

Increased temperature results in a decrease in the solubility of carbon dioxide. Since marine waters are a major sink for carbon dioxide, this decrease in solubility could have a significant impact on the concentration of carbon dioxide in the atmosphere. Increases in the temperature of marine waters can also result in coral bleaching, the process whereby the coral polyp expels the algae (zooxanthellae). The exact mechanism is unknown, but it is known that other stresses, such as high light intensity, low salinity, and the presence of pollutants exacerbate the problem. Since the coral and algae have a symbiotic relationship, if the thermal stress lasts for an extended period of time, the corals become bleached and die. Mass coral bleaching began in 1980s due to steady rise in sea temperatures, pushing reef-building corals closer to their thermal maxima. At the current rate of bleaching, some scientists predict that Australia will lose all or most of its coral reefs by 2050.

### Nanoparticles

Nanoparticles are defined as those particles that have a dimension less than 100 nm. Included in this group of chemicals are naturally occurring humic material (derived from plant and animal matter); titania particles used in painkilling creams; fullerene nanotube composites used in the manufacture of tires, tennis rackets, and video screens; fullerene cages used in cosmetics; and protein-based nanomaterials used in the production of soaps, shampoos, and detergents (Wiesner et al., 2006). Fullerenes are a novel material fabricated from carbon, and exist as hollow spheres, ellipsoids, or tubes. Due to their unique properties (including high strength, electrical conductivity, and electron affinity), the commercial applications of these chemicals have grown almost exponentially in a very short time.

Responsible use of these materials necessitates an understanding of how the chemicals behave in the natural environment along with their impact on humans and other organisms. The size, chemical composition, surface structure and chemistry, solubility and shape will affect the interaction of nanoparticles with organisms. Those that are hydrophobic and lipophilic may accumulate in the tissue. As a result of their small size and large specific surface area, nanoparticles can sorb and transport toxic pollutants, which when inhaled can cause a number of pulmonary diseases in mammals, including lung granulomas (Guzman et al., 2006). Metal oxides have been shown to cause pulmonary inflammation in rodents and humans (Wiesner et al., 2006). Inhaled nanoparticles act more like a gas and have the ability to translocate in the body, traveling freely in the blood and reaching organs such as liver or brain. It is clear that much research needs to be accomplished to assess the environmental risks and impacts of these materials so that the field of nanotechnology can grow in a sustainable and responsible way.

## 9-3 WATER QUALITY MANAGEMENT IN RIVERS

The objective of water quality management is to control the discharge of pollutants so that water quality is not degraded to an unacceptable extent below the natural background level. Controlling waste discharges, however, must be a quantitative endeavor. We must be able to measure the pollutants, predict their effect on water quality, determine the background water quality that would be present without human intervention, and decide the levels acceptable for intended uses of the water.

To most people, the tumbling mountain brook, crystal clear and icy cold, fed by melting snow is safe to drink and the epitome of high water quality.\* Certainly a stream in that condition is a treasure, but we cannot expect the Mississippi River to have the same water quality. It never did and never will. Yet both need proper management if the water is to remain usable. The mountain brook may serve as the spawning ground for desirable fish and must be protected from heat

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\*Water from this stream may or may not be safe to drink, however appealing it may appear. Runoff containing pathogenic organisms, such as *Cryptosporidium parvum* and *Giardia lamblia*, excreted in the feces of wildlife can cause disease in humans. This is a good reason to disinfect all surface waters intended for human consumption.

and sediment as well as chemical pollution. The Mississippi, however, is already warmed from hundreds of kilometers of exposure to the sun and carries the sediment from thousands of square kilometers of land. But even the Mississippi can be damaged by organic matter and toxic chemicals. Fish do live there and the river is used as a water supply for millions of people.

The effect of pollution on a river depends both on the nature of the pollutant and the unique characteristics of the individual river.\* Some of the most important characteristics include the volume and speed of water flowing in the river, the river's depth, the type of bottom, and the surrounding vegetation. Other factors include the climate of the region, the mineral heritage of the watershed, land use patterns, and the types of aquatic life in the river. Water quality management for a particular river must consider all these factors. Thus, some rivers are highly susceptible to pollutants such as sediment, salt, and heat, whereas others can tolerate large inputs of these pollutants without much damage.

Some pollutants, particularly oxygen-demanding wastes and nutrients, are so common and have such a profound effect on almost all types of rivers that they deserve special emphasis. This is not to say that they are always the most significant pollutants in any one river, but rather that no other pollutant category has as much overall effect on our nation's rivers. For these reasons, the next sections of this chapter will be devoted to a more detailed look at how oxygen-demanding material and nutrients affect water quality in rivers.

### Effect of Oxygen-Demanding Wastes on Rivers

The introduction of oxygen-demanding material, either organic or inorganic, into a river depletes the dissolved oxygen in the water. This poses a threat to fish and other higher forms of aquatic life if the concentration of oxygen falls below a critical point. To predict the extent of oxygen depletion, it is necessary to know how much waste is being discharged and how much oxygen will be required to degrade the waste. However, because oxygen is continuously being replenished from the atmosphere and from photosynthesis by algae and aquatic plants, as well as being consumed by organisms, the concentration of oxygen in the river is determined by the relative rates of these competing processes. Organic oxygen-demanding materials are commonly measured by determining the amount of oxygen consumed during degradation in a manner approximating degradation in natural waters. This section begins by considering the factors affecting oxygen consumption during the degradation of organic matter, then moves on to inorganic nitrogen oxidation. Finally, the equations for predicting dissolved oxygen concentrations in rivers from degradation of organic matter are developed and discussed.

### Biochemical Oxygen Demand

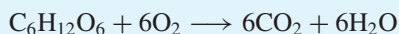
The amount of oxygen required to oxidize a substance to carbon dioxide and water may be calculated by stoichiometry if the chemical composition of the substance is known. This amount of oxygen is known as the **theoretical oxygen demand** (ThOD).

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\*Here we will use the word *river* to include streams, brooks, creeks, and any other channel of flowing, freshwater.

**EXAMPLE 9-1** Compute the ThOD of  $108.75 \text{ mg} \cdot \text{L}^{-1}$  of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ).

**Solution** We begin by writing a balanced equation for the reaction.



Next, compute the gram molecular weights of the reactants using the table on the inside front cover of the book.

Glucose	Oxygen
6C = 72	(6)(2)O = 192 g · mol <sup>-1</sup>
12H = 12	
6O = 96	
180 g · mol <sup>-1</sup>	

Thus, it takes 192 g of oxygen to oxidize 180 g of glucose to CO<sub>2</sub> and H<sub>2</sub>O.  
The ThOD of 108.75 mg · L<sup>-1</sup> of glucose is

$$(108.75 \text{ mg} \cdot \text{L}^{-1} \text{ of glucose}) \left( \frac{192 \text{ g} \cdot \text{mol}^{-1} \text{ O}_2}{180 \text{ g} \cdot \text{mol}^{-1} \text{ glucose}} \right) = 116 \text{ mg} \cdot \text{L}^{-1} \text{ O}_2$$

In contrast to the ThOD, the **chemical oxygen demand**, COD (pronounced “see oh dee”), is a measured quantity that does not depend on one’s knowledge of the chemical composition of the substances in the water. In the COD test, a strong chemical oxidizing agent (chromic acid) is mixed with a water sample and then refluxed. The difference between the amount of oxidizing agent at the beginning of the test and that remaining at the end is used to calculate the COD.

If the oxidation of an organic compound is carried out by microorganisms using the organic matter as a food source, the oxygen consumed is known as **biochemical oxygen demand**, or BOD (pronounced “bee oh dee”). The test is a bioassay that uses microorganisms in conditions similar to those in natural water to measure indirectly the amount of biodegradable organic matter present. **Bioassay** means to measure by biological means. The actual BOD is almost always less than the ThOD due to the incorporation of some of the carbon into new bacterial cells. Thus, a portion of soluble carbon is removed but will not be measured in the BOD test.

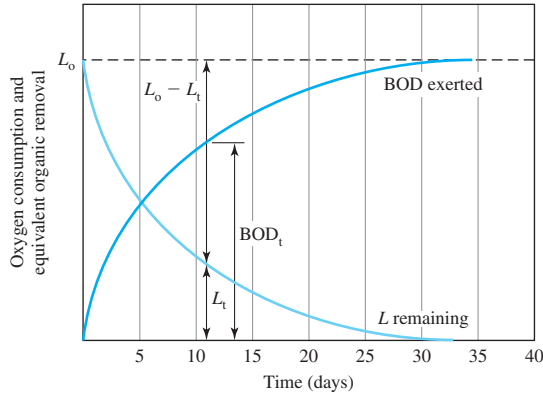
To measure the BOD of a water, a water sample is inoculated with bacteria that consume the biodegradable organic matter to obtain energy for their life processes. Because the organisms also use oxygen in the process of consuming the waste, the process is called **aerobic decomposition**. This oxygen consumption is easily measured. The greater the amount of organic matter present, the greater the amount of oxygen used. The BOD test is an indirect measurement of organic matter because we actually measure only the change in dissolved oxygen concentration caused by the microorganisms as they degrade the organic matter. Although not all organic matter is biodegradable and the actual test procedures lack precision, the BOD test is still the most widely used method of measuring organic matter because of the direct conceptual relationship between BOD and oxygen depletion in receiving waters.

Only under rare circumstances will the ThOD and the COD be equal. If the chemical composition of all of the substances in the water is known and they are capable of being completely oxidized chemically, then the two measures of oxygen demand will be the same. A waste containing only simple sugars would fall into this category. The BOD is never equal to the ThOD or COD because some carbon is always converted to biomass or waste organic compounds and this soluble organic matter, which is removed during the test, is not measured, as discussed earlier.

When a water sample containing degradable organic matter is placed in a closed container and inoculated with bacteria, the oxygen consumption typically follows the pattern shown in Figure 9–8. During the first few days the rate of oxygen depletion is rapid because of the high concentration of organic matter present. As the concentration of organic matter decreases, so does the rate of oxygen consumption. During the last part of the BOD curve, oxygen consumption is

FIGURE 9-8

BOD and oxygen-equivalent relationships.



mostly associated with the decay of the bacteria that grew during the early part of the test. It is generally assumed that the rate at which oxygen is consumed is directly proportional to the concentration of degradable organic matter remaining at any time. As a result, the BOD curve in Figure 9-8 can be described mathematically as a first-order reaction. Using our definition of reaction rate and reaction order from Chapter 4, this may be expressed as

$$\frac{dL}{dt} = -r_A \quad (9-1)$$

where  $L$  = oxygen equivalent of the organic chemicals remaining (in  $\text{mg} \cdot \text{L}^{-1}$ )

$$-r_A = -kL$$

$k$  = reaction rate constant (in  $\text{days}^{-1}$ )

Rearranging Equation 9-1 and integrating yields

$$\frac{dL}{L} = -k dt \quad (9-2)$$

$$\int_{L_0}^{L_t} \frac{dL}{L} = -k \int_0^t dt \quad (9-3)$$

$$\ln \frac{L_t}{L_0} = -kt \quad (9-4)$$

or

$$L_t = L_0 e^{-kt} \quad (9-5)$$

where  $L_0$  = oxygen equivalent of organics at time = 0

$L_t$  = oxygen equivalent of the organic chemicals remaining at time,  $t$  ( $\text{mg} \cdot \text{L}^{-1}$ )

Rather than  $L_t$ , our interest is in the amount of oxygen used in the consumption of the organics ( $\text{BOD}_t$ ). From Figure 9-8, it is obvious that  $\text{BOD}_t$  is the difference between the initial value of  $L_0$  and  $L_t$ , so

$$\begin{aligned} \text{BOD}_t &= L_0 - L_t \\ &= L_0 - L_0 e^{-kt} \\ &= L_0(1 - e^{-kt}) \end{aligned} \quad (9-6)$$

$L_0$  is often referred to as the **ultimate BOD**, that is, the maximum oxygen consumption possible when the waste has been completely degraded. Equation 9-6 is called the BOD rate equation. Note that lowercase  $k$  is used for the reaction rate constant in base  $e$ .

**EXAMPLE 9-2** If the 3-day BOD ( $BOD_3$ ) of a waste is  $75 \text{ mg} \cdot \text{L}^{-1}$  and the BOD decay constant,  $k$ , is  $0.345 \text{ day}^{-1}$ , what is the ultimate BOD?

**Solution** Substitute the given values into Equation 9-6 and solve for the ultimate BOD,  $L_o$ .

$$75 = L_o(1 - e^{-(0.345 \text{ days}^{-1})(3 \text{ days})}) = 0.645L_o$$

or

$$L_o = \frac{75}{0.645} = 116 \text{ mg} \cdot \text{L}^{-1}$$

You should note that the ultimate BOD ( $L_o$ ) is defined as the maximum BOD exerted by the waste. It is denoted by the horizontal dotted line in Figure 9-8. Because  $BOD_t$  approaches  $L_o$  asymptotically, it is difficult to assign an exact time to achieve the ultimate BOD. Indeed, based on Equation 9-1, it is achieved only in the limit as  $t$  approaches infinity. However, from a practical point of view, we can observe that when the BOD curve is approximately horizontal, the ultimate BOD has been achieved. In Figure 9-8, we would take this to be at about 35 days. In computations, we use a rule of thumb that if  $BOD_t$  and  $L_o$  agree when rounded to three significant figures, then the time to reach ultimate BOD has been achieved. Given the uncertainties of the BOD test, there are occasions when rounding to two significant figures would be realistic.

Although the ultimate BOD best expresses the concentration of degradable organic matter, it does not, by itself, indicate how rapidly oxygen will be depleted in a receiving water. Oxygen depletion is related to both the ultimate BOD and the BOD rate constant ( $k$ ). Although the ultimate BOD increases in direct proportion to the concentration of degradable organic matter, the numerical value of the rate constant is dependent on the following:

1. The nature of the waste
2. The ability of the organisms in the system to use the waste
3. The temperature

**Nature of the Waste.** There are thousands of naturally occurring organic compounds, and not all of them can be degraded with equal ease. Simple sugars and starches are rapidly degraded and will therefore have a very large BOD rate constant. Cellulose (for example, toilet paper) degrades much more slowly, and compounds such as the higher molecular weight polycyclic aromatic hydrocarbons, highly chlorinated compounds such as DDT, chlorpyrifos, PCBs, caffeine, or many of the estrogenic compounds used in birth control pills are almost undegradable in the BOD test or in conventional wastewater treatment. In some cases, as with many of the phenolic compounds, the compound is actually toxic to the microorganisms, killing them so that little or no degradation of the waste can occur. Other compounds are intermediate between these extremes. The BOD rate constant for a complex waste depends very much on the relative proportions of the various components. Table 9-3 is a summary of typical BOD rate constants. The lower rate constants for treated sewage compared with raw sewage result from the fact that easily degradable organics are more completely removed than less readily degradable organics during wastewater treatment.

**Ability of Organisms to Use Waste.** Any given microorganism is limited in its ability to use organic compounds. As a consequence, many organic compounds can be degraded by only a small group of microorganisms. In a natural environment receiving a continuous discharge

**TABLE 9-3** Typical Values for the BOD Rate Constant

Sample	$k(20^{\circ}\text{C})$ ( $\text{day}^{-1}$ )
Raw sewage	0.35–0.70
Well-treated sewage	0.12–0.23
Polluted river water	0.12–0.23

of organic waste, that population of organisms that can most efficiently use this waste will predominate. However, the culture used to inoculate the sample used in the BOD test may contain only a very small number of organisms that can degrade the particular organic compounds in the waste. This problem is especially common when analyzing industrial wastes. The result is that the BOD rate constant would be lower in the laboratory test than in the natural water. To avoid this undesirable outcome the BOD test should be conducted with organisms that have been acclimated\* to the waste so that the rate constant determined in the laboratory is comparable to that in the river.

**Temperature.** Most biological processes speed up as the temperature increases and slow down as the temperature drops. Because oxygen use is caused by the metabolism of microorganisms, the rate of its use is similarly affected by temperature. Ideally, the BOD rate constant should be experimentally determined for the temperature of the receiving water. There are two difficulties with this ideal. Often the temperature of the receiving water changes throughout the year, so a large number of tests would be required to define  $k$ . An additional difficulty is the task of comparing data from various locations having different temperatures. Laboratory testing is therefore done at a standard temperature of  $20^{\circ}\text{C}$ , and the BOD rate constant is adjusted to the temperature of the receiving water using the following expression.

$$k_T = k_{20}(\theta)^{T-20} \quad (9-7)$$

where  $T$  = temperature of interest (in  $^{\circ}\text{C}$ )

$k_T$  = BOD rate constant at the temperature of interest (in  $\text{days}^{-1}$ )

$k_{20}$  = BOD rate constant determined at  $20^{\circ}\text{C}$  (in  $\text{days}^{-1}$ )

$\theta$  = temperature coefficient. For typical domestic wastewater, this has a value of 1.135 for temperatures between  $4$  and  $20^{\circ}\text{C}$  and 1.056 for temperatures between  $20$  and  $30^{\circ}\text{C}$ . (Schroepfer, Robins, and Susag, 1964)

\*The word *acclimated* means that the organisms have had time to adapt their metabolisms to the waste or that organisms that can use the waste have been given the chance to predominate in the culture.

**EXAMPLE 9-3** A waste is being discharged into a river that has a temperature of  $10^{\circ}\text{C}$ . What fraction of the maximum oxygen consumption has occurred in 4 days if the BOD rate constant,  $k$ , determined in the laboratory under standard conditions is  $0.115 \text{ day}^{-1}$ ? (*Note:* All rate constants are base  $e$ .)

**Solution** Determine the BOD rate constant,  $k$ , for the waste at the river temperature using Equation 9-7.

$$\begin{aligned} k_{10^{\circ}\text{C}} &= 0.115(1.135)^{10-20} \\ &= 0.032 \text{ day}^{-1} \end{aligned}$$

Use this value of  $k$  in Equation 9-6 to find the fraction of maximum oxygen consumption occurring in 4 days.

$$\begin{aligned}\frac{\text{BOD}_4}{L_0} &= [1 - e^{-(0.032 \text{ days}^{-1})(4 \text{ days})}] \\ &= 0.12\end{aligned}$$

### Laboratory Measurement of Biochemical Oxygen Demand

To be as consistent as possible, it is important to standardize testing procedures when measuring BOD. In the paragraphs that follow, the standard BOD test is outlined with emphasis placed on the reason for each step rather than the details. The detailed procedures can be found in *Standard Methods for the Examination of Water and Wastewater* (Eaton et al., 2005), which is the authoritative reference of testing procedures in the water pollution control field.

**Step 1.** A special 300-mL BOD bottle (Figure 9-9) is completely filled with a sample of water that has been appropriately diluted and inoculated with microorganisms. The bottle is then stoppered to exclude air bubbles. Samples require dilution because the only oxygen available to the organisms is dissolved in the water. The most oxygen that can dissolve is about  $9 \text{ mg} \cdot \text{L}^{-1}$ , so the BOD of the diluted sample should be between 2 and  $6 \text{ mg} \cdot \text{L}^{-1}$ . Samples are diluted with a special dilution water that contains all of the trace elements required for bacterial metabolism so that degradation of the organic matter is not limited by lack of bacterial growth. The dilution water also contains an inoculum of microorganisms so that all samples tested on a given day contain approximately the same type and number of microorganisms.

**FIGURE 9-9**

#### BOD Bottles

The point on the end of the stopper is to ensure that no air is trapped in the bottle. The bottle in the center is shown with the stopper in place. Water is placed in the small cup formed by the lip. This acts as a seal to further exclude air. The bottle on the right is shown with plastic wrap over the stopper. This is to prevent evaporation of the water seal.



The ratio of undiluted to diluted sample is called the **sample size**, usually expressed as a percentage, while the inverse relationship is called the **dilution factor**. Mathematically, these are

$$\text{Sample size (\%)} = \frac{\text{volume of undiluted sample}}{\text{volume of diluted sample}} \times 100 \quad (9-8)$$

$$\text{Dilution factor} = P = \frac{\text{volume of wastewater sample}}{\text{volume of wastewater plus dilution water}} \quad (9-9)$$

The appropriate sample size to use can be determined by dividing  $4 \text{ mg} \cdot \text{L}^{-1}$  (the midpoint of the desired range of diluted BOD) by the estimated BOD concentration in the sample being tested. A convenient volume of undiluted sample is then chosen to approximate this sample size. The dilution factors given earlier are not to be used when the sample size is small compared with the total volume because under such conditions the seed/dilution water will contribute significantly to the BOD. For low dilutions, the more complex equation given in Equation 9-10a should be used.

**EXAMPLE 9-4** The BOD of a wastewater sample is estimated to be  $180 \text{ mg} \cdot \text{L}^{-1}$ . What volume of undiluted sample should be added to a 300-mL bottle? Also, what are the sample size and dilution factor using this volume? Assume that  $4 \text{ mg} \cdot \text{L}^{-1}$  BOD can be consumed in the BOD bottle.

**Solution 1** Estimate the sample size needed.

$$\text{Sample size} = \frac{4 \text{ mg} \cdot \text{L}^{-1}}{180 \text{ mg} \cdot \text{L}^{-1}} \times 100 = 2.22\%$$

Estimate the volume of undiluted sample needed because the volume of diluted sample is 300 mL.

$$\text{Volume of undiluted sample} = 0.0222 \times 300 \text{ mL} = 6.66 \text{ mL}$$

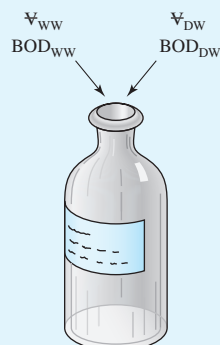
Therefore a convenient sample volume would be 7.00 mL.

Compute the actual sample size and dilution factor.

$$\text{Sample size} = \frac{7.00 \text{ mL}}{300 \text{ mL}} \times 100 = 2.33\%$$

$$\text{Dilution factor} = P = \frac{7 \text{ mL}}{300 \text{ mL}} = 0.0233$$

**Solution 2** Although environmental engineers have traditionally used this approach for determining dilution factors for BOD analysis, we could use a more fundamental approach: that of the mass-balance equation (which is inherently what was done in Solution 1). Let's think about what we are attempting to do. We have a BOD bottle to which we add wastewater and dilution water. The wastewater has an estimated BOD of  $180 \text{ mg} \cdot \text{L}^{-1}$ , and the dilution water has a BOD of zero.





The total volume in the BOD bottle is  $V_{ww} + V_{dw}$  or the volume of the wastewater plus the volume of the dilution water. The total mass of BOD in the BOD bottle can be calculated from  $BOD_{ww} \times V_{ww} + BOD_{dw} \times V_{ww} = (180 \text{ mg} \cdot \text{L}^{-1})(V_{ww}) + (0 \text{ mg} \cdot \text{L}^{-1})(V_{dw})$

We also know that the size of a BOD bottle is 300 mL, so that

$$V_{dw} + V_{ww} = 300 \text{ mL} = 0.300 \text{ L}$$

The problem statement indicates that we want a final concentration of BOD of  $4 \text{ mg} \cdot \text{L}^{-1}$ . Thus, the final mass of BOD in the bottle is

$$(4 \text{ mg} \cdot \text{L}^{-1})(0.300 \text{ L}) = 1.2 \text{ mg}$$

If we equate this to the total BOD we calculated earlier, then

$$BOD_{ww} \times V_{ww} + BOD_{dw} \times V_{ww} = (180 \text{ mg} \cdot \text{L}^{-1})(V_{ww}) + (0 \text{ mg} \cdot \text{L}^{-1})(V_{dw}) = 1.2 \text{ mg}$$

We can solve for  $V_{ww} = 1.2 \text{ mg} / 180 \text{ mg} \cdot \text{L}^{-1} = 0.00667 \text{ L}$ . Let's multiply this value by 1000 to obtain the answer in milliliters because that is the more appropriate answer: 6.67 mL. This is the same answer we obtained earlier. Again, as stated there, when actually performing a BOD analysis, you would choose a volume that is easier to dispense, such as 7.00 mL.

**Step 2.** Blank samples containing only the inoculated dilution water are also placed in BOD bottles and stoppered. Blanks are required to estimate the amount of oxygen consumed by the added inoculum in the absence of the sample.

**Step 3.** The stoppered BOD bottles containing diluted samples and blanks are incubated in the dark at 20°C for the desired number of days. For most purposes, a standard time of 5 days is used. To determine the ultimate BOD and the BOD rate constant, additional times are used. The samples are incubated in the dark to prevent photosynthesis from adding oxygen to the water and invalidating the oxygen consumption results. As mentioned earlier, the BOD test is conducted at a standard temperature of 20°C so that the effect of temperature on the BOD rate constant is eliminated and results from different laboratories can be compared.

**Step 4.** After the desired number of days has elapsed, the samples and blanks are removed from the incubator and the dissolved oxygen concentration in each bottle is measured. The BOD of the undiluted sample is then calculated using the following equation:

$$BOD_t = \frac{(DO_{b,t} - DO_{s,t})}{P} \tag{9-10}$$

where  $DO_{b,t}$  = dissolved oxygen concentration in blank (blank) after  $t$  days of incubation (in  $\text{mg} \cdot \text{L}^{-1}$ )

$DO_{s,t}$  = dissolved oxygen concentration in sample after  $t$  days of incubation (in  $\text{mg} \cdot \text{L}^{-1}$ )

$P$  = dilution factor

The preceding equation is valid only when the BOD of the seed water or the dilution water is negligible. If the BOD of the dilution or seed water is significant, then the following equation must be used.

$$BOD_t = \frac{(DO_{s,i} - DO_{s,t}) - (DO_{b,i} - DO_{b,t})f}{P} \tag{9-10a}$$

where  $DO_{b,t}$  and  $DO_{s,t}$  are defined earlier and

$DO_{s,i}$  = the initial DO of the sample

$DO_{b,i}$  = the initial DO of the blank (seed) control

$f$  = ratio of seed in diluted sample to seed in seed control

= (% seed in diluted sample)/(% seed in seed control)

= (volume of seed in diluted sample)/(volume of seed in seed control)

**EXAMPLE 9-5** What is the  $BOD_5$  of the wastewater sample of Example 9-4 if the DO values for the blank and diluted sample after 5 days are 8.7 and 4.2  $\text{mg} \cdot \text{L}^{-1}$ , respectively?

**Solution** Substitute the appropriate values into Equation 9-10.

$$BOD_5 = \frac{8.7 - 4.2}{0.0233} = 204.5, \text{ or } 205 \text{ mg} \cdot \text{L}^{-1}.$$

Note that because the sample was not seeded  $f = 1$ .

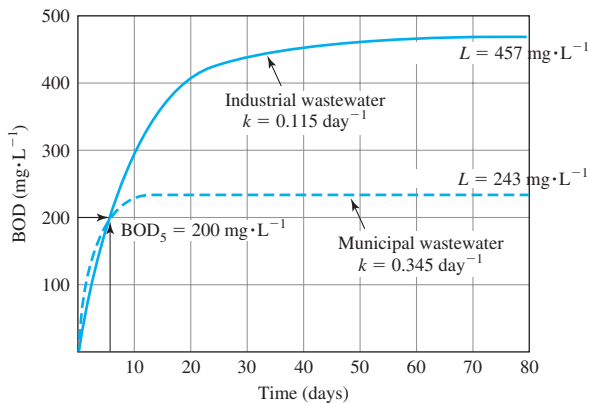
### Additional Notes on Biochemical Oxygen Demand

Although the 5-day BOD has been chosen as the standard value for most wastewater analysis and for regulatory purposes, ultimate BOD is actually a better indicator of total waste strength. For any one type of waste having a defined BOD rate constant, the ratio between ultimate BOD and  $BOD_5$  is constant so that  $BOD_5$  indicates relative waste strength. For different types of wastes having the same  $BOD_5$ , the ultimate BOD is the same only if, by chance, the BOD rate constants are the same. This is illustrated in Figure 9-10 for a municipal wastewater having a  $k = 0.345 \text{ day}^{-1}$  and an industrial wastewater having a  $k = 0.115 \text{ day}^{-1}$ . Although both wastewaters have a  $BOD_5$  of  $200 \text{ mg} \cdot \text{L}^{-1}$ , the industrial wastewater has a much higher ultimate BOD and can be expected to have a greater effect on dissolved oxygen in a river. For the industrial wastewater, a smaller fraction of the BOD was exerted in the first 5 days due to the lower rate constant.

Proper interpretation of  $BOD_5$  values can also be illustrated in another way. Consider a sample of polluted river water for which the following values were determined using standard laboratory techniques:  $BOD_5 = 50 \text{ mg} \cdot \text{L}^{-1}$ , and  $k = 0.2615 \text{ day}^{-1}$ . The ultimate BOD calculated from Equation 9-6 is, therefore,  $68 \text{ mg} \cdot \text{L}^{-1}$ . However, because the river temperature is  $10^\circ\text{C}$ , the  $k$  value in the river is calculated to be  $0.0737 \text{ day}^{-1}$  (using Equation 9-7). As shown graphically in Figure 9-11, the laboratory value of  $BOD_5$  seriously overestimates the actual oxygen

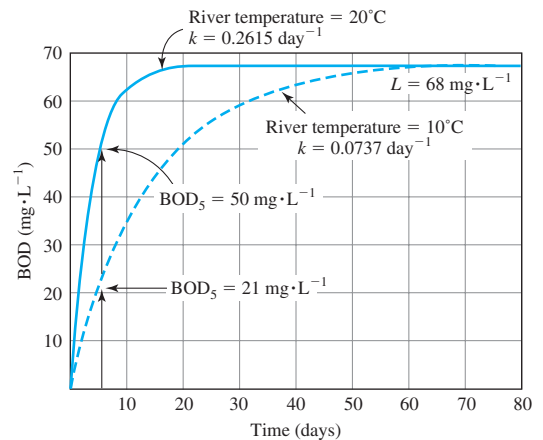
**FIGURE 9-10**

The effect of  $k$  on ultimate BOD for two wastewaters having the same  $BOD_5$ .



**FIGURE 9-11**

The effect of  $k$  on  $BOD_5$  when the ultimate BOD is constant.



consumption in the river. Again, a smaller fraction of the BOD is exerted in 5 days when the BOD rate constant is lower.

The 5-day BOD was chosen as the standard value for most purposes because the test was devised by sanitary engineers in England, where the River Thames has a travel time to the sea of less than 5 days, so there was no need to consider oxygen demand at longer times. Because no other time is any more rational than 5 days, this value has become firmly entrenched in the profession.

### Nitrogen Oxidation

Until now our unstated assumption has been that only the carbon in organic matter is oxidized. Actually many organic compounds, such as proteins, also contain nitrogen that can be oxidized with the consumption of molecular oxygen. Because the mechanisms and rates of nitrogen oxidation are distinctly different from those of carbon oxidation, the two processes must be considered separately. Logically, oxygen consumption due to oxidation of carbon is called **carbonaceous BOD** (CBOD), and that due to nitrogen oxidation is called **nitrogenous BOD** (NBOD).

The organisms that oxidize the carbon in organic compounds to obtain energy cannot oxidize the nitrogen in these compounds. Instead, the nitrogen is released into the surrounding water as ammonia ( $\text{NH}_3$ ). At normal pH values, this ammonia is actually in the form of the ammonium cation ( $\text{NH}_4^+$ ). The ammonia released from organic compounds, plus that from other sources such as industrial wastes and agricultural runoff (i.e., fertilizers), is oxidized to nitrate ( $\text{NO}_3^-$ ) by a special group of nitrifying bacteria as their source of energy in a process called **nitrification**. The overall reaction for ammonia oxidation (nitrification) is:



From this reaction the theoretical NBOD can be calculated as follows:

$$\begin{aligned} \text{NBOD} &= \frac{\text{grams of oxygen used}}{\text{grams of nitrogen oxidized}} = \frac{(2 \text{ moles})(32 \text{ g O}_2 \cdot \text{mol}^{-1})}{(1 \text{ mole})(14 \text{ g N} \cdot \text{mol}^{-1})} \\ &= 4.57 \text{ g O}_2 \cdot \text{g}^{-1} \text{ N} \end{aligned} \quad (9-12)$$

The actual nitrogenous BOD is slightly less than the theoretical value due to the incorporation of some of the nitrogen into new bacterial cells, but the difference is only a few percent.

Because nitrogen can be present in numerous forms ( $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and various organic compounds), it is often convenient to report concentrations of nitrogenous compounds in units of milligrams per liter as N. For example, it is often convenient for environmental engineers to report ammonia concentrations as “ammonia nitrogen,” that is as  $\text{NH}_3\text{-N}$ .

- EXAMPLE 9-6** (a) Compute the theoretical NBOD of a wastewater containing  $30 \text{ mg} \cdot \text{L}^{-1}$  of ammonia as nitrogen.  
 (b) If the wastewater analysis was reported as  $30 \text{ mg} \cdot \text{L}^{-1}$  of ammonia ( $\text{NH}_3$ ), what would the theoretical NBOD be?

**Solution** In the first part of the problem, the amount of ammonia was reported as  $\text{NH}_3\text{-N}$ . Therefore, we can use the theoretical relationship developed from Equation 9-11.

$$\text{Theoretical NBOD} = (30 \text{ mg NH}_3\text{-N} \cdot \text{L}^{-1})(4.57 \text{ mg O}_2 \cdot \text{mg}^{-1} \text{ N}) = 137 \text{ mg O}_2 \cdot \text{L}^{-1}$$

To answer part (b), we must convert milligrams per liter of ammonia to milligrams per liter as  $\text{NH}_3\text{-N}$  by multiplying by the ratio of gram molecular weights of N to  $\text{NH}_3$ .

$$(30 \text{ mg NH}_3 \cdot \text{L}^{-1}) \left( \frac{14 \text{ g N} \cdot \text{mol}^{-1}}{17 \text{ g NH}_3 \cdot \text{mol}^{-1}} \right) = 24.7 \text{ mg N} \cdot \text{L}^{-1}$$

Now we may use the relationship developed from Equation 9-11.

$$\text{Theoretical NBOD} = (24.7 \text{ mg N} \cdot \text{L}^{-1}) \left( \frac{4.57 \text{ mg O}_2}{\text{mg N}} \right) = 113 \text{ mg O}_2 \cdot \text{L}^{-1}$$

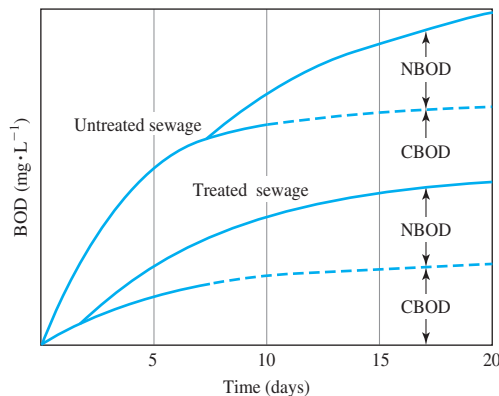
The rate at which the NBOD is exerted depends heavily on the number of nitrifying organisms present. Few of these organisms occur in untreated sewage, but the concentration is high in a well-treated effluent. When samples of untreated and treated sewage are subjected to the BOD test, oxygen consumption follows the pattern shown in Figure 9-12. In the case of untreated sewage, the NBOD is exerted after much of the CBOD has been exerted. The lag is due to the time it takes for the nitrifying bacteria to reach a sufficient population for the amount of NBOD exertion to be significant compared with that of the CBOD. In the case of the treated sewage, a higher population of nitrifying organisms in the sample reduces the lag time. Once nitrification begins, however, the NBOD can be described by Equation 9-6 with a BOD rate constant comparable to that for the CBOD of a well-treated effluent ( $k = 0.80$  to  $0.20 \text{ day}^{-1}$ ). Because the lag before the nitrogenous BOD is highly variable,  $\text{BOD}_5$  values are often difficult to interpret. When measurement of only carbonaceous BOD is desired, chemical inhibitors are added to stop the nitrification process. The rate constant for nitrification is also affected by temperature and can be adjusted using Equation 9-7.

### DO Sag Curve

The concentration of dissolved oxygen in a river is an indicator of the general health of the river. All rivers have some capacity for self-purification. As long as the discharge of oxygen-demanding wastes is well within the self-purification capacity, the DO level will remain high, and a diverse population of plants and animals, including game fish, can be found. As the amount of waste increases, the self-purification capacity can be exceeded, causing detrimental changes in plant and animal life. The stream loses its ability to cleanse itself, and the DO level decreases. When the DO drops below about  $4$  to  $5 \text{ mg} \cdot \text{L}^{-1}$ , most game fish will have been driven out. If the DO is completely removed, fish and other higher animals are killed or driven out, and

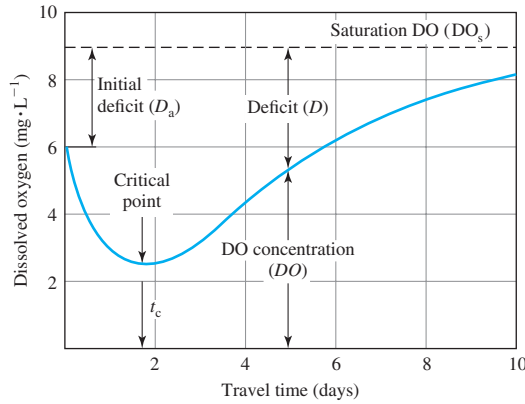
**FIGURE 9-12**

BOD curves showing both carbonaceous (CBOD) and nitrogenous (NBOD) BOD.



**FIGURE 9-13**

Typical DO sag curve.



extremely noxious conditions result. The water becomes blackish and foul-smelling as the sewage and dead animal life decompose under anaerobic conditions (i.e., without oxygen).

One of the major tools of water quality management in rivers is assessing the capability of a stream to absorb a waste load. This is done by determining the profile of DO concentration downstream from a waste discharge. This profile is called the DO sag curve (Figure 9–13) because the DO concentration dips as oxygen-demanding materials are oxidized and then rises again further downstream as the oxygen is replenished from the atmosphere and photosynthesis. As depicted in Figure 9–14, the biota of the stream are often a reflection of the dissolved oxygen conditions in the stream.

To develop a mathematical expression for the DO sag curve, the sources of oxygen and the factors affecting oxygen depletion must be identified and quantified. The only significant sources of oxygen are reaeration from the atmosphere and photosynthesis of aquatic plants. Oxygen depletion is caused by a larger range of factors, the most important being the BOD, both carbonaceous and nitrogenous, of the waste discharge, and the BOD already in the river upstream of the waste discharge. The second most important factor is that the DO in the waste discharge is

**FIGURE 9-14**

Oxygen sag downstream of an organic source.

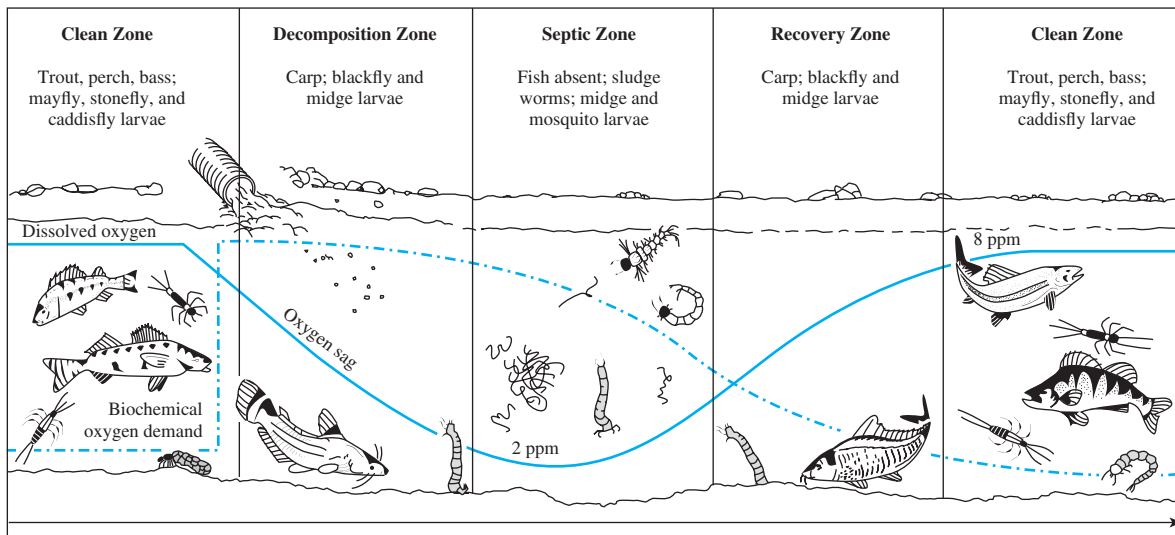


FIGURE 9-15

Schematic diagram of the mixing of the waste stream.

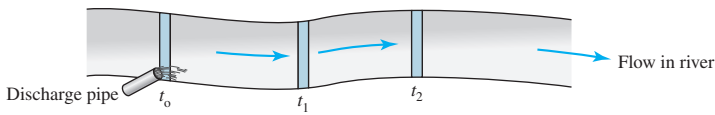
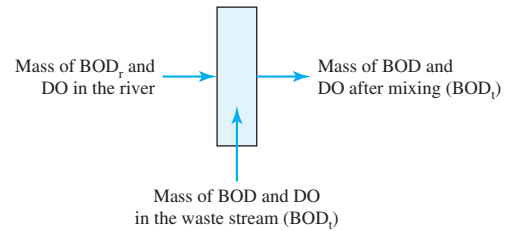


FIGURE 9-16

Mass-balance diagram for BOD and DO mixing.



usually less than that in the river. Thus, the DO at the river is often reduced as soon as the waste is added, even before any BOD is exerted. Other factors affecting dissolved oxygen depletion include nonpoint source pollution, the respiration of organisms living in the sediments (**benthic demand**), and the respiration of aquatic plants. Following the classical approach, the DO sag curve equation will be developed by considering only initial DO reduction, ultimate BOD, and reaeration from the atmosphere.

**Mass-Balance Approach.** Simplified mass balances help us understand and solve the DO sag curve problem. Three conservative (those without chemical reaction) mass balances may be used to account for initial mixing of the waste stream and the river. DO, ultimate BOD, and temperature all change as the result of mixing of the waste stream and the river. Once these are accounted for, the DO sag curve may be viewed as a nonconservative mass balance, that is, one with reactions. We can illustrate the mixing of the waste stream and the transport of the waste using the schematic diagram in Figure 9-15.

Through the discharge pipe, the waste stream flows into the river. The rectangle across the river at the location of the discharge pipe becomes the control volume around which we will develop our mass-balance expression. We will assume that the pollutant discharged from the pipe remains in this control volume and the entire volume moves downstream as a single entity. At time zero the volume is located at the pipe. The diagram illustrates the location of the volume at two subsequent times. For this case, we have two inputs and one output. The conservative mass-balance diagram for oxygen (mixing only) is shown in Figure 9-16. The product of the water flow and the DO concentration yields a mass of oxygen per unit of time.

$$\text{Mass of DO in wastewater} = Q_w \text{DO}_w \quad (9-13)$$

$$\text{Mass of DO in river} = Q_r \text{DO}_r \quad (9-14)$$

where  $Q_w$  = volumetric flow rate of wastewater (in  $\text{m}^3 \cdot \text{s}^{-1}$ )

$Q_r$  = volumetric flow rate of the river (in  $\text{m}^3 \cdot \text{s}^{-1}$ )

$\text{DO}_w$  = dissolved oxygen concentration in the wastewater (in  $\text{g} \cdot \text{m}^{-3}$ )

$\text{DO}_r$  = dissolved oxygen concentration in the river (in  $\text{g} \cdot \text{m}^{-3}$ )

The mass of DO in the river after mixing equals the sum of the mass fluxes.

$$\text{Mass of DO after mixing} = Q_w \text{DO}_w + Q_r \text{DO}_r \quad (9-15)$$

In a similar fashion for ultimate BOD,

$$\text{Mass of BOD after mixing} = Q_w L_w + Q_r L_r \quad (9-16)$$

where  $L_w$  = ultimate BOD of the wastewater (in  $\text{mg} \cdot \text{L}^{-1}$ )

$L_r$  = ultimate BOD of the river (in  $\text{mg} \cdot \text{L}^{-1}$ )

The concentrations of DO and BOD after mixing are the respective masses per unit time divided by the total flow rate (i.e., the sum of the wastewater and river flows).

$$\text{DO} = \frac{Q_w \text{DO}_w + Q_r \text{DO}_r}{Q_w + Q_r} \quad (9-17)$$

$$L_a = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r} \quad (9-18)$$

where  $L_a$  = initial ultimate BOD after mixing.

**EXAMPLE 9-7** The town of Aveta discharges  $17,360 \text{ m}^3 \cdot \text{day}^{-1}$  of treated wastewater into the Tefnet Creek. The treated wastewater has a  $\text{BOD}_5$  of  $12 \text{ mg} \cdot \text{L}^{-1}$  and a BOD decay constant,  $k$ , of  $0.12 \text{ day}^{-1}$  at  $20^\circ\text{C}$ . Tefnet Creek has a flow rate of  $0.43 \text{ m}^3 \cdot \text{s}^{-1}$  and an ultimate BOD,  $L_o$ , of  $5.0 \text{ mg} \cdot \text{L}^{-1}$ . The DO of the river is  $6.5 \text{ mg} \cdot \text{L}^{-1}$  and the DO of the wastewater is  $1.0 \text{ mg} \cdot \text{L}^{-1}$ . Compute the DO and initial ultimate BOD,  $L_o$ , after mixing.

**Solution** The DO after mixing is given by Equation 9-17. To use this equation we must convert the wastewater flow to compatible units, that is, to cubic meters per second.

$$Q_w = \frac{(17,360 \text{ m}^3 \cdot \text{day}^{-1})}{(86,400 \text{ s} \cdot \text{day}^{-1})} = 0.20 \text{ m}^3 \cdot \text{s}^{-1}$$

The DO after mixing is then

$$\text{DO} = \frac{(0.20 \text{ m}^3 \cdot \text{s}^{-1})(1.0 \text{ mg} \cdot \text{L}^{-1}) + (0.43 \text{ m}^3 \cdot \text{s}^{-1})(6.5 \text{ mg} \cdot \text{L}^{-1})}{0.20 \text{ m}^3 \cdot \text{s}^{-1} + 0.43 \text{ m}^3 \cdot \text{s}^{-1}} = 4.75 \text{ mg} \cdot \text{L}^{-1}$$

Before we can determine the initial ultimate BOD after mixing, we must first determine the ultimate BOD of the wastewater. Solving Equation 9-6 for the ultimate BOD,  $L_o$ :

$$L_o = \frac{\text{BOD}_5}{(1 - e^{-kt})} = \frac{12 \text{ mg} \cdot \text{L}^{-1}}{(1 - e^{-(0.12 \text{ day}^{-1})(5 \text{ days})})} = \frac{12 \text{ mg} \cdot \text{L}^{-1}}{(1 - 0.55)} = 26.6 \text{ mg} \cdot \text{L}^{-1}$$

Note that we used the subscript of 5 days in  $\text{BOD}_5$  to determine the value of  $t$  in the equation. Now setting  $L_w = L_o$ , we can determine the initial ultimate BOD after mixing,  $L_a$ , using Equation 9-18.

$$L_a = \frac{(0.20 \text{ m}^3 \cdot \text{s}^{-1})(26.6 \text{ mg} \cdot \text{L}^{-1}) + (0.43 \text{ m}^3 \cdot \text{s}^{-1})(5.0 \text{ mg} \cdot \text{L}^{-1})}{0.20 \text{ m}^3 \cdot \text{s}^{-1} + 0.43 \text{ m}^3 \cdot \text{s}^{-1}} = 11.86, \text{ or } 12 \text{ mg} \cdot \text{L}^{-1}$$

For temperature, we must consider a heat balance rather than a mass balance. This is an application of a fundamental principle of physics:

$$\text{Loss of heat by hot bodies} = \text{gain of heat by cold bodies} \quad (9-19)$$

The **change in enthalpy** or “heat content” of a mass of a substance may be defined by the following equation:

$$H = mC_p \Delta T \quad (9-20)$$

where  $H$  = change in enthalpy (in J)

$m$  = mass of substance (in g)

$C_p$  = specific heat at constant pressure (in  $J \cdot g^{-1} \cdot K^{-1}$ )

$\Delta T$  = change in temperature (in K)

The specific heat of water varies slightly with temperature. A value of 4.19 will be a satisfactory approximation for the range of temperatures usually found in the natural environment. Using our fundamental heat loss = heat gain equation, we may write

$$(m_w)(4.19)\Delta T_w = (m_r)(4.19)\Delta T_r \quad (9-21)$$

The temperature after mixing is found by solving this equation for the final temperature by recognizing that  $\Delta T$  on each side of the equation is the difference between the final river temperature ( $T_f$ ) and the starting temperature of the wastewater and the river water, respectively.

$$T_f = \frac{Q_w T_w + Q_r T_r}{Q_w + Q_r} \quad (9-22)$$

**Oxygen Deficit.** The DO sag equation has been developed using oxygen deficit rather than dissolved oxygen concentration, to make it easier to solve the integral equation that results from the mathematical description of the mass balance. The oxygen deficit is the difference between the saturation value (at the particular temperature of the water) and the actual dissolved oxygen concentration

$$D = DO_s - DO \quad (9-23)$$

where  $D$  = oxygen deficit (in  $mg \cdot L^{-1}$ )

$DO_s$  = saturation concentration of dissolved oxygen (in  $mg \cdot L^{-1}$ )

$DO$  = actual concentration of dissolved oxygen (in  $mg \cdot L^{-1}$ )

The saturation value of dissolved oxygen is heavily dependent on water temperature; it decreases as the temperature increases. Values of  $DO_s$  for freshwater are given in Table A-2 of Appendix A.

**Initial Deficit.** The beginning of the DO sag curve occurs at the point where a waste discharge mixes with the river. The initial deficit is calculated as the difference between saturated DO and the concentration of the DO after mixing (Equation 9-17).

$$D_a = DO_s - \frac{Q_w DO_w + Q_r DO_r}{Q_{mix}} \quad (9-24)$$

where  $D_a$  = initial deficit after river and waste have mixed (in  $mg \cdot L^{-1}$ )

$DO_s$  = saturation concentration of dissolved oxygen at the temperature of the river after mixing (in  $mg \cdot L^{-1}$ )

**EXAMPLE 9-8** Calculate the initial deficit of the Tefnet Creek after mixing with the wastewater from the town of Aveta (see Example 9-7 for data). The stream temperature is  $10^\circ C$ , and the wastewater temperature is  $10^\circ C$ .

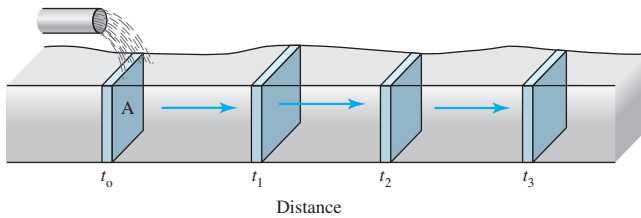
**Solution** With the stream temperature, the saturation value of dissolved oxygen ( $DO_s$ ) can be determined from the table in Appendix A. At  $10^\circ C$ ,  $DO_s = 11.33 mg \cdot L^{-1}$ . Because we calculated the concentration of DO after mixing as  $4.75 mg \cdot L^{-1}$  in Example 9-7, the initial deficit after mixing is

$$D_a = DO_s - DO_{mix} = 11.33 mg \cdot L^{-1} - 4.75 mg \cdot L^{-1} = 6.58 mg \cdot L^{-1}$$



FIGURE 9-17

Cross section of stream flow. Each rhomboid represents the location of a control volume as it moves downstream in the river.



Because wastewater commonly has a higher temperature than river water, especially during the winter, the river temperature downstream of the discharge is usually higher than that upstream. Because we are interested in downstream conditions, it is important to use the downstream temperature when determining the saturation concentration of dissolved oxygen.

**DO Sag Equation.** Numerous models have been developed to describe the change in BOD in a river or stream with distance (or time) from a wastewater outfall. The level of complexity of these models varies greatly. The simplest model and the basis for all other models is the classical Streeter–Phelps model (Streeter and Phelps, 1925). This model assumes that

1. The river is completely and uniformly mixed in the horizontal direction across the river, and in the vertical direction with depth.
2. There is no dispersion of the pollutant as it moves downstream as shown in Figure 9–17.

This means that in the three-dimensional section shown in Figure 9–17 as box A, the chemical (e.g., DO and BOD) is completely mixed and that the concentration of the chemical is the same in all locations in the box. The assumption that no dispersion takes place means that each rectangular cross-section moves down the stream as a packet. The shape of this packet does not change with distance downstream.

The Streeter–Phelps model has essentially two reaction terms: reaeration and deoxygenation. Reaeration describes the rate at which oxygen is replenished and is a function of the stream properties. As you might expect, the greater the turbulence, the more rapids, the greater the rate of reaeration. Reaeration will also depend on the oxygen deficit. The greater the oxygen deficit, the greater the reaeration rate. Thus, the rate at which oxygen is transferred from the air into the stream or river (reaeration) is linearly proportional to the dissolved oxygen deficit (the difference between the concentration of dissolved oxygen in the water and the solubility of oxygen in water at that temperature). The kinetics and modeling of oxygen dissolution are discussed in Chapter 2, Reaction Kinetics. Thus,

$$\text{Rate of reaeration} = k_r(\text{DO}_s - \text{DO}) = k_r D \quad (9-25)$$

where  $k_r$  = the reaeration coefficient (in  $\text{time}^{-1}$ )

$\text{DO}_s$  = the dissolved oxygen concentration at saturation (in  $\text{mass} \cdot \text{volume}^{-1}$ )

$D$  = DO deficit =  $(\text{DO}_s - \text{DO})$

The reaeration coefficient is very much dependent on the physical characteristics of the river. The greater the velocity in the stream, the greater the reaeration coefficient will be. O'Connor and Dobbins (1958) found that the reaeration coefficient is related to the stream velocity and depth using the following equation.

$$k_r = \frac{3.9u^{1/2}}{h^{3/2}} \quad (9-26)$$

where  $k_r$  = the reaeration coefficient at 20°C ( $\text{day}^{-1}$ )  
 $u$  = the average stream velocity (in  $\text{m} \cdot \text{s}^{-1}$ )  
 $h$  = the average stream depth (in m)

Note the factor of 3.9 is necessary to make the equation dimensionally correct. The units of velocity must be in meters per second, whereas depth must be in meters. Reaeration coefficients, typically, vary from 0.1 for small ponds to  $>1.15$  for rapids and waterfalls. The reaeration coefficient can be adjusted for temperature changes using the relationship.

$$k_r = k_{r,20}\theta^{(T-20)} \quad (9-27)$$

where  $k_{r,20}$  = the reaeration coefficient for a temperature of 20°C  
 $\theta$  = temperature coefficient (1.024)  
 $T$  = temperature (in °C)

**EXAMPLE 9-9** A stream containing no biochemical oxygen demand (this is a hypothetical situation and rarely occurs) has a DO of  $5.00 \text{ mg} \cdot \text{L}^{-1}$  and a flow rate,  $Q$ , of  $8.70 \text{ m}^3 \cdot \text{s}^{-1}$ . The temperature of the stream is 18°C. The average velocity in the stream is  $0.174 \text{ m} \cdot \text{s}^{-1}$ . The average depth,  $H$ , of the stream is 5 m. Determine the reaeration coefficient,  $k_r$ , and the rate of reaeration.

**Solution** To solve this problem we must first determine the reaeration coefficient at 20°C, using Equation 9-26.

$$\begin{aligned} k_r &= \frac{3.9u^{1/2}}{h^{3/2}} = \frac{3.9(0.174 \text{ m} \cdot \text{s}^{-1})^{1/2}}{(5.00 \text{ m})^{1.5}} \\ &= \frac{3.9(0.417)}{11.18} = 0.146 \text{ day}^{-1} \end{aligned}$$

We must also take into account the fact that the stream is not at 20°C but at 18°C. Thus we must use the equation

$$k_r = k_{r,20}\theta^{(T-20)} = (0.146)(1.024)^{(18-20)} = 0.139 \text{ day}^{-1}$$

The oxygen deficit is calculated by taking the difference between the saturation value ( $9.54 \text{ mg} \cdot \text{L}^{-1}$ —from Appendix A-2) and the dissolved oxygen concentration:

$$D = 9.54 - 5.0 = 4.54 \text{ mg} \cdot \text{L}^{-1}$$

Thus, according to Equation 9-25, the rate of reaeration equals

$$(0.139 \text{ day}^{-1})(4.54 \text{ mg} \cdot \text{L}^{-1}) = 0.632 \text{ mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$$

Now, let's consider the rate at which DO disappears from the stream as a result of microbial action (M) or what is commonly referred to as the **rate of deoxygenation**. The rate of deoxygenation at any point in the river is assumed to be proportional to the BOD remaining at that point, so that

$$\text{Rate of deoxygenation} = k_d L_t \quad (9-28)$$

where  $k_d$  = the deoxygenation rate ( $\text{time}^{-1}$ )

$L_t$  = BOD remaining at some time after the wastes enter the stream ( $\text{mass} \cdot \text{time}^{-1}$ )

Most models make the assumption that  $k_d$  is equal to the constant,  $k$ , that is, the rate constant obtained using the BOD test. Thus, using Equation 9-5, we can write Equation 9-28 in terms of the ultimate BOD.

$$\text{Rate of deoxygenation} = k_d L_0 e^{-k_d t} \quad (9-29)$$

(Because the rate of deoxygenation is temperature-dependent,  $k_d$  must be corrected for temperature by correcting  $k$  for temperature.) Although the assumption that  $k = k_d$  is reasonable for deep, slow-moving streams, it is a poor assumption for turbulent, shallow, rapidly moving streams. For such streams:

$$k_d = k + \frac{u}{h} \eta \quad (9-30)$$

where  $k$  = BOD rate constant (at  $20^\circ\text{C}$ )

$u$  = average velocity of stream flow (in  $\text{length} \cdot \text{time}^{-1}$ )

$h$  = average depth of stream (in length)

$\eta$  = bed activity coefficient (ranges from 0.1 for stagnant or deep water to 0.6 for rapidly flowing water)

The deoxygenation coefficient can be corrected for temperature using Equation 9-7 and coefficients used to correct BOD rate constants for temperature.

**EXAMPLE 9-10** Determine the deoxygenation rate constant for the reach of Tefnet Creek (Examples 9-7 and 9-8) below the wastewater outfall (discharge pipe). The average speed,  $u$ , of the stream flow in the creek is  $0.03 \text{ m} \cdot \text{s}^{-1}$ . The depth,  $h$ , is 5.0 m and the bed-activity coefficient,  $\eta$ , is 0.35. What is the rate of deoxygenation, in units of  $\text{mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$ ?

**Solution** From Example 9-7, the value of the BOD decay constant,  $k$ , is  $0.12 \text{ day}^{-1}$ . Using Equation 9-30, the deoxygenation rate constant,  $k_d$ , at  $20^\circ\text{C}$  is

$$k_d = 0.12 \text{ day}^{-1} + \frac{0.03 \text{ m} \cdot \text{s}^{-1}}{5.0 \text{ m}} (0.35) = 0.1221, \text{ or } 0.12 \text{ day}^{-1}$$

Note that the units are not consistent. As we have noted before, empirical expressions, such as that in Equations 9-26 and 9-30, may have implicit conversion factors. Thus, you must be careful to use the same units as those used by the author of the equation.

We also note that the deoxygenation rate constant of  $0.1221 \text{ day}^{-1}$  is at  $20^\circ\text{C}$ . In Example 9-8, we noted that the stream temperature was  $10^\circ\text{C}$ . Thus, we must correct the estimated  $k_d$  value using Equation 9-7.

$$\begin{aligned} k_d \text{ at } 10^\circ\text{C} &= (0.1221 \text{ day}^{-1})(1.135)^{10-20} = (0.1221)(0.2819) \\ &= 0.03442, \text{ or } 0.034 \text{ day}^{-1} \end{aligned}$$

From Example 9-7, we know that the ultimate BOD immediately after mixing,  $L_t$ , is  $12 \text{ mg} \cdot \text{L}^{-1}$ . Then using Equation 9-28, we obtain

$$\begin{aligned} \text{Rate of deoxygenation} &= k_d L_t \\ &= 0.034 \text{ day}^{-1} \times 12 \text{ mg} \cdot \text{L}^{-1} \\ &= 0.408 \text{ mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1} \end{aligned}$$

The DO sag curve (Streeter–Phelps model) is simply a mass-balance approach to calculating or predicting the DO level downstream in a river. Using the mass-balance approach introduced in Chapter 4, we can develop the sag curve using a one-dimensional general continuity equation for a constituent in water. Here, the constituent is oxygen and the equation is

$$\frac{\partial C}{\partial t} = \bar{D}_x \frac{\partial^2 C}{\partial x^2} - \bar{v}_x \frac{\partial C}{\partial x} + \sum (\text{reactions}) \quad (9-31)$$

where  $\bar{v}_x$  = downstream velocity in the  $x$  direction  
 $\bar{D}_x$  = dispersion coefficient in the  $x$  direction

Here we will ignore the dispersion term and impose steady-state conditions. As such, the first two terms of Equation 9–31 drop out, and the equation is reduced to an ordinary differential equation.

$$\bar{v}_x \frac{dC}{dx} = \sum (\text{reactions}) \quad (9-32)$$

We can obtain the reaction terms by combining Equations 9–25 and 9–28 because the oxygen deficit is a function of the competition between oxygen use and reaeration from the atmosphere. Also if we use the notation used previously, that is,  $D$  for deficit, we obtain the equation

$$\bar{v}_x \frac{dD}{dx} = k_d L - k_r D \quad (9-33)$$

where  $\frac{dD}{dx}$  = the change in oxygen deficit ( $D$ ) with respect to unit of distance (in  $\text{mg} \cdot \text{L}^{-1} \cdot \text{day}$ )

$k_d$  = deoxygenation rate constant (in  $\text{day}^{-1}$ )  
 $L$  = ultimate BOD of river water (in  $\text{mg} \cdot \text{L}^{-1}$ )  
 $k_r$  = reaeration rate constant (in  $\text{day}^{-1}$ )  
 $D$  = oxygen deficit in river water (in  $\text{mg} \cdot \text{L}^{-1}$ )

Often, environmental engineers and scientists want to represent the previous equation in terms of travel time downstream. This can be easily accomplished if we recognize that

$$\text{Time} = \frac{x}{\bar{v}_x} \quad (9-34)$$

Therefore, we can write Equation 9–33 as

$$\frac{dD}{dt} = k_d L - k_r D \quad (9-35)$$

By integrating Equation 9–35, and using the boundary conditions (at  $t = 0$ ;  $D = D_a$  and  $L = L_a$ ; and at  $t = t$ ,  $D = D_t$ , and  $L = L_t$ ), the DO sag equation is obtained:

$$D_t = \frac{k_d L_a}{k_r - k_d} (e^{-k_d t} - e^{-k_r t}) + D_a (e^{-k_r t}) \quad (9-36)$$

where  $D_t$  = oxygen deficit in river water after exertion of BOD for time,  $t$  (in  $\text{mg} \cdot \text{L}^{-1}$ )  
 $L_a$  = initial ultimate BOD after river and wastewater have mixed (Equation 8–28) (in  $\text{mg} \cdot \text{L}^{-1}$ )  
 $k_d$  = deoxygenation rate constant (in  $\text{day}^{-1}$ )  
 $k_r$  = reaeration rate constant (in  $\text{day}^{-1}$ )  
 $t$  = time of travel of wastewater discharge downstream (in days)  
 $D_a$  = initial deficit after river and wastewater have mixed (Equation 9–24) (in  $\text{mg} \cdot \text{L}^{-1}$ )

When  $k_r = k_d$ , Equation 9–36 reduces to

$$D_t = (k_d t L_a + D_a) (e^{-k_d t}) \quad (9-37)$$

where the terms are as previously defined.

**EXAMPLE 9-11** A city of 200,000 people disposes of  $1.05 \text{ m}^3 \cdot \text{s}^{-1}$  of treated sewage that still has a  $\text{BOD}_u$  of  $28.0 \text{ mg} \cdot \text{L}^{-1}$  and  $1.8 \text{ mg} \cdot \text{L}^{-1}$  of DO into a river. Upstream from the outfall, the river has a flowrate of  $7.08 \text{ m}^3 \cdot \text{s}^{-1}$  and a velocity of  $0.37 \text{ m} \cdot \text{s}^{-1}$ . At this point, the  $\text{BOD}_u$  and DO in the river are  $3.6$  and  $7.6 \text{ mg} \cdot \text{L}^{-1}$ , respectively. The saturation value of DO (at the temperature of the river) is  $8.5 \text{ mg} \cdot \text{L}^{-1}$ . The deoxygenation coefficient,  $k_d$ , is  $0.61 \text{ day}^{-1}$ , and the reaeration coefficient,  $k_r$ , is  $0.76 \text{ day}^{-1}$ . Assume complete mixing and that the velocity in the river is the same upstream and downstream of the outfall.

1. What is the oxygen deficit and the  $\text{BOD}_u$  just downstream from the outfall (just after mixing, before any reaction can occur)?
2. What is the DO 16 km downstream?

**Solution**

1. Using Equation 9-17, we can calculate the concentration of dissolved oxygen in the river after mixing.

$$\text{DO}_{\text{mix}} = \frac{(1.8 \text{ mg} \cdot \text{L}^{-1})(1.05 \text{ m}^3 \cdot \text{s}^{-1}) + (7.08 \text{ m}^3 \cdot \text{s}^{-1})(7.6 \text{ mg} \cdot \text{L}^{-1})}{1.05 \text{ m}^3 \cdot \text{s}^{-1} + 7.08 \text{ m}^3 \cdot \text{s}^{-1}} = 6.85 \text{ mg} \cdot \text{L}^{-1}$$

$$\text{Initial deficit} = D_a = 8.5 - 6.85 = 1.6 \text{ mg} \cdot \text{L}^{-1}.$$

Similarly, using Equation 9-18, we can calculate the concentration of ultimate BOD in the river after mixing.

$$L_{a,\text{mix}} = \frac{(28 \text{ mg} \cdot \text{L}^{-1})(1.05 \text{ m}^3 \cdot \text{s}^{-1}) + (3.6 \text{ mg} \cdot \text{L}^{-1})(7.08 \text{ m}^3 \cdot \text{s}^{-1})}{8.13 \text{ m}^3 \cdot \text{s}^{-1}} = 6.75 \text{ mg} \cdot \text{L}^{-1}$$

2. DO 16 km downstream

$$t = \frac{(16 \text{ km})(1000 \text{ m} \cdot \text{km}^{-1})}{(0.37 \text{ m} \cdot \text{s}^{-1})(3600 \text{ s} \cdot \text{h}^{-1})(24 \text{ h} \cdot \text{day}^{-1})} = 0.50 \text{ days}$$

Using Equation 9-36,

$$\begin{aligned} D_t &= \frac{(0.61)(6.75)}{(0.76 - 0.61)} [\exp(-(0.61)(0.50)) - \exp(-(0.76)(0.50))] \\ &\quad + 1.6 \exp(-(0.76)(0.50)) \\ &= 2.56 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

$$\text{therefore DO} = 8.5 \text{ mg} \cdot \text{L}^{-1} - 2.56 \text{ mg} \cdot \text{L}^{-1} = 5.9 \text{ mg} \cdot \text{L}^{-1}$$

To relate travel time to a physical distance downstream, we must also know the average stream velocity. Once  $D$  has been found at any point downstream, the DO can be found from Equation 9-36. Note that it is physically impossible for the DO to be less than zero. If the deficit calculated from Equation 9-36 is greater than the saturation DO, then all the oxygen was depleted at some earlier time and the DO is zero. If the result of your calculation yields a negative DO, report it as zero because concentration values cannot be less than zero.

The lowest point on the DO sag curve with respect to dissolved oxygen, which is called the **critical point**, is of major interest because it indicates the worst conditions in the river with respect to dissolved oxygen. The time to the critical point ( $t_c$ ) can be found by differentiating Equation 9-36, setting it equal to zero, and solving for  $t$  using the values for  $k_r$  and  $k_d$ .

$$t_c = \frac{1}{k_r - k_d} \ln \left[ \frac{k_r}{k_d} \left( 1 - D_a \frac{k_r - k_d}{k_d L_a} \right) \right] \quad (9-38)$$

or when  $k_r = k_d$ ,

$$t_c = \frac{1}{k_d} \left( 1 - \frac{D_a}{L_a} \right) \quad (9-39)$$

and the critical deficit ( $D_c$ ) is then found by using this critical time in Equation 9-36.

$$D_c = \frac{k_d L_a}{k_r - k_a} (e^{-k_d t_c} - e^{-k_r t_c}) + D_a (e^{-k_r t_c}) \quad (9-40)$$

In some instances there may not be a sag in the DO downstream. The lowest DO may occur in the mixing zone. In these instances Equation 9-38 will not give a useful value.

**EXAMPLE 9-12** Using the data presented in Example 9-11,

1. Calculate the critical time and distance.
2. What is the minimum DO?

**Solution**

1. Using Equation 9-38, we can calculate the critical time,  $t_c$ .

$$t_c = \frac{1}{0.76 - 0.61} \ln \left\{ \frac{0.76}{0.61} \left[ 1 - \frac{1.6(0.76 - 0.61)}{(0.61)(6.75)} \right] \right\}$$

$$= 1.07 \text{ days}$$

$$\text{Flow} = 0.37 \text{ m} \cdot \text{s}^{-1}$$

$$\begin{aligned} \text{Critical distance} &= (1.07 \text{ days})(0.37 \text{ m} \cdot \text{s}^{-1})(3600 \text{ s} \cdot \text{h}^{-1})(24 \text{ h} \cdot \text{day}^{-1})(10^{-3} \text{ m} \cdot \text{km}^{-1}) \\ &= 34.2 \text{ km} \end{aligned}$$

2. Using the critical time,  $t_c$ , for  $t$ , we can use Equation 9-36 to calculate the “critical deficit”:

$$\begin{aligned} D &= \frac{(0.61)(6.75)}{(0.76 - 0.61)} \{ \exp[-(0.61)(1.07)] - \exp[-(0.76)(1.07)] \} \\ &\quad + 1.6 \exp[-(0.76)(1.07)] \\ &= 2.8 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

$$\text{therefore, the minimum DO} = 8.5 \text{ mg} \cdot \text{L}^{-1} - 2.8 \text{ mg} \cdot \text{L}^{-1} = 5.7 \text{ mg} \cdot \text{L}^{-1}$$

**EXAMPLE 9-13** Determine the DO concentration at a point 5 km downstream from the Aveta discharge into the Tefnet Creek (Examples 9-7, 9-8, 9-10). Also determine the critical DO and the distance downstream at which it occurs.

**Solution**

All of the appropriate data are provided in the three previous examples. With the exceptions of the travel time,  $t$ , and the reaeration rate, the values needed for Equations 9-36 and 9-38 have been computed in Examples 9-7, 9-8, and 9-10. The first step then is to calculate  $k$ .

$$k_r \text{ at } 20^\circ\text{C} = \frac{(3.9)(0.03 \text{ m} \cdot \text{s}^{-1})^{0.5}}{(5.0 \text{ m})^{1.5}} = 0.0604 \text{ day}^{-1}$$

Because  $k_r$  is given for 20°C and the stream temperature is at 10°C, Equation 9–7 must be used to correct for the temperature difference.

$$k_r \text{ at } 10^\circ\text{C} = (0.0604 \text{ day}^{-1})(1.024)^{10-20} = (0.0604)(0.7889) = 0.04766 \text{ day}^{-1}$$

Note that the temperature coefficient is the one associated with Equation 9–27.

The travel time  $t$  is computed from the distance downstream and the speed of the stream.

$$t = \frac{(5 \text{ km})(1,000 \text{ m} \cdot \text{km}^{-1})}{(0.03 \text{ m} \cdot \text{s}^{-1})(86,400 \text{ s} \cdot \text{day}^{-1})} = 1.929 \text{ day}$$

Although it is not warranted by the significant figures in the computation, we have elected to keep four significant figures because of the computational effects of truncating the extra digits.

The deficit is estimated using Equation 9–36.

$$\begin{aligned} D_t &= \frac{(0.03442)(11.86)}{0.04766 - 0.03442} \left[ e^{-(0.03442)(1.929)} - e^{-(0.04766)(1.929)} \right] + 6.58 \left[ e^{-(0.04766)(1.929)} \right] \\ &= (30.83)(0.9358 - 0.9122) + 6.58(0.9122) \\ &= 6.7299 \text{ or } 6.73 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

and the dissolved oxygen is

$$\text{DO} = 11.33 - 6.73 = 4.60 \text{ mg} \cdot \text{L}^{-1}$$

The critical time is computed using Equation 9–38.

$$\begin{aligned} t_c &= \frac{1}{0.04766 - 0.03442} \ln \left\{ \left( \frac{0.04766}{0.03442} \right) \left[ 1 - 6.58 \times \frac{(0.04766 - 0.03442)}{(0.03442)(11.86)} \right] \right\} \\ &= 6.45 \text{ days} \end{aligned}$$

Using  $t_c$  for the time in Equation 9–36, we can calculate the critical deficit as

$$\begin{aligned} D_c &= \frac{(0.03442)(11.86)}{0.04766 - 0.03442} \left[ e^{-(0.03442)(6.45)} - e^{-(0.04766)(6.45)} \right] + 6.58 \left[ e^{-(0.04766)(6.45)} \right] \\ &= 6.85 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

and the critical DO is

$$\text{DO}_c = 11.33 - 6.85 = 4.48 \text{ mg} \cdot \text{L}^{-1}$$

The critical DO occurs downstream at a distance of

$$(6.45 \text{ days})(86,400 \text{ s} \cdot \text{day}^{-1})(0.03 \text{ m} \cdot \text{s}^{-1}) \left( \frac{1 \text{ km}}{1000 \text{ m}} \right) = 16.7 \text{ km}$$

from the wastewater discharge point. (Remember that  $0.03 \text{ m} \cdot \text{s}^{-1}$  is the speed of the stream.)

**Management Strategy.** The beginning point for water quality management in rivers using the DO sag curve is to determine the minimum DO concentration that will protect the aquatic life in the stream. This value, called the **DO standard**, is generally set to protect the most sensitive species that exist or could exist in the particular river. For a known waste discharge and a known set of river characteristics, the DO sag equation can be solved to find the DO at the critical point. If this value is greater than the standard, the stream can adequately assimilate the waste. If the DO at the critical point is less than the standard, then additional waste treatment is needed. Usually, the environmental engineer has control over just two parameters:  $L_a$  and  $D_a$ . By increasing the efficiency of

the existing treatment processes or by adding additional treatment steps, the ultimate BOD of the waste discharge can be reduced, thereby reducing  $L_a$ . Often a relatively inexpensive method for improving stream quality is to reduce  $D_a$  by adding oxygen to the wastewater to bring it close to saturation prior to discharge. To determine whether a proposed improvement will be adequate, the new values for  $L_a$  and  $D_a$  are used to determine whether the DO standard will be violated at the critical point. As a last resort, mechanical reaeration of rivers can be accomplished to artificially increase  $k_r$  and therefore decrease  $D_a$ . However, this measure is both costly to install and operate.

When using the DO sag curve to determine the adequacy of wastewater treatment, it is important to use the river conditions that will result in the least DO concentration. Usually these conditions occur in the late summer when river flows are low and temperatures are high. A frequently used criterion is the 10-year, 7-day low flow, which is the recurrence interval of the average low flow for a 7-day period. Low river flows reduce the dilution of the waste entering the river, causing higher values for  $L_a$  and  $D_a$ . The value of  $k_r$  is usually reduced by low river flows because of reduced velocities. In addition, higher temperatures increase  $k_d$  more than  $k_r$  and also decrease DO saturation, thus making the critical point more severe.

**EXAMPLE 9-14** The Flins Company is considering opening one of two possible plants on either the Veles River or on its twin, the Perun River. Among the decisions to be made are what effect the plant discharge will have on each river and which river would be affected less. Effluent data from the Rongo canning plants A and B are considered to be representative of the potential discharge characteristics. In addition, measurements from each river at summer low-flow conditions are available.

Effluent Parameter	Plant A	Plant B
Flow (in $\text{m}^3 \cdot \text{s}^{-1}$ )	0.0500	0.0500
Ultimate BOD at 25°C (in $\text{kg} \cdot \text{day}^{-1}$ )	129.60	129.60
DO (in $\text{mg} \cdot \text{L}^{-1}$ )	0.900	0.900
Temperature (in °C)	25.0	25.0
$k$ at 20°C (in $\text{day}^{-1}$ )	0.110	0.0693

River Parameter	Veles River	Perun River
Flow (in $\text{m}^3 \cdot \text{s}^{-1}$ )	0.500	0.500
Ultimate BOD at 25°C (in $\text{mg} \cdot \text{L}^{-1}$ )	19.00	19.00
DO (in $\text{mg} \cdot \text{L}^{-1}$ )	5.85	5.85
Temperature (in °C)	25.0	25.0
Speed (in $\text{m} \cdot \text{s}^{-1}$ )	0.100	0.200
Average depth (in m)	4.00	4.00
Bed-activity coefficient	0.200	0.200

Four combinations must be evaluated:

Plant A on the Veles River	Plant B on the Veles River
Plant A on the Perun River	Plant B on the Perun River

**Solution** Note that for the purpose of explaining the calculations, the number of significant figures given for the data is greater than can probably be measured. The only difference in the combinations is the change in deoxygenation and reaeration coefficients. Thus, we need calculate only one value of  $L_a$  and one value of  $D_a$ .

We begin by converting the mass flux of ultimate BOD (in  $\text{kg} \cdot \text{day}^{-1}$ ) to a concentration (in  $\text{mg} \cdot \text{L}^{-1}$ ). Following our general approach for calculating concentration from mass flow, we



divide the mass flux (in  $\text{kg} \cdot \text{day}^{-1}$ ) by the flow of the water carrying the waste ( $Q_w$ ,  $Q_r$ , or the sum  $Q_w + Q_r$ ):

$$\frac{\text{Mass flux of ultimate BOD discharged (in } \text{kg} \cdot \text{day}^{-1}\text{)}}{\text{Flow of water-carrying waste (in } \text{m}^3 \cdot \text{s}^{-1}\text{)}}$$

The mass flux units are then converted to milligrams per day and the water flow to liters per day so that the days cancel.

$$\frac{(\text{Mass flux in units of } \text{kg} \cdot \text{day}^{-1}) \times (1 \times 10^6 \text{ mg} \cdot \text{kg}^{-1})}{(\text{Flow rate } Q \text{ in units of } \text{m}^3 \cdot \text{s}^{-1}) \times (86,400 \text{ s} \cdot \text{day}^{-1})(1 \times 10^3 \text{ L} \cdot \text{m}^{-3})}$$

For either plant A or B,

$$\begin{aligned} L_w &= \frac{(129.60 \text{ kg} \cdot \text{day}^{-1})(1 \times 10^6 \text{ mg} \cdot \text{kg}^{-1})}{(0.0500 \text{ m}^3 \cdot \text{s}^{-1})(86,400 \text{ s} \cdot \text{day}^{-1})(1 \times 10^3 \text{ L} \cdot \text{m}^{-3})} \\ &= \frac{129.60 \times 10^6 \text{ mg}}{4.320 \times 10^6 \text{ L}} \\ &= 30.00 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

Now we can compute the mixed BOD using Equation 9–18.

$$\begin{aligned} L_a &= \frac{(0.0500)(30.00) + (0.500)(19.00)}{0.0500 + 0.500} \\ &= 20.0 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

From Table A–2 of Appendix A, we find that the DO saturation at  $25^\circ\text{C}$  is  $8.38 \text{ mg} \cdot \text{L}^{-1}$ . Then using Equation 9–24, we determine the initial deficit:

$$\begin{aligned} D_a &= 8.38 - \frac{(0.0500)(0.900) + (0.500)(5.85)}{0.0500 + 0.500} \\ &= 8.38 - 5.4 \\ &= 2.98 \text{ mg} \cdot \text{L}^{-1} \end{aligned}$$

For the combination of plant A discharging to the Veles River, the reaeration and deoxygenation coefficients are calculated using Equation 9–26 and Equation 9–30, respectively

$$\begin{aligned} k_d &= 0.110 + \frac{0.100 \times 0.200}{4.00} \\ &= 0.115 \text{ day}^{-1} \text{ at } 20^\circ\text{C} \end{aligned}$$

and

$$\begin{aligned} k_r &= \frac{3.9(0.100)^{0.5}}{(4.00)^{1.5}} \\ &= 0.154 \text{ day}^{-1} \text{ at } 20^\circ\text{C} \end{aligned}$$

Because the temperature of the river is  $25^\circ\text{C}$  and the wastewater effluent temperature is also  $25^\circ\text{C}$ , we do not have to calculate a temperature after mixing. However, we will have to adjust  $k_d$  and  $k_r$  to  $25^\circ\text{C}$ . For  $k_d$ , we use Equation 9–7 with a value of  $\theta$  of 1.056.

$$\begin{aligned} k_d &= 0.115(1.056)^{25-20} \\ &= 0.151 \text{ day}^{-1} \end{aligned}$$

From the discussion that follows Equation 9-27, we note that  $\theta = 1.024$  for reaeration, and thus  $k_r = 0.154(1.024)^{25-20} = 0.173 \text{ day}^{-1}$

Although perhaps not justified by the coefficients, we round to three significant figures because we will want to calculate travel time to two decimal places.

Now we have all the information we need to calculate the time to the critical point. Using Equation 9-38, we obtain

$$t_c = \frac{1}{0.173 - 0.151} \ln \left\{ \frac{0.173}{0.151} \left[ 1 - 2.98 \left( \frac{0.173 - 0.151}{0.151 \times 20.0} \right) \right] \right\}$$

$$= 45.45 \ln \{ 1.146 [ 1 - 2.98(0.02185) ] \}$$

$$= 5.18 \text{ days}$$

Using this value for  $t$  in Equation 9-36, we can calculate the deficit at the critical point.

$$D_c = \frac{(0.151)(20.0)}{0.173 - 0.151} [ e^{-(0.151)(5.18)} - e^{-(0.173)(5.18)} ] + 2.98 [ e^{-(0.173)(5.18)} ]$$

$$= 137.3 [ (0.0493) ] + 2.98 [ 1.224 ]$$

$$= 6.763 + 1.242$$

$$= 7.99 \text{ mg} \cdot \text{L}^{-1}$$

Using  $D_c$  and the appropriate value for the DO saturation that we obtained earlier from Table A-2, we can calculate the DO at the critical point.

$$\text{DO} = \text{DO}_s - D$$

$$= 8.38 - 7.99 = 0.39 \text{ mg} \cdot \text{L}^{-1}$$

Thus, the lowest DO for the plant A-Veles River combination is  $0.39 \text{ mg} \cdot \text{L}^{-1}$ , and it occurs at a travel time of 5.18 days downstream from the plant A outfall. Because the Veles River travels at a speed of  $0.100 \text{ m} \cdot \text{s}^{-1}$ , this would be

$$\frac{(0.100 \text{ m} \cdot \text{s}^{-1})(5.18 \text{ days})(86,400 \text{ s} \cdot \text{day}^{-1})}{1000 \text{ m} \cdot \text{km}^{-1}} = 44.8 \text{ km}$$

downstream.

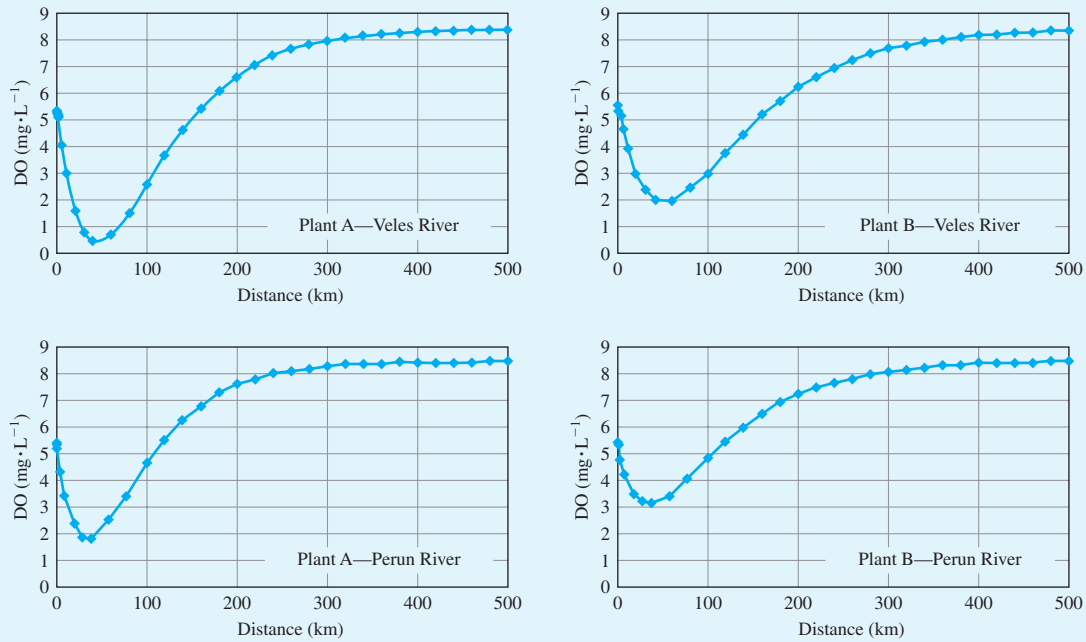
The results of the other combinations are summarized in the following table.

	Plant A		Plant B	
	Veles River	Perun River	Veles River	Perun River
$k_d$	0.151	0.151	0.104	0.104
$k_r$	0.173	0.245	0.173	0.245
$t_c$	5.18	4.11	5.86	4.47
$D$	7.98	6.62	6.51	5.32
DO	0.40	1.76	1.87	3.06

The best combination is the plant B on the Perun River. This is because of the four options, the deficit is the lowest and the minimum DO the greatest for plant B on the Perun River.

**FIGURE 9-18**

Effect of  $k_d$  and  $k_r$  on DO sag curve. Note that the velocity in the Perun River is twice that in the Veles River.



Using a spreadsheet program, we have generated the DO values for a series of times for each of the combinations and plotted the results in Figure 9–18. From this figure we can make the following general observations:

1. Increasing the reaeration rate, while holding everything else as it is, reduces the deficit and decreases the critical time.
2. Decreasing the reaeration rate, while holding everything else as it is, increases the deficit and increases the critical time.
3. Increasing the deoxygenation rate, while holding everything else as it is, increases the deficit and decreases the critical time.
4. Decreasing the deoxygenation rate, while holding everything else as it is, decreases the deficit and increases the critical time.

**Nitrogenous BOD.** Up to this point, only carbonaceous BOD has been considered in the DO sag curve. However, in many cases nitrogenous BOD has at least as much influence on dissolved oxygen levels. Modern wastewater treatment plants can routinely produce effluents with CBOD<sub>5</sub> of less than 30 mg · L<sup>-1</sup>. A typical effluent also contains approximately 30 mg · L<sup>-1</sup> of nitrogen, which would mean an NBOD of about 137 mg · L<sup>-1</sup> if it were discharged as ammonia (see Example 9–6). Nitrogenous BOD can be incorporated into the DO sag curve by adding an additional term to Equation 9–36.

$$D = \frac{k_d L_a}{k_r - k_d} (e^{-k_d t} - e^{-k_r t}) + D_a (e^{-k_r t}) + \frac{k_n L_n}{k_r - k_n} (e^{-k_n t} - e^{-k_r t}) \quad (9-41)$$

where  $k_n$  = the nitrogenous deoxygenation coefficient (in  $\text{day}^{-1}$ )

$L_n$  = ultimate nitrogenous BOD after waste and river have mixed (in  $\text{mg} \cdot \text{L}^{-1}$ )

and the other terms are as previously defined.

It is important to note that with the additional term for NBOD, it is not possible to find the critical time using Equation 9-38. Instead, it must be found by a trial and error solution of Equation 9-41.

**Other Factors Affecting DO Levels in Rivers.** The classical DO sag curve assumes that there is only one point-source discharge of waste into the river. In reality, this is rarely the case. Multiple point sources can be handled by dividing the river up into reaches with a point source at the head of each reach. A **reach** is a length of river specified by the engineer on the basis of its homogeneity, that is, channel shape, bottom composition, slope, and so on. The oxygen deficit and residual BOD can be calculated at the end of each reach. These values are then used to determine new values of  $D_a$  and  $L_a$  at the beginning of the following reach. Nonpoint source pollution can also be handled this way if the reaches are made small enough. Nonpoint source pollution can also be incorporated directly into the DO sag equation for a more sophisticated analysis. Dividing the river into reaches is also necessary whenever the flow regime changes because the reaeration coefficient would also change. In small rivers, rapids play a major role in maintaining high DO levels. Eliminating rapids by dredging or damming a river can have a severe effect on DO, although DO levels immediately downstream of dams are usually high because of the turbulence of the falling water.

Some rivers contain large deposits of organic matter in the sediments. These can be natural deposits of leaves and dead aquatic plants or can be sludge deposits from wastewaters receiving little or no treatment. In either case, decomposition of this organic matter places an additional burden on the stream's oxygen resources because the oxygen demand must be supplied from the overlying water. When this benthic demand is significant, compared with the oxygen demand in the water column, it must be included quantitatively in the sag equation.

Aquatic plants can also have a substantial effect on DO levels. During the day, their photosynthetic activities produce oxygen that supplements the reaeration and can even cause oxygen supersaturation. However, plants also consume oxygen for respiration processes. Although there is a net overall production of oxygen, plant respiration can severely lower DO levels during the night. Plant growth is usually highest in the summer when flows are low and temperatures are high, so that large nighttime respiration requirements coincide with the worst cases of oxygen depletion from BOD exertion. In addition, when aquatic plants die and settle to the bottom, they increase the benthic demand. As a general rule, large growths of aquatic plants are detrimental to the maintenance of a consistently high DO level.

### **Effect of Nutrients on Water Quality in Rivers**

Although oxygen-demanding wastes are definitely the most important river pollutants on an overall basis, nutrients can also contribute to deteriorating water quality in rivers by causing excessive plant growth. Nutrients are those elements required by plants for their growth. They include, in order of abundance in plant tissue: carbon, nitrogen, phosphorus, and a variety of trace elements. When sufficient quantities of all nutrients are available, plant growth is possible. By limiting the availability of any one nutrient, further plant growth is prevented.

Some plant growth is desirable because plants form the base of the food chain and thus support the animal community. However, excessive plant growth can create a number of undesirable conditions, such as thick slime layers on rocks and dense growths of aquatic weeds.

The availability of nutrients is not the only requirement for plant growth. In many rivers, the turbidity caused by eroded soil particles, bacteria, and other factors prevents light from penetrating far into the water, thereby limiting total plant growth in deep water. It is for this reason that slime growths on rocks usually occur only in shallow water. Strong water currents also prevent rooted plants from taking hold, and thus limit their growth to quiet backwaters where the currents are weak and the water is shallow enough for light to penetrate.

**Effects of Nitrogen.** Nitrogen is detrimental to a receiving body for four reasons:

1. In high concentrations, ammonia in its unionized form is toxic to fish.
2. Ammonia,  $\text{NH}_3$ , in low concentrations, and nitrate,  $\text{NO}_3^-$ , serve as nutrients for excessive growth of algae.
3. The conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  consumes large quantities of dissolved oxygen.
4. During the common practice of disinfecting wastewater effluent using chlorination, the chlorine ( $\text{Cl}_2$ ) and hypochlorous acid/hypochlorite ( $\text{HOCl}/\text{OCl}^-$ ) can react with any ammonia present in the water, forming chloramines. The chloramines, which are not removed during dechlorination prior to discharge, are more toxic than either chlorine and hypochlorous acid/hypochlorite.

**Effects of Phosphorus.** The major harmful effect of phosphorus is that it serves as a vital nutrient for the growth of algae. If the phosphorus availability meets the growth demands of the algae, algae are produced in excess. When the algae die, they become an oxygen-demanding organic material as bacteria seek to degrade them. This oxygen demand frequently overtaxes the DO supply of the water body and, as a consequence, causes fish to die.

**Management Strategy.** The strategy for managing water quality problems associated with excessive nutrients is based on the sources for each nutrient. Except under rare circumstances, there is plenty of carbon available for plant growth. Plants use carbon dioxide, which is available from the bicarbonate alkalinity of the water and from the bacterial decomposition of organic matter. As carbon dioxide is removed from the water, it is replenished from the atmosphere. Generally, the major source of trace elements is the natural weathering of rock minerals, a process over which the environmental scientist and engineer has little control. However, because acid rain caused by air pollution accelerates the weathering process, air pollution control can help reduce the supply of trace elements. The removal of trace elements from wastewater is difficult. In addition, such small amounts of trace elements are needed for plant growth that nitrogen or phosphorus is more likely to be the limiting nutrient. Therefore, the practical control of nutrient-caused water quality problems in streams is based on removal of nitrogen or phosphorus from wastewaters before they are discharged.

## 9-4 WATER QUALITY MANAGEMENT IN LAKES

### **Control of Phosphorus in Lakes**

In Chapter 5 the problem of eutrophication and its effect on ecosystems was discussed. Because phosphorus is usually the limiting nutrient, control of cultural eutrophication must be accomplished by reducing the input of phosphorus to the lake. Once the input is reduced, the phosphorus concentration will gradually fall as phosphorus is buried in the sediment or flushed from the lake. Other strategies for reversing or slowing the eutrophication process, such as precipitating phosphorus with additions of aluminum (alum) or removing phosphorus-rich sediments by dredging, have been proposed. However, if the input of phosphorus is not also curtailed, the eutrophication process will continue. Thus, dredging or precipitation alone can result only in temporary improvement in water quality. In conjunction with reduced phosphorus inputs, these measures can help speed up the removal of phosphorus already in the lake system. Of course, the need to speed the recovery process must be weighed against the potential damage from inundating shoreline areas with sludge and stirring up chemicals buried in the sediment.

To be able to reduce phosphorus inputs, it is necessary to know the sources of phosphorus and the potential for their reduction. The natural source of phosphorus is the weathering of rock. Phosphorus released from the rock can enter the water directly, but more commonly it is taken up by plants and enters the water in the form of dead plant matter. It is exceedingly difficult to reduce the natural inputs of phosphorus. If these sources are large, the lake is generally naturally eutrophic. For many lakes the principal sources of phosphorus are the result of human activity.

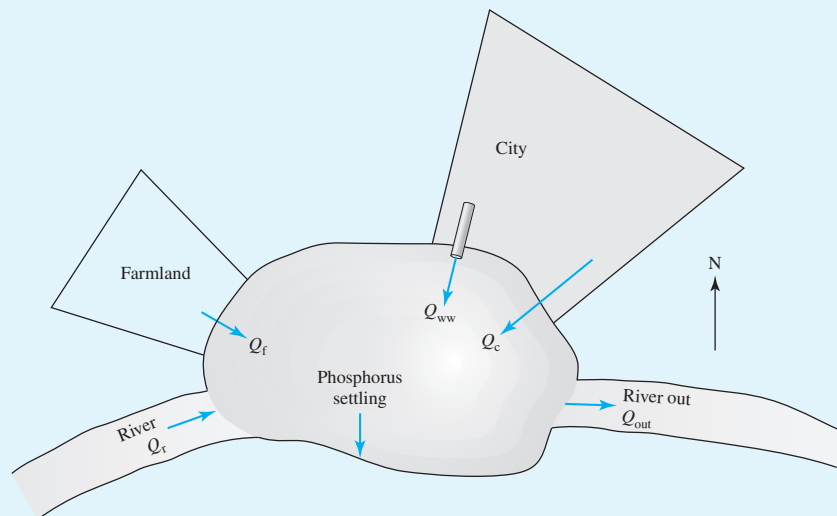
The most important sources are municipal and industrial wastewaters, seepage from septic tanks, and agricultural runoff that carries phosphorus fertilizers into the water. The relative contributions of various sources of phosphorus are illustrated in the following example.

**EXAMPLE 9-15** The fictitious Pinga Lake in Camelot has a surface area of  $9.34 \times 10^7 \text{ m}^2$  and depth of 10 m. The lake receives a yearly average of 107 cm of precipitation. The lake receives phosphorus from the following sources:

1. The wastewater treatment plant for the city of Astrid discharges into the lake. The average water usage for the residents of the city is  $350 \text{ L} \cdot \text{capita}^{-1} \cdot \text{day}^{-1}$ . There are 54,000 residents of this city. The total phosphate level in the sewage influent is  $10 \text{ mg} \cdot \text{L}^{-1}$  (yearly average). The wastewater treatment plant removes 90% of the phosphorus.
2. The city has recently renovated its sewage collection system, separating the storm water from the sewage, installing a separate sewer system. The storm water is discharged into the lake after treatment through a sand filter that removes 50% of the phosphorus. The storm sewers serve an area that is  $9.5 \text{ km}^2$ , having a runoff coefficient of 0.40. The phosphorus concentration in the untreated storm water is  $0.75 \text{ mg} \cdot \text{L}^{-1}$ .
3. The lake is fed by a pristine stream, having an average yearly flow rate of  $0.65 \text{ m}^3 \cdot \text{s}^{-1}$ . The stream has an average total phosphorus concentration of  $0.05 \text{ mg} \cdot \text{L}^{-1}$ .
4. Farmland lies to the east of the lake. It has a drainage area of  $150 \text{ km}^2$ . Manure is applied in early spring before the crops are sown. The phosphorus loading to the land is  $0.42 \text{ kg} \cdot \text{km}^{-2} \cdot \text{year}^{-1}$ . The crops remove 60% of the phosphorus applied. The runoff coefficient on this land is 0.30. (This loading to the lake can be averaged throughout the year.)
5. The phosphorus settling rate from the lake is  $2.8 \times 10^{-8} \text{ s}^{-1}$ .

Calculate the total phosphorus concentration in the lake. What is the trophic state of the lake? You may assume that the rate of evaporation is equal to the rate of precipitation.

**Solution** Let's draw a picture of this lake.



We must first calculate all of our **flow rates**:

The flow rate in the pristine stream,  $Q_r$ , is given as  $0.65 \text{ m}^3 \cdot \text{s}^{-1}$ .

The flow rate from the wastewater treatment plant is

$$Q_{ww} = (350 \text{ L} \cdot \text{capita}^{-1} \cdot \text{day}^{-1})(54,000 \text{ people}) \left( \frac{1 \text{ m}^3}{1000 \text{ L}} \right) \left( \frac{1 \text{ day}}{86,400 \text{ s}} \right) = 0.219 \text{ m}^3 \cdot \text{s}^{-1}$$