentration. The concentration exiting the CMFR is shown with a dashed line; the concentration exiting the PFR is shown with a solid line. The maximum concentration reached in the CMFR effluent is less than that reached in the PFR effluent because the increased inlet concentration is diluted by the volume of lower-concentration fluid within the CMFR.

immediately after the inlet concentration increases, as the more concentrated flow is mixed throughout the CMFR. The outlet concentration does not immediately double in response to the doubled inlet concentration, however, as the higher-concentration influent flow is diluted by the volume of low-concentration fluid within the CMFR. The CMFR outlet concentration rises exponentially and would eventually double, but the inlet spike does not last long enough for this to occur. In contrast, the outlet concentration exiting the PFR does not change until enough time has passed for the first plug of higher-concentration fluid to traverse the length of the PFR. At that time, the outlet concentration doubles, and it remains elevated for a period equal to the duration of the inlet spike.

4.1.5.1.2 Selection of CMFR or PFR. Selection of a CMFR or PFR in an engineered system is based on the considerations just described—control efficiency as a function of reactor size, and response to changing inlet conditions. In many cases, a CMFR may be used to reduce sensitivity to spikes and be followed by a PFR for efficient use of resources.

In natural systems, the choice is based upon whether or not the system is mixed (in which case a CMFR would be used to model the system) or flows downstream without mixing (requiring use of a PFR). In some cases, it is necessary to use both the CMFR and PFR models. A common example of this occurs in cases involving effluent flow into a river. A CMFR is used to define a mixing problem, as was done in Example 4.2. This sets the inlet concentration for a PFR, which is used to model degradation of the pollutant as it flows further downstream. (This type of problem is investigated further in Chapter 5.)

EXAMPLE 4.3 REQUIRED VOLUME FOR PFR

Determine the volume required for a PFR to obtain the same degree of pollutant reduction as the CMFR in Example 4.3. Assume that the flow rate and first-order decay rate constant are unchanged ($Q = 50 \text{ m}^3 \text{ day}^{-1}$, $k = 0.216 \text{ day}^{-1}$).

SOLUTION

The CMFR in Example 4.3 achieved a pollutant decrease of $C_{\text{out}}/C_{\text{in}} = 32/100 = 0.32$. From Equation 4-19,

$$\frac{C_{\text{out}}}{C_{\text{in}}} = e^{-(kV/Q)}$$

or

$$0.32 = \exp - \frac{0.216 \text{ day}^{-1} V}{50 \text{ m}^3 \text{ day}^{-1}}$$

Solving for V ,

$$V = \ln(0.32) \times \frac{50 \text{ m}^3 \text{ day}^{-1}}{-0.216 \text{ day}^{-1}} = 264 \text{ m}^3$$

As expected, this volume is smaller than the 500 m³ required for the CMFR in Example 4.3.

4.1.6 Retention Time and Other Expressions for V/Q

A number of terms, including *retention time*, *detention time*, and *residence time*, are used to refer to the average period spent in a given control volume, θ . The retention time is given by

$$\theta = \frac{V}{Q} \quad (4-20) \text{Fu}$$

where V is the volume of the reactor, and Q is the total volumetric flow rate exiting the reactor.

Typical retention times in some engineered systems are shown in Table 4-3. Examples 4.7 and 4.8 illustrate the calculation and application of retention time.

Table 4-3. Typical Retention Times in Unit Processes Used for Treating Drinking Water and Wastewater

Unit Operation	Used for	Approximate Retention Time
<i>Wastewater Treatment</i>		
Grit removal	Removal of large particles (grit)	30 min
Primary settling	Removal of large solids	≤ 1 h
Secondary Settling	Removal of smaller solids	≤ 2 h
Activated sludge	Removal of organic matter using microorganisms and oxygen	4–8 h
Anaerobic digester	Stabilization of organic matter in sludge in absence of oxygen	15–30 days
<i>Drinking-water Treatment</i>		
Rapid-mix tank	Blending of chemical coagulants with water prior to treatment	< 1 min
Flocculator	Gentle mixing to promote flocculation of small particles	30 min
Disinfection	Destruction of pathogens	< 15 min

EXAMPLE 4-3 RETENTION TIME IN A CONTINUOUS FLOW REACTOR

Calculate the retention times in the CMFR of Example 4.3 and the PFR of Example 4.6.

SOLUTION

For the CMFR,

$$\theta = \frac{V}{Q} = \frac{500 \text{ m}^3}{50 \text{ m}^3 \text{ day}^{-1}} = 10 \text{ days}$$

For the PFR,

$$\theta = \frac{V}{Q} = \frac{264 \text{ m}^3}{50 \text{ m}^3 \text{ day}^{-1}} = 5.3 \text{ days}$$

EXAMPLE 4-4 RETENTION TIMES IN LAKE ONTARIO

The Great Lakes region is shown in Figure 4-10. Calculate the retention times for Lake Michigan and Lake Ontario using the data provided in Table 4-4.

SOLUTION

For Lake Michigan,

$$\theta = \frac{4,900 \times 10^9 \text{ m}^3}{36 \times 10^9 \text{ m}^3 \text{ yr}^{-1}} = 136 \text{ yr}$$

For Lake Ontario,

$$\theta = \frac{1,634 \times 10^9 \text{ m}^3}{212 \times 10^9 \text{ m}^3 \text{ yr}^{-1}} = 8 \text{ yr}$$

These values mean that Lake Michigan changes its water volume completely once every 136 years and Lake Ontario once every 8 years. The higher flow and smaller volume of Lake Ontario result in a significantly shorter retention time. This means that pollutant concentrations can increase in Lake Ontario much more quickly than they can in Lake Michigan, but it also means that concentrations will drop much more quickly in Lake Ontario if a pollutant source is eliminated, provided that flow out of the lakes is the dominant pollutant sink.

These values of θ can be used to determine whether it would be appropriate to model the lakes as CMFRs in a mass-balance problem. As discussed in Chapter

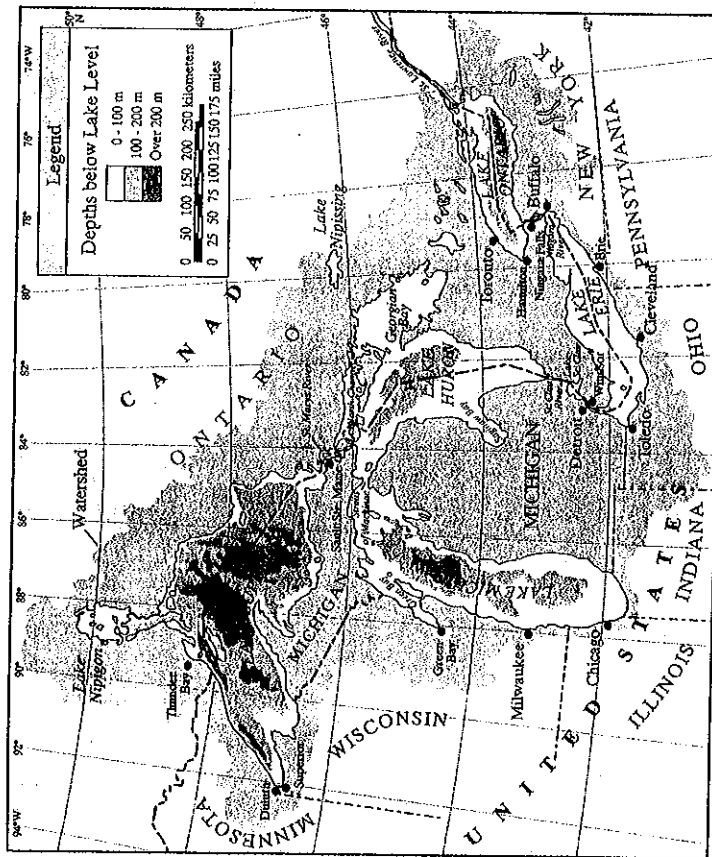


Figure 4-10. The North American Great Lakes. The Great Lakes are an important part of the physical and cultural heritage of North America. The Great Lakes contain approximately 18% of the world's supply of freshwater, making them the world's largest system of available surface freshwater (only the polar ice caps contain more freshwater). The first humans arrived in the area approximately 10,000 years ago. Around 6,000 years ago, copper mining began along the south shore of Lake Superior and hunting/fishing communities were established throughout the area. Population in the region in the sixteenth century is estimated at between 60,000 and 117,000, a level that resulted in few human disturbances. Today, the combined Canadian and U.S. population in the region exceeds 33 million. Increases in settlement and exploitation over the past two hundred years have caused many disturbances to the ecosystem. The outflow from the Great Lakes is less than 1% per year. Therefore, pollutants that enter the lakes by air, direct discharge, or from nonpoint pollution sources may remain in the system for a long period of time, as demonstrated in Example 4.8.

5. temperate lakes generally are mixed twice per year. Therefore, over the period required for water to flush through Lakes Michigan and Ontario, the lakes would be mixed many times. It would therefore be appropriate to model the lakes as CMFRs in mass balances involving pollutants that do not decay significantly in less than approximately 1 year.

Table 4-4. Volume and Flows for the Great Lakes

Lake	Volume 10^9 m^3	Outflow $10^9 \text{ m}^3 \text{ yr}^{-1}$
Superior	12,000	67
Michigan	4,900	36
Huron	3,500	161
Erie	468	182
Ontario	1,634	211

Source: Chapra and Reckhow, 1983.

4.2 ENERGY BALANCES

Modern society is dependent on the use of energy. Such use requires transformations in the form of energy and control of energy flows. For example, when coal is burned at a power plant, the chemical energy present in the coal is converted to heat, which is then converted in the plant's generators to electrical energy. Eventually, the electrical energy is converted back into heat for warmth or used to do work. However, energy flows and transformation can also cause environmental problems. For example, thermal heat energy from electrical power plants can result in increased temperatures in rivers used for cooling water, "greenhouse" pollutants in the atmosphere alter the energy balance of the Earth and may cause significant increases in global temperatures, and burning of fossil fuels to produce energy is associated with emissions of pollutants.

The movement of energy and changes in its form can be tracked using *energy balances*, which are analogous to mass balances. The first law of thermodynamics states that energy can neither be produced nor destroyed. Conservation of energy provides a basis for energy balances, just as the law of conservation of mass provides a basis for mass balances. However, all energy balances are treated as conservative; as long as all the possible forms of energy are considered (and in the absence of nuclear reactions), there is no term in energy balances that is analogous to the chemical-reaction term in mass balances.

4.2.1 Forms of Energy

The forms of energy can be divided into two types: *internal energy* and *external energy*. Energy that is a part of the molecular structure or organization of a given substance is internal. Energy that results from the location or motion of the substance is external. Examples of external energy include *gravitational potential energy* and *kinetic energy*. Gravitational potential energy is the energy gained when a mass is moved to a higher location above the Earth. Kinetic energy is the energy that results from the movement of objects. When a rock thrown off of a cliff accelerates toward the ground, the sum of kinetic and potential energy is

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