BOD and Oxygen Saturation

LECTURE OVERVIEW: After a brief introduction to the dissolved oxygen problem, I describe how BOD serves as a means to quantify the oxygen demand of a wastewater. Simple mass balances are developed for the BOD of a batch system. Following a brief review of Henry's law, I also present a general overview of the saturation of oxygen in water.

In Lec. 1, I stated that engineers originally became involved in water-quality modeling to assess the impact of sewage on receiving waters. We will now study the models that were developed to solve this problem. To place these models in context, I'll first describe the cycle of organic production and decomposition that occurs in the biosphere.

19.1 THE ORGANIC PRODUCTION/DECOMPOSITION CYCLE

As depicted in Fig. 19.1 the biosphere can be viewed as a cycle of life and death. Powered by the sun, autotrophic[†] organisms (primarily plants) convert simple inorganic nutrients into more complex organic molecules. In *photosynthesis*, solar energy is stored as chemical energy in the organic molecules. In addition oxygen is liberated and carbon dioxide is consumed.

The organic matter then serves as an energy source for heterotrophic organisms (bacteria and animals) in the reverse processes of *respiration* and *decomposition*.

[†] The term *autotrophic* refers to organisms like plants that do not depend on other organisms for nutrition. In contrast *heterotrophic* organisms consist of animals and most bacteria that subsist on organic matter.
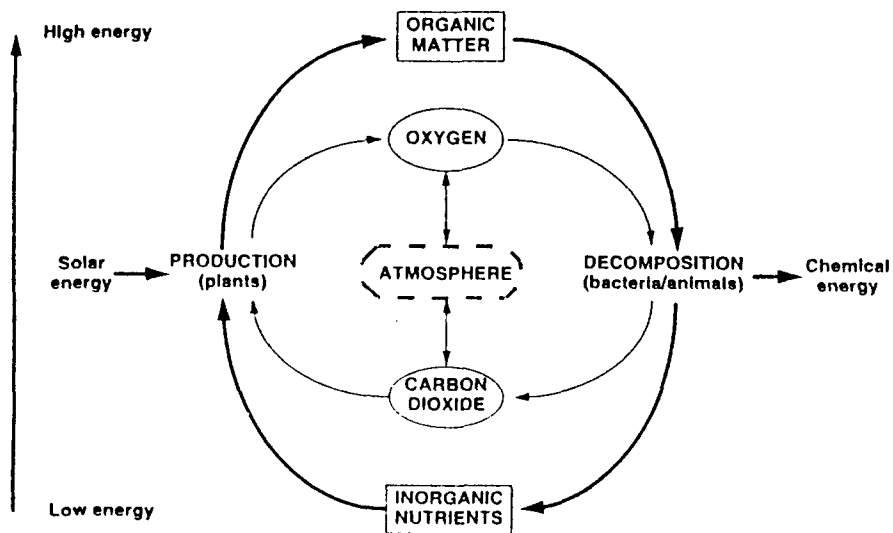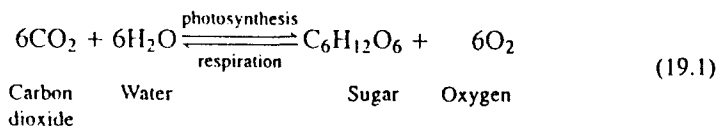
FIGURE 19.1
The natural cycle of organic production and decomposition.

These return the organic matter to the simpler inorganic state. During breakdown, oxygen is consumed and carbon dioxide is liberated.

The cycle can be represented in chemical terms by the following simple expression:

$$6CO_2 + 6H_2O \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftharpoons}} C_6H_{12}O_6 + 6O_2 \qquad (19.1)$$

<div style="text-align:center">Carbon   Water   Sugar   Oxygen
dioxide</div>

According to this reversible reaction, carbon dioxide and water are used to synthesize organic matter (the sugar glucose) and to create oxygen in the forward photosynthesis reaction. Conversely the organic matter is broken down and oxygen is consumed in the reverse respiration and decomposition reactions.

The chemistry of the production/decomposition cycle is far more complicated than Eq. 19.1. For example many different organic compounds are created and broken down in the process. In addition other elements beyond carbon, hydrogen, and oxygen are involved. In later lectures I'll present a more complete representation. However, Eq. 19.1 provides a starting point for our efforts to quantify the process.

19.2 THE DISSOLVED OXYGEN SAG

Now that we have the big picture, let's link the life/death cycle with the environment in a stream below a wastewater discharge (Fig. 19.2). If the stream is originally unpolluted, dissolved oxygen levels above the discharge will be near saturation. The introduction of the untreated sewage will elevate the levels of both dissolved and
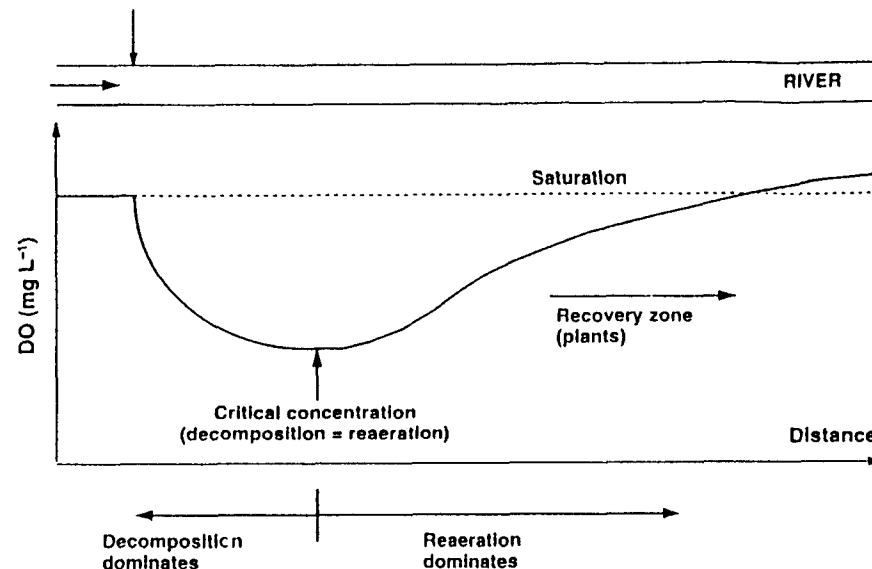

FIGURE 19.2
The dissolved oxygen "sag" that occurs below sewage discharges into streams.

solid organic matter. This has two impacts. First, the solid matter makes the water turbid. Thus light cannot penetrate and plant growth is suppressed. Some of the solids settle downstream from the sewage outfall and create sludge beds that can emit noxious odors (Fig. 19.3a). Second, the organic matter provides food for heterotrophic organisms. Consequently the right side of the cycle in Fig. 19.1 becomes dominant. Large populations of decomposer organisms break down the organic matter in the water and in the process deplete the dissolved oxygen. In addition decomposition of the organic matter takes place in the sludge bed and a sediment oxygen demand supplements the decay in the water.

As oxygen levels drop, atmospheric oxygen enters the water to compensate for the oxygen deficit. At first the oxygen consumption in the water and to the sediments dwarfs this *reaeration*. However, as the organic matter is assimilated and the oxygen levels drop, there will come a point at which the depletion and the reaeration will be in balance. At this point the lowest or "critical" level of oxygen will be reached. Beyond this point reaeration dominates and oxygen levels begin to rise. In this recovery zone the water becomes clearer because much of the solid matter from the discharge will have settled. In addition inorganic nutrients liberated during the decomposition process will be high. Consequently the recovery zone will often be dominated by the growth of plants. Thus the left side of the cycle from Fig. 19.1 can become overemphasized.

Beyond the chemical changes, sewage also leads to significant effects on the biota. As in Fig. 19.3b and c, molds and bacteria dominate near the discharge. In addition the bacteria themselves provide a food source for a succession of organisms
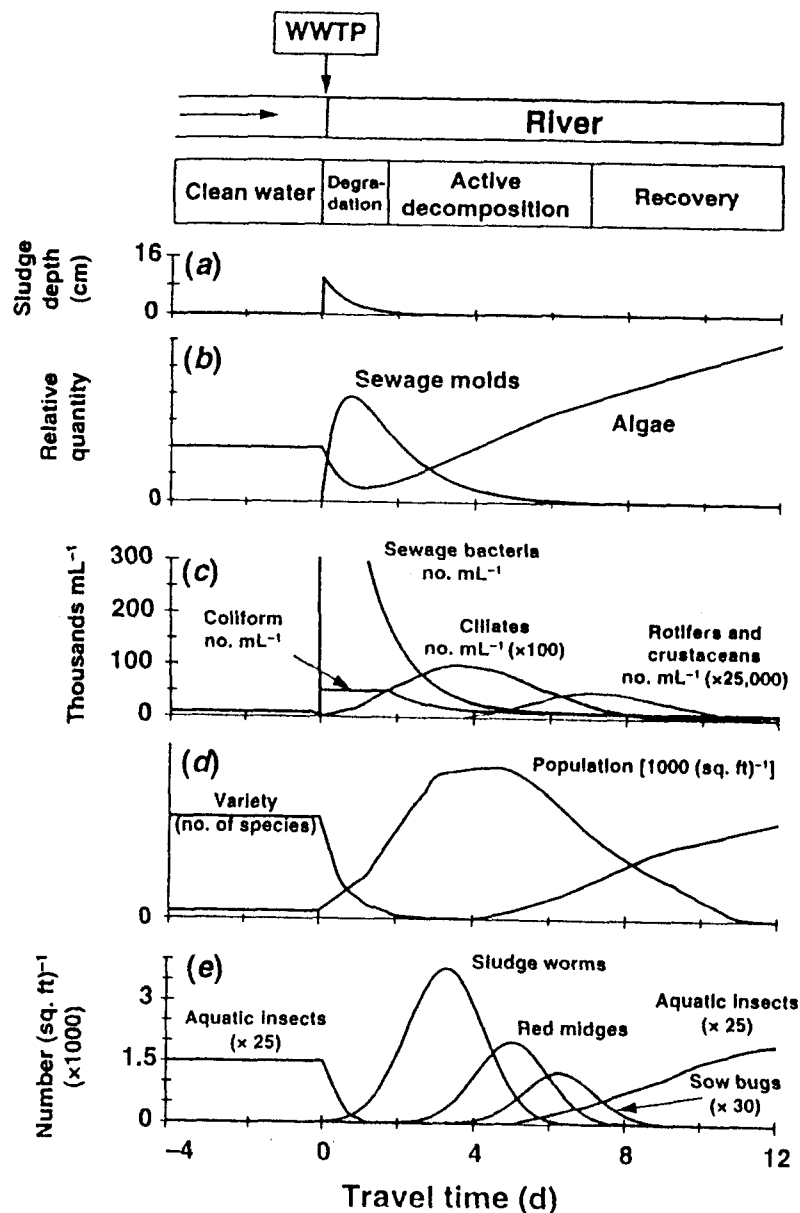
FIGURE 19.3

The changes in the biota below a sewage treatment plant effluent (redrawn from Bartsch and Ingram 1977).

consisting of ciliates, rotifers, and crustaceans. The diversity of higher organisms decreases drastically in the degradation and active decomposition zones below the discharge. At the same time the total number of organisms increases (Fig. 19.3d and e). As recovery ensues, these trends are reversed.

All the chemical interactions form the characteristic dissolved oxygen "sag" shown in Fig. 19.2. The key feature of the sag is the critical or minimum concentration. The location and magnitude of this critical concentration depends on a number of factors, including the size of the loading, the stream's flow and morphometry, water temperature, etc. The goal of the models formulated below will be to simulate the sag as a function of these factors.

19.3 EXPERIMENT

The first step in modeling the DO sag will be to characterize the strength of the wastewater. To do this we will focus on the respiration/decomposition portion of the life/death cycle. In terms of the general chemical representation from Eq. 19.1, this is

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{respiration}} 6CO_2 + 6H_2O \qquad (19.2)$$
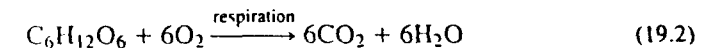
Now let's imagine a closed-batch experiment to investigate how this reaction affects a simple environment (recall Lec. 2). Suppose that you placed a quantity of sugar into a bottle of water with an initial oxygen content of o_0. You also add a small amount of bacteria and stopper the bottle. Assuming that decomposition proceeds as a first-order reaction, a mass balance for the glucose can be written as

$$V\frac{dg}{dt} = -k_1 V g \qquad (19.3)$$

where g = glucose concentration (mg-glucose L^{-1}) and k_1 = the decomposition rate in the bottle (d^{-1}). If the initial level of glucose is g_0, this equation can be solved for

$$g = g_0 e^{-k_1 t} \qquad (19.4)$$

Next a mass balance can be written for oxygen,

$$V\frac{do}{dt} = -r_{og} k_1 V g \qquad (19.5)$$

where o = oxygen concentration (mgO L^{-1}) and r_{og} = the stoichiometric ratio of oxygen consumed to glucose decomposed (mgO mg-glucose^{-1}). Equation 19.4 can be substituted into Eq. 19.5 to give

$$V\frac{do}{dt} = -r_{og} k_1 V g_0 e^{-k_1 t} \qquad (19.6)$$

If the initial level of oxygen is o_0, this equation can be solved for

$$o = o_0 - r_{og} g_0 (1 - e^{-k_1 t}) \qquad (19.7)$$

According to this equation, the bottle will originally have a dissolved oxygen level of o_0. Thereafter the oxygen will decrease exponentially and asymptotically approach a level of

$$o \rightarrow o_0 - r_{og}g_0 \qquad (19.8)$$

Before proceeding further, let's work an example.

EXAMPLE 19.1. OXYGEN DEPLETION IN A CLOSED BATCH SYSTEM.

You place 2 mg of glucose in a 250-mL bottle. After adding a small quantity of bacteria, you fill the remainder of the volume with water and stopper the bottle. The initial concentration of oxygen is 10 mg L^{-1}. If glucose decomposes at a rate of 0.1 d^{-1}, determine the oxygen concentration as a function of time in this closed batch system.

Solution: First, we must determine the initial concentration of glucose,

$$g_0 = \frac{2 \text{ mg}}{250 \text{ mL}} \left(\frac{1000 \text{ mL}}{L} \right) = 8 \text{ mg L}^{-1}$$

Next we must determine the ratio of mass of oxygen consumed per mass of glucose decomposed. Using the stoichiometry of Eq. 19.2 we can calculate

$$r_{og} = \frac{6(32)}{6 \times 12 + 1 \times 12 + 6 \times 16} = 1.0667 \text{ mgO mg-glucose}^{-1}$$

Therefore total decomposition of the glucose would consume the following amount of oxygen:

$$r_{og}g_0 = 1.0667 \times 8 = 8.5333 \text{ mg L}^{-1}$$

Consequently the oxygen level in the bottle will ultimately approach (Eq. 19.8)

$$o \rightarrow 10 - 8.5333 = 1.4667 \text{ mg L}^{-1}$$

Equation 19.7 can then be used to compute the oxygen level as a function of time. Some results, along with the glucose levels (expressed as oxygen equivalents) computed with Eq. 19.4 are displayed below:

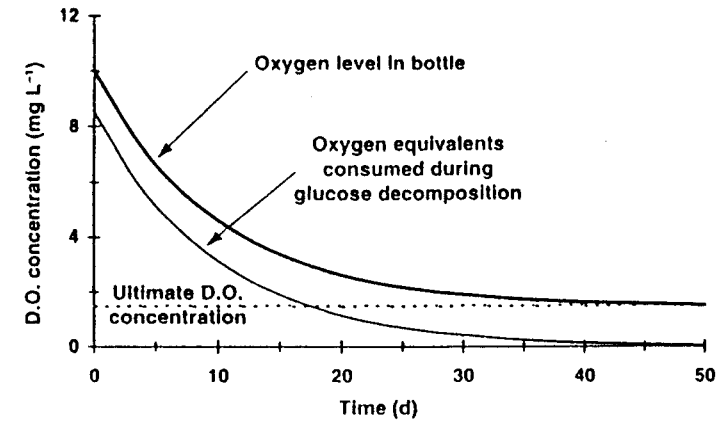| Time (d)	Glucose (mgO L^{-1})	Oxygen (mgO L^{-1})
0	8.5333	10.0000
4	5.7201	7.1867
8	3.8343	5.3009
12	2.5702	4.0369
16	1.7229	3.1895
20	1.1549	2.6215

A graph of the results can also be generated:

FIGURE E19.1

19.4 BIOCHEMICAL OXYGEN DEMAND

The experiment outlined at the end of the last section was intended to show how the decomposition process could be modeled for a simple batch system. At face value a similar approach could be used to model how sewage would affect oxygen levels. However, such an approach would be problematic because, as mentioned previously, sewage is not composed of simple sugar. Thus to rigorously apply the approach, we would have to characterize the concentrations of the myriad organic compounds in each sewage sample. We would further need to determine the stoichiometry of the decomposition for each reaction. Finally each of the compounds could decompose at a different rate. Obviously such a rigorous approach would be impractical.

In the early days of modeling, the constraints on such an approach were even more severe because of the limitations of the technology for characterizing organic compounds. As a consequence the first water-quality analysts took an empirical approach and simply disregarded the composition of the sewage. As in our simple experiment from Example 19.1, the analysts introduced some sewage into a batch reactor and merely measured how much oxygen was consumed. The resulting quantity was dubbed *biochemical oxygen demand* or *BOD*.

In terms of our simple model we can now define a new variable L (mgO L^{-1}) that is the amount of oxidizable organic matter remaining in the bottle expressed as oxygen equivalents. A mass balance for L for the batch system can be written as

$$V\frac{dL}{dt} = -k_1 VL \qquad (19.9)$$

If the initial level is L_0, this equation can be solved for

$$L = L_0 e^{-k_1 t} \qquad (19.10)$$

Note that the oxygen consumed during the decomposition process can be defined as

$$y = L_0 - L \tag{19.11}$$

or substituting Eq. 19.10,

$$y = L_0(1 - e^{-k_1 t}) \tag{19.12}$$

where y = BOD (mgO L^{-1}). We can now see that the value L_0 can be defined as either the initial concentration of oxidizable organic matter (expressed in oxygen units) or as the ultimate BOD. This notion is reinforced by Fig. 19.4, which shows both Eq. 19.10 and 19.12.

Next a mass balance can be written for oxygen,

$$V\frac{do}{dt} = -k_1 V L_0 e^{-k_1 t} \tag{19.13}$$

If the initial level of oxygen is o_0, this equation can be solved for

$$o = o_0 - L_0(1 - e^{-k_1 t}) \tag{19.14}$$

According to this equation the bottle will originally have a dissolved oxygen level of o_0. Thereafter the oxygen will decrease exponentially and asymptotically approach a level of

$$o \rightarrow o_0 - L_0 \tag{19.15}$$

Notice that this development is identical to the glucose experiment. In fact the glucose experiment could be modeled in terms of BOD by substituting
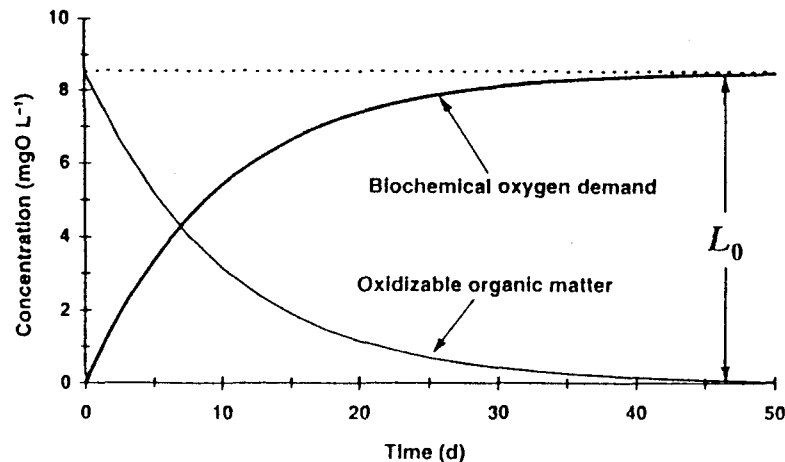

FIGURE 19.4
The value L_0 can be defined as either the initial concentration of oxidizable organic matter or as the ultimate BOD.

$$L_0 = r_{og} g_0 \tag{19.16}$$

Thus by disregarding the exact composition of the organic matter, we avoid the necessity of characterizing the organic matter and its stoichiometry relative to oxygen.

Finally it should be noted that although the exact composition of the organic matter in wastewater is not characterized, the organic carbon content can be measured directly. In these cases Eq. 19.16 can be reformulated to estimate the BOD on the basis of organic carbon content, as in

$$L_0 = r_{oc} C_{org} \tag{19.17}$$

where C_{org} = organic carbon concentration of the wastewater (mgC L^{-1}) and r_{oc} = ratio of mass of oxygen consumed per mass of carbon assimilated (mgO mgC^{-1}). Again, Eq. 19.2 provides a basis for estimating the ratio

$$r_{oc} = \frac{6(32)}{6(12)} = 2.67 \text{ mgO mgC}^{-1} \tag{19.18}$$

Finally it should be noted that along with the decomposition of carbonaceous matter, an additional oxygen demand is exerted due to the oxidation of ammonia to nitrate in the process called **nitrification**. The oxygen demand due to nitrification is sometimes referred to as **nitrogenous BOD** or **NBOD** to distinguish it from the carbonaceous BOD or CBOD described above. In Lec. 23 we will describe nitrification and NBOD in detail.

19.5 BOD MODEL FOR A STREAM

Now we can take our model and apply it to a stream below a sewage treatment plant. When we do this we must now consider that, in addition to decomposition, the BOD can also be removed by sedimentation. Therefore the mass balance for a constant-flow, constant-geometry channel can be written as

$$\frac{\partial L}{\partial t} = -U\frac{\partial L}{\partial x} - k_r L \tag{19.19}$$

where k_r = total removal rate (d^{-1}), which is composed of both decomposition and settling,

$$k_r = k_d + k_s \tag{19.20}$$

where k_d = decomposition rate in the stream (d^{-1}) and k_s = settling removal rate (d^{-1}). Recognize that the decomposition rate represents the same type of process as the k_1 from the bottle experiment (recall Eqs. 19.3 and 19.9). We have used a different subscript in Eq. 19.20 to highlight that decomposition in a natural environment such as a river will generally be different from that in a bottle. In addition note that the settling rate is related to more fundamental parameters by

$$k_s = \frac{v_s}{H} \tag{19.21}$$

where v_s = BOD settling velocity (m d^{-1}) and H = water depth (m).

At steady-state, Eq. 19.19 becomes

$$0 = -U\frac{dL}{dx} - k_r L \tag{19.22}$$

If complete mixing is assumed at the location of the discharge, an initial concentration can be calculated as the flow-weighted average (recall Eq. 9.42) of the loading (subscript w) and the BOD in the river upstream of the discharge (subscript r),

$$L_0 = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r} \tag{19.23}$$

Using this value as an initial condition, we can solve Eq. 19.22 for

$$L = L_0 e^{-\frac{k_r}{U}x} \tag{19.24}$$

Thus the BOD is reduced by decomposition and settling as it is carried downstream.

Aside from modeling the distribution of BOD below a point source in a plug-flow stream with constant parameters, Eq. 19.24 provides a framework for estimating the removal rate in such systems. To do this, the natural logarithm can be taken,
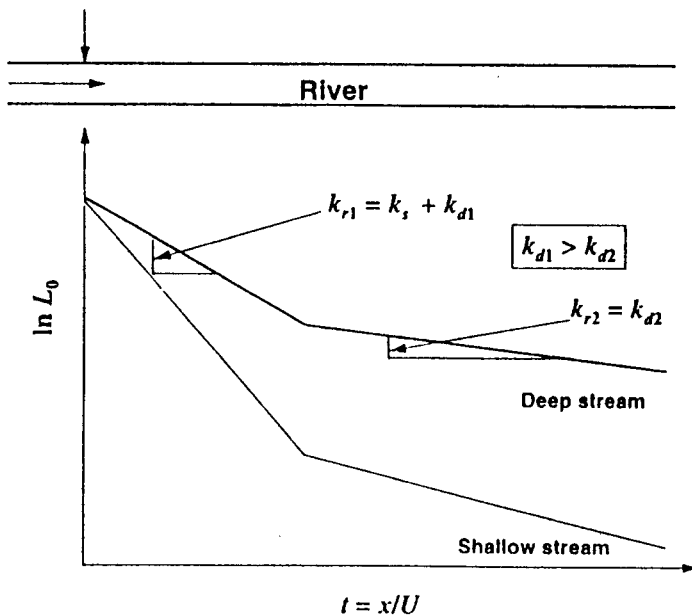

FIGURE 19.5
Plot of BOD downstream from a point source of untreated sewage into a plug-flow river having constant hydrogeometric characteristics. In the initial stretch, high BOD removal rates will occur due to settling and fast decomposition of easily degradable organic matter. Further downstream the lower removal rates will occur as the more refractory organic matter degrades at a slower rate.

$$\ln L = \ln L_0 - \frac{k_r}{U}x \tag{19.25}$$

Consequently if the simple model holds, a plot of $\ln L$ versus x/U (that is, travel time) should yield a straight line with a slope of k_r.

Figure 19.5 shows a typical pattern that might be observed in a stream receiving untreated sewage. Note how the rate is higher immediately below the discharge. Several factors underlie such a pattern. In particular the higher rates are usually caused by the fast degradation of readily decomposable organics and the settling of sewage particulates.

19.6 BOD LOADINGS, CONCENTRATIONS, AND RATES

Before proceeding to other aspects of DO modeling, let's review some of the parameters that relate to biochemical oxygen demand.

19.6.1 BOD₅ (5-Day BOD)

As in Table 19.1, typical values for the BOD bottle decay rate range from 0.05 to 0.5 d⁻¹, with a geometric mean of about 0.15 d⁻¹. This information can be used to estimate a 95% response time for the bottle test as $t_{95} = 3/0.15 = 20$ d. Because such a long measurement period is unacceptable, water-quality analysts early on adopted a 5-day BOD test.

Although shortening the incubation time to 5 d makes the test practical, we must then have a means to extrapolate the 5-d result to the ultimate BOD level. This is usually done by performing a long-term BOD to estimate the decay rate. If the first-order decomposition model holds, Eq. 19.12 can be used to compute

$$L_0 = \frac{y_5}{1 - e^{-k_1(5)}} \tag{19.26}$$

where $y_5 = $ 5-day BOD. Table 19.1 includes typical values for the ratio of 5-day to ultimate BOD.

19.6.2 BOD Loadings and Concentrations

Table 19.2 provides typical values of flow rate and BOD for raw sewage from both the United States and developing countries. In general the flow rate for the United

TABLE 19.1
Typical values of the BOD bottle decomposition rate for various levels of treatment. BOD$_u$ is the ultimate BOD. Values here are for CBOD

Treatment	$k_1(20°C)$	BOD₅/BOD$_u$
Untreated	0.35 (0.20–0.50)	0.83
Primary	0.20 (0.10–0.30)	0.63
Activated sludge	0.075 (0.05–0.10)	0.31

TABLE 19.2
Typical loading rates for untreated domestic sewage

	Per-capita flow rate (m³ capita⁻¹ d⁻¹)	Per-capita CBOD (m³ capita⁻¹ d⁻¹)	CBOD concentration (mg L⁻¹)
United States	0.57 (150)[*]	125 (0.275)[†]	220
Developing countries	0.19 (50)[*]	60 (0.132)[†]	320

[*]Gallons capita⁻¹ day⁻¹; [†]pounds capita⁻¹ day⁻¹.

States is higher because higher water use typically accompanies a higher standard of living. Per capita generation rate of BOD is also higher because of garbage disposals and other accouterments of a developed economy like that of the United States. The average concentration of the developing countries is generally higher because the lower water use in these countries outweighs the higher per capita BOD contribution for the United States.

19.6.3 BOD Removal Rates

The bottle BOD decomposition rate provides a first estimate of the removal rate in natural waters. As listed in Table 19.1, the rates depend on the degree of treatment of the sewage prior to discharge. Raw sewage is a mixture of compounds ranging from easily decomposable sugars to refractory substances that take longer to break down. Because waste treatment tends to selectively remove the former, BOD bottle rates tend to be lower for treated sewage.
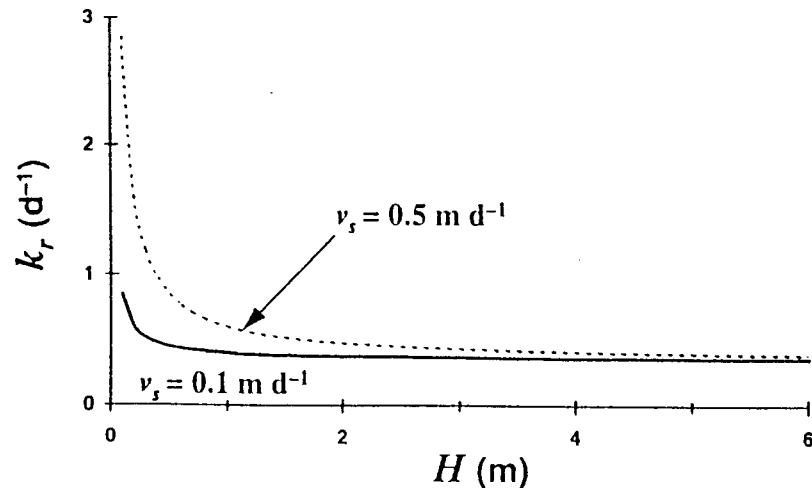
FIGURE 19.6
Plot of total removal rate versus stream depth for BOD that is 50% in settleable form. A range of settling velocities is depicted. Note that a decomposition rate of 0.35 d⁻¹ is used.
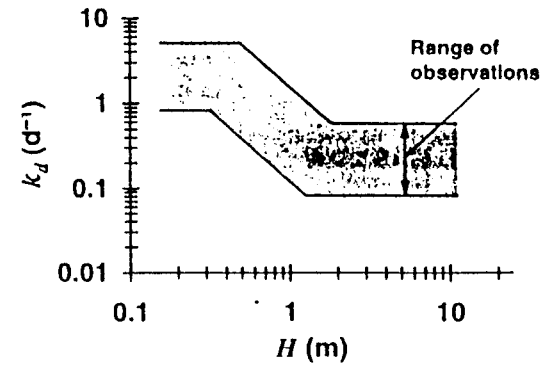
FIGURE 19.7
In-stream decomposition rate versus depth (Bowie et al. 1985).

As might be expected, the bottle rate can rarely be directly applied to rivers because the bottle environment is not a good representation of the river. In fact only in deep, slow rivers would the two converge. In most other rivers, environmental factors tend to make removal higher than for the bottle. The primary causes of this increase are settling and bed effects.

Settling. Settling effects relate to the fact that for sewage with a significant fraction of organic solids, the total removal rate in streams is a combination of settling and decomposition (recall Eqs. 19.20 and 19.21),

$$k_r = k_d + \frac{v_s}{H} \tag{19.27}$$

Using some typical settling velocities, we can see (Fig. 19.6) that the settling effect can be particularly significant for raw sewage in shallow streams (that is, < 1 m).

Bed effects. All other things equal, attached bacteria generally are more effective decomposers than free-floating bacteria. Bottom decomposition can be parameterized as a mass-transfer flux of BOD. Thus in a way similar to settling, bottom decomposition becomes more pronounced in shallower systems because the effect becomes more significant relative to the volumetric decomposition in the water.

This trend, which is displayed in Fig. 19.7, has been fit by the equations (Hydroscience 1971)

$$k_d = 0.3\left(\frac{H}{8}\right)^{-0.434} \qquad 0 \le H \le 8 \text{ ft}$$
$$k_d = 0.3 \qquad\qquad H > 8 \text{ ft} \cdot \tag{19.28}$$

Thus up to about 2.4 m (8 ft) the rate decreases with depth. Above 2.4 m the rate approaches a constant value that is typical of bottle rates.

Finally, BOD decomposition rates can be extrapolated to other temperatures using Eq. 2.44 ($k = k_{20}\theta^{T-20}$), with $\theta \cong 1.047$.

In summary BOD removal rates tend to increase with temperature and tend to be higher immediately downstream from point sources. The latter effect is more

pronounced for untreated wastewater. In addition enhanced settling and bed effects means that shallower systems typically exhibit higher BOD removal rates than deeper waters.

19.7 HENRY'S LAW AND THE IDEAL GAS LAW

If a beaker of gas-free distilled water is opened to the atmosphere, gaseous compounds such as oxygen, carbon dioxide, and nitrogen cross the air-water interface and enter into solution (Fig. 19.8). The process will continue until an equilibrium is established between the partial pressure of the gas in the atmosphere and the concentration in the aqueous phase. This equilibrium is quantified by Henry's law, which can be represented as

$$H_e = \frac{p}{c} \qquad (19.29)$$

where H_e = Henry's constant (atm m^3 mole^{-1})
p = partial pressure (atm)
c = water concentration (mole m^{-3})

Henry's constants for some gases commonly encountered in water-quality modeling are summarized in Table 19.3.

Equation 19.29 can also be represented in dimensionless form by invoking the ideal gas law

$$c = \frac{p}{RT_a} \qquad (19.30)$$

where R = universal gas constant [8.206 × 10^{-5} atm m^3 (K mole)$^{-1}$] and T_a = absolute temperature (K). Thus the ideal gas law provides a means to express the partial pressure in concentration units of moles m^{-3}. Substituting Eq. 19.30 into 19.29 and rearranging yields the dimensionless Henry's constant

$$H_e'c_l < c_g \qquad H_e'c_l < c_g \qquad H_e'c_l = c_g$$

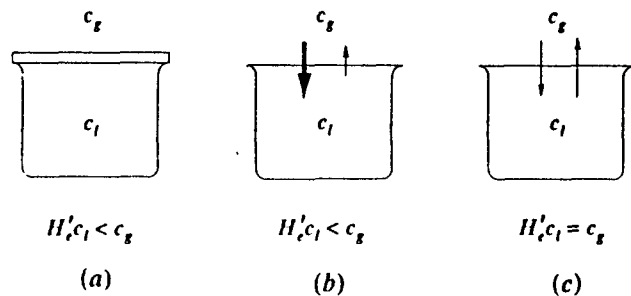$$(a) \qquad\qquad (b) \qquad\qquad (c)$$

FIGURE 19.8
The closed system in (a) is undersaturated with oxygen. When it is opened to the atmosphere (b), oxygen comes into solution until an equilibrium (c) is reached. Henry's law provides the means to quantify this equilibrium condition.

TABLE 19.3
Henry's constants for some gases commonly encountered in water-quality modeling (modified from Kavanaugh and Trussell 1980)

Compound	Formula	Henry's constant (20°C)	
		(Dimensionless)	(atm m^3 mole^{-1})
Methane	CH$_4$	64.4	1.55 × 10^0
Oxygen	O$_2$	32.2	7.74 × 10^{-1}
Nitrogen	N$_2$	28.4	6.84 × 10^{-1}
Carbon dioxide	CO$_2$	1.13	2.72 × 10^{-2}
Hydrogen sulfide	H$_2$S	0.386	9.27 × 10^{-3}
Sulfur dioxide	SO$_2$	0.0284	6.84 × 10^{-4}
Ammonia	NH$_3$	0.000569	1.37 × 10^{-5}

$$H_e' = \frac{H_e}{RT_a} = \frac{c_g}{c_l} \qquad (19.31)$$

where c_g and c_l are the gas and liquid concentrations, respectively (mole m^{-3}).

Notice that Henry's law specifies that at equilibrium the ratio of the gaseous to the water concentration will be maintained at a constant value. The water concentration for a particular gaseous level is referred to as the *saturation concentration*. In the following example we determine the saturation concentration for oxygen.

EXAMPLE 19.2. HENRY'S LAW AND OXYGEN SATURATION. Determine the saturation concentration of oxygen in water at 20°C. Note that clean, dry air near sea level is composed of approximately 20.95% oxygen by volume.

Solution: Assuming that Dalton's law holds, the partial pressure of oxygen can be computed as

$$p = 0.2095(1 \text{ atm}) = 0.2095 \text{ atm}$$

This value can then be substituted into Eq. 19.29 along with the value of Henry's constant from Table 19.3 to yield

$$c = \frac{p}{H_e} = \frac{0.2095}{0.774} = 0.2707 \text{ mole m}^{-3}$$

or in mass units,

$$c = 0.2707 \text{ mole m}^{-1}\left(\frac{32 \text{ g-oxygen}}{\text{mole}}\right) = 8.66 \text{ mg L}^{-1}$$

19.8 DISSOLVED OXYGEN SATURATION

As calculated in the previous example, the saturation concentration of oxygen in a natural water is on the order of 10 mg L^{-1}. In general several environmental factors can affect this value. From the perspective of water-quality modeling, the most important of these are:
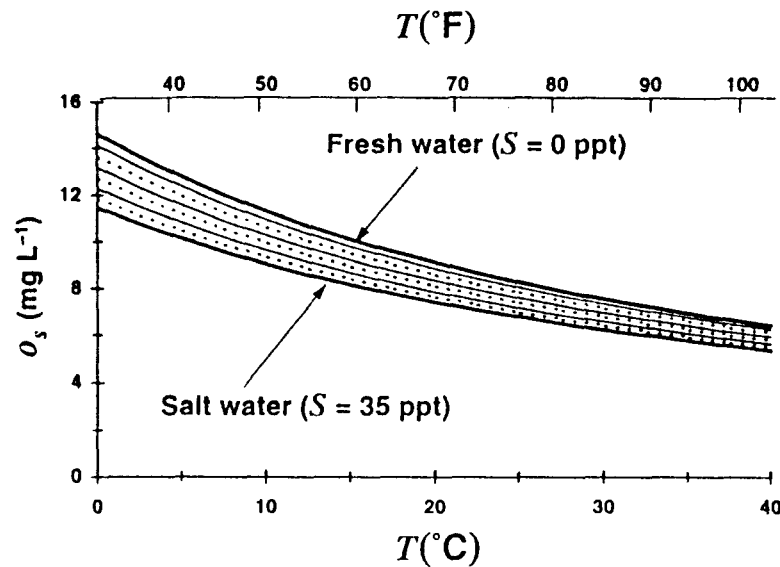
FIGURE 19.9
Relationship of oxygen saturation in water to temperature and salinity.

- Temperature
- Salinity
- Partial pressure variations due to elevation

Several empirically derived equations have been developed to predict how these factors influence saturation. These are reviewed in the following sections.

19.8.1 Temperature Effect

The following equation can be used to establish the dependence of oxygen saturation on temperature (APHA 1992):

$$\ln o_{sf} = -139.34411 + \frac{1.575701 \times 10^5}{T_a} - \frac{6.642308 \times 10^7}{T_a^2}$$

$$+ \frac{1.243800 \times 10^{10}}{T_a^3} - \frac{8.621949 \times 10^{11}}{T_a^4} \quad (19.32)$$

where o_{sf} = saturation concentration of dissolved oxygen in fresh water at 1 atm (mg L^{-1}) and T_a = absolute temperature (K). Remember that

$$T_a = T + 273.15 \quad (19.33)$$

where T = temperature (°C). According to this equation, saturation decreases with increasing temperature. As displayed in Fig. 19.9, freshwater concentration ranges from about 14.6 mg L^{-1} at 0°C to 7.6 mg L^{-1} at 30°C.

19.8.2 Salinity Effect

The following equation can be used to establish the dependence of saturation on salinity (APHA 1992):

$$\ln o_{ss} = \ln o_{sf} - S\left(1.7674 \times 10^{-2} - \frac{1.0754 \times 10^1}{T_a} + \frac{2.1407 \times 10^3}{T_a^2}\right) \quad (19.34)$$

where o_{ss} = saturation concentration of dissolved oxygen in saltwater at 1 atm (mg L^{-1}) and S = salinity (g L^{-1} = parts per thousand, ppt, sometimes given as ‰).
Salinity can be related to chloride concentration by the following approximation:

$$S = 1.80655 \times \text{Chlor} \quad (19.35)$$

where Chlor = chloride concentration (ppt). The higher the salinity, the less oxygen can be held by water (Fig. 19.9).

> **EXAMPLE 19.3. OXYGEN SATURATION FOR AN ESTUARY.** Determine the saturation for an estuary with a temperature of 20°C and a salinity of 25 ppt.
>
> **Solution:** Equation 19.32 can be used to compute
>
> $$\ln o_{sf} = -139.34411 + \frac{1.575701 \times 10^5}{293.15} - \frac{6.642308 \times 10^7}{293.15^2}$$
>
> $$+ \frac{1.243800 \times 10^{10}}{293.15^3} - \frac{8.621949 \times 10^{11}}{293.15^4} = 2.207$$
>
> This corresponds to a freshwater saturation value of
>
> $$o_{sf} = e^{2.207} = 9.092 \text{ mg L}^{-1}$$
>
> Equation 19.34 can be used to correct for salinity,
>
> $$\ln o_{ss} = 2.207 - 25\left(1.7674 \times 10^{-2} - \frac{1.0754 \times 10^1}{293.15} + \frac{2.1407 \times 10^3}{293.15^2}\right) = 2.060$$
>
> which corresponds to a saltwater saturation value of
>
> $$o_{ss} = e^{2.060} = 7.846 \text{ mg L}^{-1}$$
>
> Thus the saltwater value is about 86% of the freshwater value.

19.8.3 Pressure Effect

The following equation can be used to establish the dependence of saturation on pressure (APHA 1992):

$$o_{sp} = o_{sl}p\left[\frac{\left(1 - \frac{p_{wv}}{p}\right)(1 - \theta p)}{(1 - p_{wv})(1 - \theta)}\right] \quad (19.36)$$
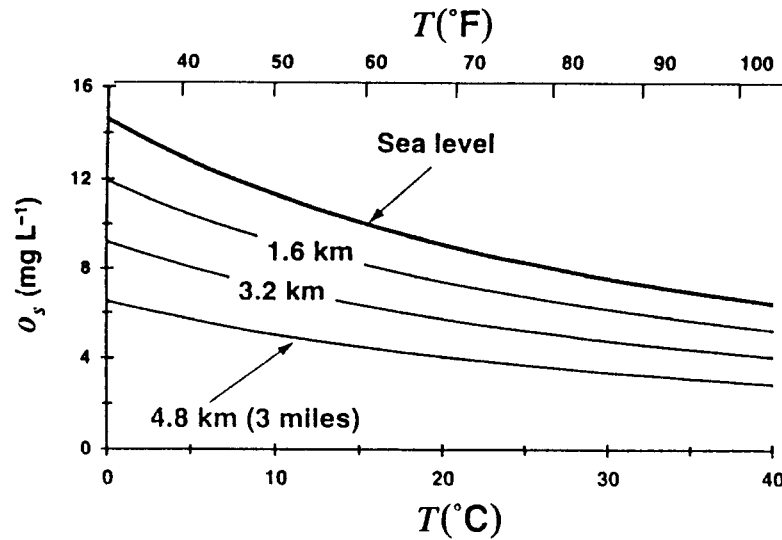
FIGURE 19.10
Relationship of oxygen saturation in water to temperature and elevation above sea level.

where p = atmospheric pressure (atm)

o_{sp} = saturation concentration of dissolved oxygen at p (mg L^{-1})

o_{sl} = saturation concentration of dissolved oxygen at 1 atm (mg L^{-1})

p_{wv} = partial pressure of water vapor (atm)

p_{wv} can be calculated by

$$\ln p_{wv} = 11.8571 - \frac{3840.70}{T_a} - \frac{216{,}961}{T_a^2} \tag{19.37}$$

The parameter θ can be computed as

$$\theta = 0.000975 - 1.426 \times 10^{-5}T + 6.436 \times 10^{-8}T^2 \tag{19.38}$$

Notice that this formula is written in terms of temperature in degrees Celsius rather than Kelvin.

Zison et al. (1978) have developed a handy approximation based on elevation.

$$o_{sp} = o_{sl}[1 - 0.1148 \times elev(km)] \tag{19.39}$$

or in English units,

$$o_{sp} = o_{sl}[1 - 0.000035 \times elev(ft)] \tag{19.40}$$

where elev = elevation above sea level. As displayed in Fig. 19.10 this relationship indicates that as pressure decreases at higher elevations, the saturation drops.

PROBLEMS

19.1. Use separation of variables to solve Eq. 19.6 for Eq. 19.7.

19.2. A tanker truck careens off the road and dumps 30,000 L of glucose syrup into a small mountain lake. The concentration of the syrup is 100 g-glucose L^{-1}.
(a) Compute the grams of CBOD spilled.
(b) Determine the lake's saturation concentration of oxygen (T = 10°C; elev = 11,000 ft.).

19.3. A lake with a bay has the following characteristics:

	Lake	Bay
Mean depth	8 m	3 m
Surface area	1.6×10^6 m^2	0.4×10^6 m^2
Inflow	50,000 m^3 d^{-1}	4800 m^3 d^{-1}
Inflow BOD concentration	0 mg L^{-1}	57 mg L^{-1}

A subdivision housing 1000 people is planned that will discharge raw sewage into the bay. Each individual contributes about 0.568 m^3 capita^{-1} d^{-1} of wastewater and 113.4 g capita^{-1} d^{-1} of carbonaceous biochemical oxygen demand.
(a) The bay inflow has a chloride concentrations of 50 mg L^{-1}. The lake and the bay have chloride concentrations of 5 and 10 mg L^{-1}, respectively. Determine the bulk diffusion coefficient between the lake and the bay.
(b) If the BOD decays at a rate of 0.1 d^{-1} and settles at a rate of 0.1 m d^{-1}, determine the steady-state BOD concentration of the lake and bay in mg L^{-1}. Make this determination with and without the subdivision.

19.4. The following data have been collected for dissolved and total BOD below a point source of untreated sewage into a stream. Use this data to estimate the BOD removal rates (k_r, k_s, and k_d) for the river. The velocity and depth are 6600 m d^{-1} and 2 m, respectively.

x (km)	0	5	10	15	20	25	30	35
Dissolved (mg L^{-1})	20.0	17.0	14.7	12.9	11.6	10.5	9.6	8.9
Total (mg L^{-1})	40.0	29.4	22.5	17.8	14.6	12.3	10.7	9.6

x (km)	40	45	50	60	70	80	90	100
Dissolved (mg L^{-1})	8.3	7.8	7.3	6.6	6.0	5.5	5.1	4.7
Total (mg L^{-1})	8.7	8.0	7.5	6.7	6.0	5.5	5.1	4.7

19.5. Determine the saturation concentrations at 20°C for (a) nitrogen gas (78.1% by volume in the atmosphere) and (b) carbon dioxide (0.0314%).

19.6. A flow of 2 cms with a 5-d BOD of 10 mg L^{-1} is discharged from an activated-sludge treatment plant to a stream with a flow of 5 cms and zero BOD. Stream characteristics are $k_{r,20}$ = 0.2 d^{-1}, cross-sectional area = 25 m^2, and T = 28°C.
(a) What is the concentration of BOD at the mixing point?
(b) How far below the effluent will the stream BOD concentration fall to 5% of its original value?