substances in question. In a COD test, a strong chemical oxidizing agent is used to oxidize the organics rather than relying on microorganisms to do the job. The COD test is much quicker than a BOD test, taking only a matter of hours. However, it does not distinguish between the oxygen demand that will actually be felt in a natural environment due to biodegradation, and the chemical oxidation of inert organic matter. It also does not provide any information on the rate at which actual biodegradation will take place. The measured value of COD is higher than BOD, though for easily biodegradable matter the two will be quite similar. In fact, the COD test is sometimes used as a way to estimate the ultimate BOD.

5.6 THE EFFECT OF OXYGEN-DEMANDING WASTES ON RIVERS

The amount of dissolved oxygen in water is one of the most commonly used indicators of a river's health. As DO drops below 4 or 5 mg/L, the forms of life that can survive begin to be reduced. In the extreme case, when anaerobic conditions exist, most higher forms of life are killed or driven off. Noxious conditions, including floating sludges, bubbling, odorous gases, and slimy fungal growths, then prevail.

A number of factors affect the amount of DO available in a river. Oxygen-demanding wastes remove DO; photosynthesis adds DO during the day, but those plants remove oxygen at night; and the respiration of organisms living in the water as well as in sediments removes oxygen. In addition, tributaries bring their own oxygen supplies, which mix with those of the main river. In the summer, rising temperatures reduce the solubility of oxygen while lower flows reduce the rate at which oxygen enters the water from the atmosphere. In the winter, ice may form, blocking access to new atmospheric oxygen. To model properly all of these effects and their interactions is a difficult task. A simple analysis, however, can provide insight into the most important parameters that affect DO. We should remember, however, that our results are only a first approximation to reality.

The simplest model of the oxygen resources in a river focuses on two key processes: the removal of oxygen by microorganisms during biodegradation, and the replenishment of oxygen through reaeration at the interface between the river and the atmosphere. In this simple model, it is assumed that there is a continuous discharge of waste at a given location on the river. As the water and wastes flow downriver, it is assumed that they are uniformly mixed at any given cross section of river, and it is assumed that there is no dispersion of wastes in the direction of flow. These assumptions are part of what is referred to as the *point-source, plug flow* model, illustrated in Figure 5.14.

Deoxygenation

The rate of deoxygenation at any point in the river is assumed to be proportional to the BOD remaining at that point. That is,

$$\text{Rate of deoxygenation} = k_d L_t \qquad (5.19)$$

where

k_d = the deoxygenation rate constant (day^{-1})

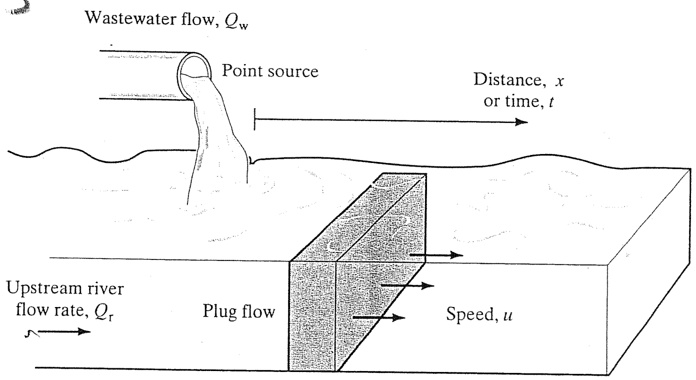

FIGURE 5.14 The point-source, plug flow model for dissolved-oxygen calculations.

L_t = the BOD remaining t (days) after the wastes enter the river, (mg/L)

The deoxygenation rate constant k_d is often assumed to be the same as the (temperature adjusted) BOD rate constant k obtained in a standard laboratory BOD test. For deep, slowly moving rivers, this seems to be a reasonable approximation, but for turbulent, shallow, rapidly moving streams, the approximation is less valid. Such streams have deoxygenation constants that can be significantly higher than the values determined in the laboratory.

Substituting (5.10), which gives BOD remaining after time t, into (5.19) gives

$$\text{Rate of deoxygenation} = k_d L_0 e^{-k_d t} \qquad (5.20)$$

where L_0 is the BOD of the mixture of streamwater and wastewater at the point of discharge. Assuming complete and instantaneous mixing,

$$L_0 = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r} \qquad (5.21)$$

where

L_0 = ultimate BOD of the mixture of streamwater and wastewater (mg/L)
L_r = ultimate BOD of the river just upstream of the point of discharge (mg/L)
L_w = Ultimate BOD of the wastewater (mg/L)
Q_r = volumetric flow rate of the river just upstream of the discharge point (m^3/s)
Q_w = volumetric flow rate of wastewater (m^3/s)

EXAMPLE 5.6 Downstream BOD

A wastewater treatment plant serving a city of 200,000 discharges 1.10 m^3/s of treated effluent having an ultimate BOD of 50.0 mg/L into a stream that has a flow of 8.70 m^3/s and a BOD of its own, equal to 6.0 mg/L. The deoxygenation constant, k_d is 0.20/day.

a. Assuming complete and instantaneous mixing, estimate the ultimate BOD of the river just downstream from the outfall.

b. If the stream has constant cross section so that is flows at a fixed speed equal to 0.30 m/s, estimate the BOD remaining in the stream at a distance 30,000 m downstream.

Solution

a. The BOD of the mixture of effluent and stream water can be found using (5.21):

$$L_0 = \frac{1.10\text{ m}^3/\text{s} \times 50.0\text{ mg/L} + 8.70\text{ m}^3/\text{s} \times 6.0\text{ mg/L}}{(1.10 + 8.70)\text{ m}^3/\text{s}} = 10.9\text{ mg/L}$$

b. At a speed of 0.30 m/s, the time required for the waste to reach a distance 30,000 m downstream would be

$$t = \frac{30.000\text{ m}}{0.30\text{ m/s}} \times \frac{\text{hr}}{3600\text{ s}} \times \frac{\text{day}}{24\text{ hr}} = 1.16\text{ days}$$

So the BOD remaining at that point, 30 km downstream, would be

$$L_t = L_0 e^{-k_d t} = 10.9\, e^{-(0.2/\text{d} \times 1.16\text{d})} = 8.7\text{ mg/L}$$

■

Reaeration

The rate at which oxygen is replenished is assumed to be proportional to the difference between the actual DO in the river at any given location and the saturated value of dissolved oxygen. This difference is called the oxygen deficit, D:

$$\text{Rate of reaeration} = k_r D \tag{5.22}$$

where

k_r = reaeration constant (time$^{-1)}$

D = dissolved oxygen deficit = $(\text{DO}_s - \text{DO})$ (5.23)

DO_s = saturated value of dissolved oxygen

DO = actual dissolved oxygen at a given location downstream

The reaeration constant, k_r, is very much dependent on the particular conditions in the river. A fast-moving, whitewater river will have a much higher reaeration constant than a sluggish stream or a pond. Many attempts have been made empirically to relate key stream parameters to the reaeration constant, with one of the most commonly used formulations being the following (O'Connor and Dobbins, 1958):

$$k_r = \frac{3.9\, u^{1/2}}{H^{3/2}} \tag{5.24}$$

where

k_r = reaeration coefficient at 20 °C (day^{-1})

u = average stream velocity (m/s)

H = average stream depth (m)

Typical values of the reaeration constant k_r for various bodies of water are given in Table 5.10. Adjustments to the reaeration rate constant for temperatures other than 20 °C can be made using (5.15) but with a temperature coefficient θ equal to 1.024.

The solubility of oxygen in water DO_s was first introduced in Chapter 2, where it was noted that the saturated value of dissolved oxygen varies with temperature, atmospheric pressure, and salinity. Table 5.11 gives representative values of the solubility of oxygen in water at various temperatures and chloride concentrations.

Both the wastewater that is being discharged into a stream and the stream itself are likely to have some oxygen deficit. If we assume complete mixing of the two, we can calculate the initial deficit of the polluted river using a weighted average based on their individual concentrations of dissolved oxygen:

$$D_0 = \text{DO}_s - \frac{Q_w \text{DO}_w + Q_r \text{DO}_r}{Q_w + Q_r} \tag{5.25}$$

where

D_0 = initial oxygen deficit of the mixture of river and wastewater

DO_s = saturated value of DO in water at the temperature of the river

TABLE 5.10 Typical Reaeration Constants for Various Bodies of Water

Water body	Range of k_r at 20 °C (day^{-1})[a]
Small ponds and backwaters	0.10–0.23
Sluggish streams and large lakes	0.23–0.35
Large streams of low velocity	0.35–0.46
Large streams of normal velocity	0.46–0.69
Swift streams	0.69–1.15
Rapids and waterfalls	> 1.15

[a] Base *e*.

Source: Tchobanoglous and Schroeder (1985).

TABLE 5.11 Solubility of Oxygen in Water (mg/L) at 1 atm pressure

	Chloride concentration in water (mg/L)			
Temperature (°C)	0	5000	10,000	15,000
0	14.62	13.73	12.89	12.10
5	12.77	12.02	11.32	10.66
10	11.29	10.66	10.06	9.49
15	10.08	9.54	9.03	8.54
20	9.09	8.62	8.17	7.75
25	8.26	7.85	7.46	7.08
30	7.56	7.19	6.85	6.51

Source: Thomann and Mueller (1987).

DO_w = DO in the wastewater

DO_r = DO in the river just upstream of the wastewater discharge point

---

EXAMPLE 5.7 Initial Oxygen Deficit

The waste water in Example 5.6 has a dissolved oxygen concentration of 2.0 mg/L and a discharge rate of 1.10 m³/s. The river that is receiving this waste has DO equal to 8.3 mg/L, a flow rate 8.70 m³/s, and a temperature of 20 °C. Assuming complete and instantaneous mixing, estimate the initial dissolved oxygen deficit of the mixture of wastewater and river water just downstream from the discharge point.

Solution The initial amount of dissolved oxygen in the mixture of waste and river would be

$$\text{DO} = \frac{1.10\ \text{m}^3/\text{s} \times 2.0\ \text{mg/L} + 8.70\ \text{m}^3/\text{s} \times 8.3\ \text{mg/L}}{(1.10 + 8.70)\ \text{m}^3/\text{s}} = 7.6\ \text{mg/L}$$

The saturated value of dissolved oxygen DO_s at 20 °C is given in Table 5.11 as 9.09 mg/L, so the initial deficit would be

$$D_0 = 9.09\ \text{mg/L} - 7.6\ \text{mg/L} = 1.5\ \text{mg/L}$$

■

The Oxygen Sag Curve

The deoxygenation caused by microbial decomposition of wastes and oxygenation by reaeration are competing processes that are simultaneously removing and adding oxygen to a stream. Combining the two equations (5.20) and (5.22) yields the following expression for the rate of increase of the oxygen deficit:

Rate of increase of the deficit = Rate of deoxygenation − Rate of oxygenation

$$\frac{dD}{dt} = k_d L_0 e^{-k_d t} - k_r \text{D} \tag{5.26}$$

which has the solution

$$D = \frac{k_d L_0}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_0 e^{-k_r t} \tag{5.27}$$

Since the deficit D is the difference between the saturation value of dissolved oxygen DO_s and the actual value DO, we can write the equation for the DO as

$$\text{DO} = \text{DO}_s - \left[\frac{k_d L_0}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_0 e^{-k_r t}\right] \tag{5.28}$$

Equation (5.28) is the classic *Streeter-Phelps oxygen sag equation* first described in 1925. A plot of this DO is given in Figure 5.15. As can be seen, there is a stretch of river immediately downstream of the discharge point where the DO drops rapidly. At the *critical point* downstream, dissolved oxygen reaches its minimum value and river conditions are at their worst. Beyond the critical point, the remaining organic matter in the river has diminished to the point where oxygen is being added to the river by reaeration faster than it is being withdrawn by decomposition, and the river begins to recover.

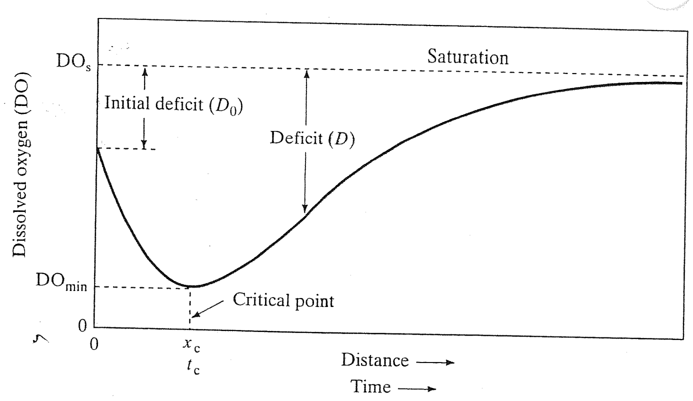

FIGURE 5.15 Streeter-Phelps oxygen sag curve.

There are a few more things we can add to this analysis of oxygen deficit. For the special case where $k_r = k_d$, the denominator in (5.27) goes to zero, which is mathematically unacceptable, so the equation needs to be rederived under those conditions. Under these circumstances the solution to (5.26) becomes

$$D = (k_d L_0 t + D_0)e^{-k_d t} \tag{5.29}$$

If the stream has a constant cross-sectional area and is traveling at a speed u, then time and distance downstream are related by

$$x = ut \tag{5.30}$$

where

x = distance downstream

u = stream speed

t = elapsed time between discharge point and distance x downstream

Equation (5.27) can be rewritten as

$$D = \frac{k_d L_0}{k_r - k_d}\left(e^{-k_d x/u} - e^{-k_r x/u}\right) + D_0 e^{-k_r x/u} \tag{5.31}$$

The location of the critical point, and the corresponding minimum value of DO is of obvious importance. It is at this point where stream conditions are at their worst. Setting the derivative of the oxygen deficit equal to zero, and solving for the critical time, yields

$$t_c = \frac{1}{k_r - k_d}\ln\left\{\frac{k_r}{k_d}\left[1 - \frac{D_0(k_r - k_d)}{k_d L_0}\right]\right\} \tag{5.32}$$

The maximum deficit can then be found by substituting the value obtained for the critical time, t_c, into (5.28).

The oxygen sag curve should make some intuitive sense, even without the mathematical analysis. Near the outfall, there is so much organic matter being degraded that the rate of removal of oxygen from the water is higher than the rate that it can be returned by reaeration, so the dissolved oxygen drops. As we move further downstream there is less and less organic matter remaining, so the rate of removal of oxygen keeps dropping as well. At the critical point the rate of removal of oxygen equals the rate of addition of oxygen by reaeration. Beyond the critical point, reaeration begins to dominate, returning oxygen to the river at a faster rate than the bacteria remove it so the dissolved oxygen begins its climb back to the saturation value. Figure 5.16 shows the rate of deoxygenation, the rate of reaeration, and the oxygen sag curve.

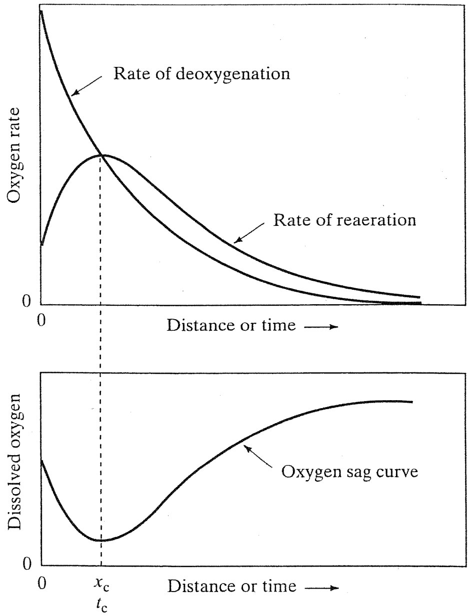

FIGURE 5.16 While the rate of deoxygenation exceeds the rate of reaeration the DO in the river drops. At the critical point those rates are equal. Beyond the critical point, reaeration exceeds decomposition, the DO curve climbs toward saturation, and the river recovers.

EXAMPLE 5.8 Streeter-Phelps Oxygen Sag Curve

Just below the point where a continuous discharge of pollution mixes with a river, the BOD is 10.9 mg/L and DO is 7.6 mg/L. The river and waste mixture has a temperature of 20 °C, a deoxygenation constant k_d of 0.20/day, an average flow speed of 0.30 m/s, and an average depth of 3.0 m. (In other words, this is just a continuation of the problem started in Examples 5.6 and 5.7).

a. Find the time and distance downstream at which the oxygen deficit is a maximum.

b. Find the minimum value of DO.

Solution From Table 5.11, the saturation value of DO at 20 °C is 9.1 mg/L, so the initial deficit is

$$D_0 = 9.1 - 7.6 = 1.5 \text{ mg/L}$$

To estimate the reaeration constant, we can use the O'Connor and Dobbins relationship given in (5.24):

$$k_r = \frac{3.9\,u^{1/2}}{H^{3/2}} = \frac{3.9\,(0.30)^{1/2}}{(3.0)^{3/2}} = 0.41/\text{day}$$

a. Using (5.32), we can find the time at which the deficit is a maximum:

$$t_c = \frac{1}{k_r - k_d} \ln\left\{\frac{k_r}{k_d}\left[1 - \frac{D_0(k_r - k_d)}{k_d L_0}\right]\right\}$$

$$= \frac{1}{(0.41 - 0.20)} \ln\left\{\frac{0.41}{0.20}\left[1 - \frac{1.5\,(0.41 - 0.20)}{0.20 \times 10.9}\right]\right\} = 2.67 \text{ days}$$

so the critical distance downstream would be

$$x_c = ut_c = 0.30 \text{ m/s} \times 3600 \text{ s/hr} \times 24 \text{ hr/d} \times 2.67 \text{ d} = 69{,}300 \text{ m} = 69.3 \text{ km}$$

which is about 43 miles

b. The maximum deficit can be found from (5.27):

$$D = \frac{k_d L_0}{k_r - k_d}\left(e^{-k_d t} - e^{-k_r t}\right) + D_0 e^{-k_r t}$$

$$= \frac{0.20 \times 10.9}{(0.41 - 0.20)}\left(e^{-0.20 \times 2.67} - e^{-0.41 \times 2.67}\right) + 1.5e^{-0.41 \times 2.67} = 3.1 \text{ mg/L}$$

so the minimum value of DO will be the saturation value minus this maximum deficit:

$$\text{DO}_{\text{min}} = (9.1 - 3.1) \text{ mg/L} = 6.0 \text{ mg/L}$$

■

In the preceding example, the lowest value of DO was found to be 6.0 mg/L, an amount sufficient for most aquatic life. If the amount of BOD added to the river is excessive, the oxygen sag curve may drop below a minimum acceptable level, leading to a stretch of river with unhealthful conditions, as shown in Figure 5.17. Fish that cannot tolerate water with such oxygen will be driven elsewhere or they will die. The variety of animals that can inhabit the unhealthy region is diminished and less desirable forms take over, forming thick mats of fungi, filamentous bacteria, sludge, and blood worms that blanket the bottom. The extreme case of excessive pollution is one in which the dissolved oxygen is driven to zero, creating a nearly lifeless, anaerobic stretch of river. Decomposition continues at a much slower rate by anaerobic microbes, releasing noxious and toxic gases such as hydrogen sulfide and ammonia.

Figure 5.17 may seem to suggest that the cause of an unhealthful drop in DO is an increase in the BOD from a waste source. That may be the case, but the oxygen sag curve is also sensitive to other sorts of changes. The DO curve changes with the

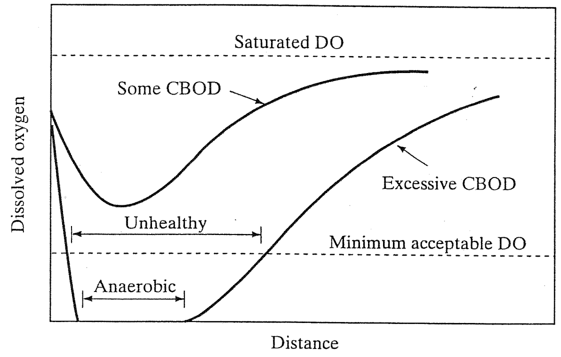

FIGURE 5.17 As a river gets more polluted, the oxygen sag curve drops below an acceptable level, and in the extreme case anaerobic conditions can occur.

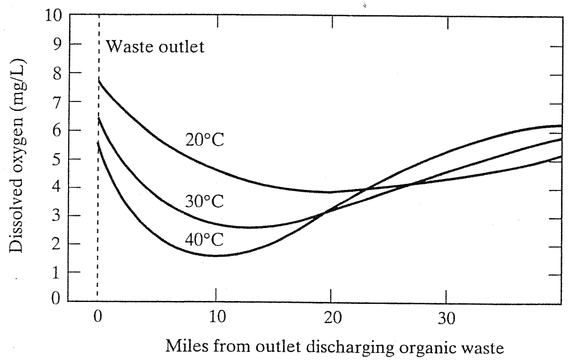

FIGURE 5.18 Changes in the oxygen sag curve as temperature increases. At higher temperatures the minimum DO is lower.

seasons, with the temperature, and with the time of day, even if the pollutant load is constant. In summer months, for example, river flows are usually diminished so the amount of waste dilution decreases, the BOD of the river/waste mix goes up, and the minimum DO drops.

The effect of temperature on the oxygen sag curve is also important (Figure 5.18). As temperatures rise, wastes decompose faster and the rate of deoxygenation increases. At the same time, the saturated value of DO drops, so reaeration slows down. The combination of these effects causes the critical point downstream to be reached sooner and the minimum value of DO to be lower as well. Thus a stream that may have sufficient DO in colder months may have an unacceptable deficit in the warmer months of summer..It also illustrates the potential adverse impact caused by thermal pollution from power plants. A river that might have been able to accept a certain sewage load without adverse effects could have unacceptably low oxygen levels when a power plant is added.

Photosynthesis also affects DO. Algae and other aquatic plants add DO during the daytime hours, while photosynthesis is occurring, but at night their continued respiration draws it down again. The net effect is a diurnal variation that can lead to elevated levels of DO in the late afternoon and depressed concentrations at night. For a lake or a slow-moving stream that is already overloaded with BOD and choked with algae, it is not unusual for respiration to cause offensive, anaerobic conditions late at night, even though the river seems fine during the day.

There are other factors not included in our simple oxygen sag model. Accumulated sludge along the bottom contributes to the oxygen demand; tributaries contribute their own BOD and DO; multiple sources cause multiple dips in the sag curve; nonpoint sources contribute pulses of BOD and other contaminants when it rains; and this model has not included the effects of nitrification. Nitrification causes a second dip in the oxygen sag curve a little further downstream as ammonia and organic nitrogen convert to nitrite and nitrate. If there is not enough DO downstream for nitrification to proceed, nitrogen remains as ammonia, which is toxic.

Modeling the impacts of BOD on the oxygen resources in a stream or river is an important part of the permitting process for new sources. Stream models can help determine the maximum amount of additional BOD that will be allowed, which, in turn, affects facility siting decisions and the extent of on-site waste treatment that will be required.

5.7 WATER QUALITY IN LAKES AND