...is a measured quantity that does not depend either on ...microorganisms. The
the ability of microorganisms to degrade the waste or on knowledge of the particular

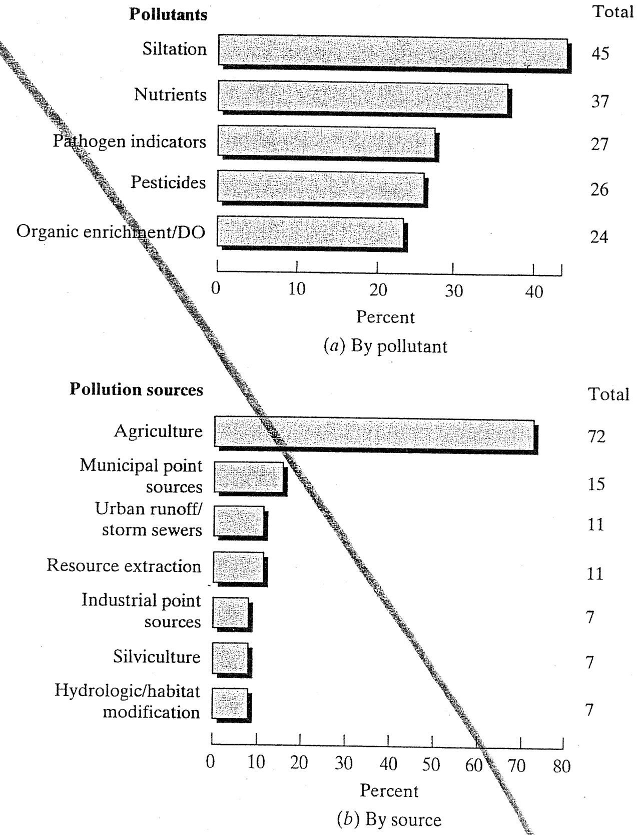

FIGURE 5.8 Percent of assessed river miles impaired by pollution: (a) By pollutants, (b) by sources of pollution. (U.S. EPA, 1994)

5.5 BIOCHEMICAL OXYGEN DEMAND

Surface water is obviously highly susceptible to contamination. It has historically been the most convenient sewer for industry and municipalities alike, while at the same time it is the source of the majority of our water for all purposes. One particular category of pollutants, oxygen-demanding wastes, has been such a pervasive surface-water problem, affecting both moving water and still water, that it will be given special attention.

When biodegradable organic matter is released into a body of water, microorganisms, especially bacteria, feed on the wastes, breaking them down into simpler organic and inorganic substances. When this decomposition takes place in an *aerobic* environment—that is, in the presence of oxygen—the process produces nonobjectionable, stable end products such as carbon dioxide (CO_2), sulfate (SO_4), orthophosphat (PO_4), and nitrate (NO_3). A simplified representation of aerobic decomposition i given by the following:

Aerobic Decomposition

$$\text{Organic matter} + O_2 \xrightarrow{\text{Microorganisms}} CO_2 + H_2O + \text{New cells} + \text{Stable products } (NO_3, PO_4, SO_4, \ldots)$$

When insufficient oxygen is available, the resulting *anaerobic* decomposition i performed by completely different microorganisms. They produce end products tha can be highly objectionable, including hydrogen sulfide (H_2S), ammonia (NH_3), an methane (CH_4). Anaerobic decomposition can be represented by the following:

Anaerobic Decomposition

$$\text{Organic matter} \xrightarrow{\text{Microorganisms}} CO_2 + H_2O + \text{New cells} + \text{Unstable products } (H_2S, NH_3, CH_4, \ldots$$

The methane produced is physically stable, biologically degradable, and is a poten greenhouse gas. When emitted from bodies of water, it is often called swamp gas. It i also generated in the anaerobic environment of landfills, where it is sometimes collected and used as an energy source.

The amount of oxygen required by microorganisms to oxidize organic waste aerobically is called the *biochemical oxygen demand* (BOD). BOD may have variou units, but most often it is expressed in milligrams of oxygen required per liter of waste water (mg/L). The biochemical oxygen demand, in turn, is made up of two parts: th *carbonaceous oxygen demand* (CBOD), and the *nitrogenous oxygen demand* (NBOD) Those distinctions will be clarified later.

Five-day BOD Test

The total amount of oxygen that will be required for biodegradation is an importan measure of the impact that a given waste stream will have on the receiving body o water. While we could imagine a test in which the oxygen required to degrade *complete* a sample of waste would be measured, for routine purposes such a test would take to long to be practical (at least several weeks would be required). As a result, it has becom standard practice simply to measure and report the oxygen demand over a shorter restricted period of five days, realizing that the ultimate demand is considerably higher.

The five-day BOD, or BOD_5, is the total amount of oxygen consumed b microorganisms during the first five days of biodegradation. In its simplest form, a BOD_5 test would involve putting a sample of waste into a stoppered bottle and measuring the concentration of dissolved oxygen (DO) in the sample at the beginning o the test and again five days later. The difference in DO divided by the volume of wast would be the five-day BOD. Light must be kept out of the bottle to keep algae from adding oxygen by photosynthesis, and the stopper is to keep air from replenishing D that has been removed by biodegradation. To standardize the procedure, the test is ru at a fixed temperature of 20 °C. Since the oxygen demand of typical waste is severa hundred milligrams per liter, and since the saturated value of DO for water at 20 °C i

chemical oxygen demand, COD, is a measured quantity that does not depend either on
the ability of microorganisms to degrade the waste or on knowledge of the particular

only 9.1 mg/L, it is usually necessary to dilute the sample to keep final DO above zero. If during the five days the DO drops to zero, the test is invalid since more oxygen would have been removed had more been available.

The five-day BOD of a diluted sample is given by

$$\text{BOD}_5 = \frac{\text{DO}_i - \text{DO}_f}{P} \tag{5.3}$$

where

DO_i = the initial dissolved oxygen (DO) of the diluted wastewater
DO_f = the final DO of the diluted wastewater, 5 days later
P = the dilution fraction = $\dfrac{\text{volume of wastewater}}{\text{volume of wastewater plus dilution water}}$

A standard BOD bottle holds 300 mL, so P is just the volume of wastewater divided by 300 mL.

EXAMPLE 5.1 Unseeded Five-day BOD Test

A 10.0-mL sample of sewage mixed with enough water to fill a 300-mL bottle has an initial DO of 9.0 mg/L. To help assure an accurate test, it is desirable to have at least a 2.0-mg/L drop in DO during the five-day run, and the final DO should be at least 2.0 mg/L. For what range of BOD_5 would this dilution produce the desired results?

Solution The dilution fraction is $P = 10/300$. To get at least a 2.0-mg/L drop in DO, the minimum BOD needs to be

$$\text{BOD}_5 \geq \frac{\text{DO}_i - \text{DO}_f}{P} = \frac{2.0\ \text{mg/L}}{(10/300)} = 60\ \text{mg/L}$$

To assure at least 2.0 mg/L of DO remaining after five days requires that

$$\text{BOD}_5 \leq \frac{(9.0 - 2.0)\ \text{mg/L}}{(10/300)} = 210\ \text{mg/L}$$

So this dilution will be satisfactory for BOD_5 values between 60 and 210 mg/L. ■

So far we have assumed that the dilution water added to the waste sample has no BOD of its own, which would be the case if pure water were added. In some cases it is necessary to seed the dilution water with microorganisms to assure that there is an adequate bacterial population to carry out the biodegradation. In such cases, to find the BOD of the waste itself, it is necessary to subtract the oxygen demand caused by the seed from the demand in the mixed sample of waste and dilution water.

To be able to sort out the effect of seeded dilution water from the waste itself, two BOD bottles must be prepared, one containing just the seeded dilution water and the other containing the mixture of both the wastewater and seeded dilution water (Figure 5.9). The change in DO in the bottle containing just seeded dilution water (called the "blank") as well as the change in DO in the mixture are then noted. T oxygen demand of the waste itself (BOD_w) can then be determined as follows:

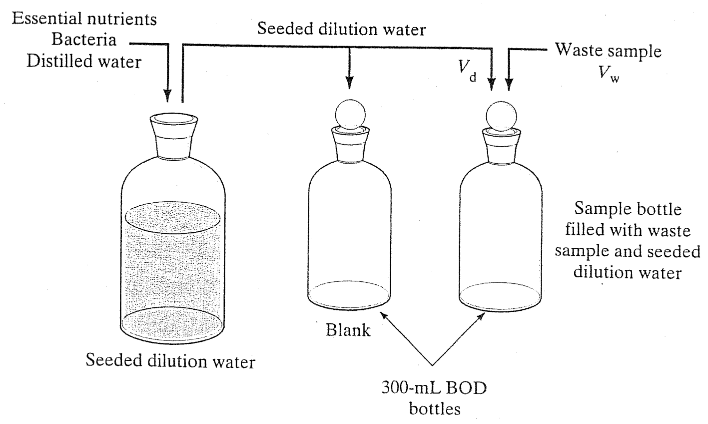

FIGURE 5.9 Laboratory test for BOD using seeded dilution water.

$$\text{BOD}_m V_m = \text{BOD}_w V_w + \text{BOD}_d V_d \qquad (5$$

where

BOD_m = BOD of the mixture of wastewater and seeded dilution water
BOD_w = BOD of the wastewater alone
BOD_d = BOD of the seeded dilution water alone (the blank)
V_w = the volume of wastewater in the mixture
V_d = the volume of seeded dilution water in the mixture
V_m = the volume of the mixture = $V_d + V_w$

Let P = the fraction of the mixture that is wastewater = V_w/V_m so tl $(1 - P)$ = the fraction of the mixture that is seeded dilution water = V_d/l Rearranging (5.4) gives

$$\text{BOD}_w = \text{BOD}_m\left(\frac{V_m}{V_w}\right) - \text{BOD}_d\left(\frac{V_d}{V_w} \times \frac{V_m}{V_m}\right) \qquad (5$$

where the last term has been multiplied by unity (V_m/V_m). A slight rearrangement (5.5) yields

$$\text{BOD}_w = \frac{\text{BOD}_m}{(V_w/V_m)} - \text{BOD}_d\frac{(V_d/V_m)}{(V_w/V_m)} \qquad (5$$

Substituting the definitions of P and $(1 - P)$ into (5.6) gives

$$\mathrm{BOD_w} = \frac{\mathrm{BOD_m} - \mathrm{BOD_d}(1-P)}{P} \tag{5.7}$$

Since

$$\mathrm{BOD_m} = \mathrm{DO_i} - \mathrm{DO_f} \quad \text{and} \quad \mathrm{BOD_d} = B_\mathrm{i} - B_\mathrm{f}$$

where

B_i = initial DO in the seeded dilution water (blank)
B_f = final DO in the seeded dilution water

our final expression for the BOD of the waste itself is thus

$$\mathrm{BOD_w} = \frac{(\mathrm{DO_i} - \mathrm{DO_f}) - (B_\mathrm{i} - B_\mathrm{f})(1-P)}{P} \tag{5.8}$$

EXAMPLE 5.2 A seeded BOD test

A test bottle containing just seeded dilution water has its DO level drop by 1.0 mg/L in a five-day test. A 300-mL BOD bottle filled with 15 mL of wastewater and the rest seeded dilution water (sometimes expressed as a dilution of 1:20) experiences a drop of 7.2 mg/L in the same time period. What would be the five-day BOD of the waste?

Solution The dilution factor P is

$$P = 15/300 = 0.05$$

Using (5.8), the five-day BOD of the waste would be

$$\mathrm{BOD_5} = \frac{7.2 - 1.0(1 - 0.05)}{0.05} = 125 \text{ mg/L}$$

■

Modeling BOD as a First-order Reaction

Suppose we imagine a flask with some biodegradable organic waste in it. As bacteria oxidize the waste, the amount of organic matter remaining in the flask will decrease with time until eventually it all disappears. Another way to describe the organic matter in the flask is to say as time goes on, the amount of organic matter already oxidized goes up until finally all of the original organic matter has been oxidized. Figure 5.10 shows these two equivalent ways to describe the organic matter. We can also describe oxygen demand from those same two perspectives. We could say that the remaining demand for oxygen to decompose the wastes decreases with time until there is no more demand, or we could say the amount of oxygen demand already exerted, or utilized, starts at zero and rises until all of the original oxygen demand has been satisfied.

Translating Figure 5.10 into a mathematical description is straightforward. To do so, it is often assumed that the rate of decomposition of organic wastes is proportional

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…gen demand, COD, is a measured quantity that does not depend either on … are toxic to microorganisms. The
the ability of microorganisms to degrade the waste or on knowledge of the particular

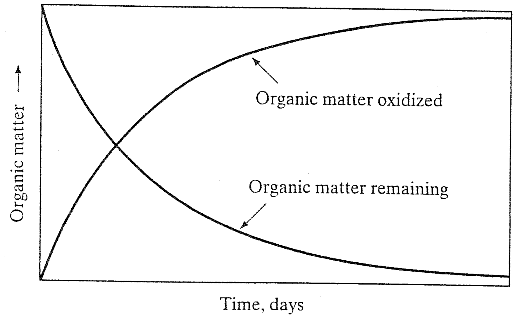


FIGURE 5.10 Two equivalent ways to describe the time dependence of organic matter in a fla

to the amount of waste that is left in the flask. If we let L_t represent the amount
gen demand left after time t, then, assuming a first-order reaction, we can write

$$\frac{dL_t}{dt} = -kL_t$$

where k = the BOD reaction constant (time^{-1}).

The solution to (5.9) is

$$L_t = L_0 e^{-kt}$$

where L_0 is the *ultimate carbonaceous oxygen demand.* It is the total amount of
required by microorganisms to oxidize the carbonaceous portion of the waste t
ple carbon dioxide and water. (Later we will see that there is an additional dema
oxygen associated with the oxidation of nitrogen compounds.) The ultimate ca
ceous oxygen demand is the sum of the amount of oxygen already consumed
waste in the first t days (BOD_t), plus the amount of oxygen remaining to be con
after time t. That is,

$$L_0 = \mathrm{BOD}_t + L_t$$

Combining (5.10) and (5.11) gives us

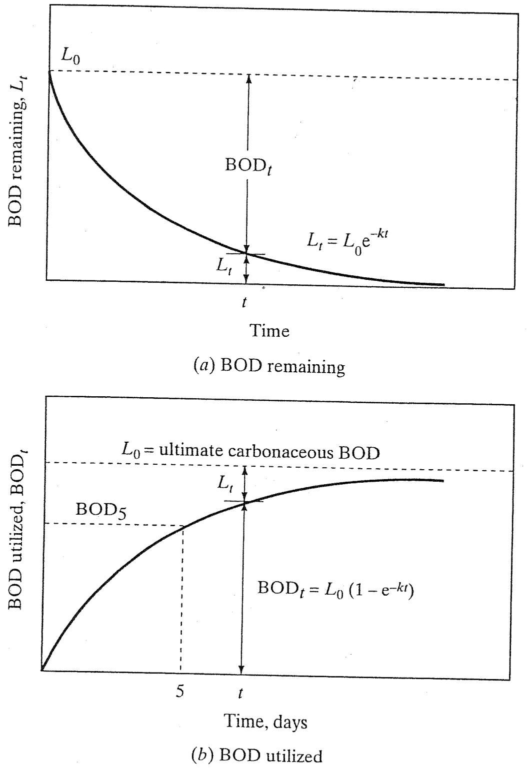
$$\mathrm{BOD}_t = L_0(1 - e^{-kt})$$

A graph of Eqs. (5.10) and (5.12) is presented in Figure 5.11. If these two
are combined, the result would look exactly like Figure 5.10. Notice that
demand can be described by the BOD remaining (you might want to think
how much oxygen demand is Left at time t), as in Figure 5.11a, or equivalently
gen demand already satisfied (or utilized, or exerted), BOD_t, as in Figure 5.11
notice how the five-day BOD is more easily described using the BOD utilized cu

Sometimes the analysis leading to (5.12) is made using logarithms to the
rather than the base e, as they were here. The relationship equivalent to (5.12),
base 10, is

$$\mathrm{BOD}_t = L_0(1 - 10^{-Kt})$$

nonbiodegradable because they are toxic to microorganisms. The pesticides and various indus-
chemical oxygen demand, COD, is a measured quantity that does not depend either on
the ability of microorganisms to degrade the waste or on knowledge of the particular



(*a*) BOD remaining

(*b*) BOD utilized

FIGURE 5.11 Idealized carbonaceous oxygen demand: (*a*) The BOD remaining as a function of time, and (*b*) the oxygen already consumed as a function of time.

where upper case K is the reaction rate coefficient to the base 10. It is easy to show that

$$k = K \ln 10 = 2.303K \tag{5.14}$$

EXAMPLE 5.3 Estimating L_0 from BOD_5

The dilution factor P for an unseeded mixture of waste and water is 0.030. The DO of the mixture is initially 9.0 mg/L, and after five days it has dropped to 3.0 mg/L. The reaction rate constant k has been found to be 0.22 day^{-1}.

a. What is the five-day BOD of the waste?
b. What would be the ultimate carbonaceous BOD?
c. What would be the remaining oxygen demand after five days?

Solution

a. From (5.3), the oxygen consumed in the first five days is

$$BOD_5 = \frac{DO_i - DO_f}{P} = \frac{9.0 - 3.0}{0.030} = 200 \text{ mg/L}$$

b. The total amount of oxygen needed to decompose the carbonaceous pc waste can be found by rearranging (5.12):

$$L_0 = \frac{BOD_5}{(1 - e^{-kt})} = \frac{200}{(1 - e^{-0.22\times 5})} = 300 \text{ mg/L}$$

c. After five days, 200 mg/L of oxygen demand out of the total 300 mg/L already been used. The remaining oxygen demand would therefore 200) mg/L = 100 mg/L.

The BOD Reaction Rate Constant *k*

The BOD reaction rate constant k is a factor that indicates the rate of bioc of wastes. As k increases, the rate at which dissolved oxygen is used increas the ultimate amount required, L_0, does not change. The reaction rate will d number of factors, including the nature of the waste itself (for example, sir and starches degrade easily while cellulose does not), the ability of th microorganisms to degrade the wastes in question (it may take some time fc population of organisms to be able to thrive on the particular waste in que the temperature (as temperatures increase, so does the rate of biodegradati

Some typical values of the BOD reaction rate constant, at 20 °C, a Table 5.9. Notice that raw sewage has a higher rate constant than either v sewage or polluted river water. This is because raw sewage contains a larger of easily degradable organics that exert their oxygen demand quite quickl remainder that decays more slowly.

The rate of biodegradation of wastes increases with increasing temp account for these changes, the reaction rate constant k is often modified us lowing equation:

$$k_T = k_{20}\theta^{(T-20)}$$ 5.15

TABLE 5.9 Typical values for the BOD rate constant k at 20 °C

Sample	k (day^{-1})[a]	K (day^{-1})[b]
Raw sewage	0.35–0.70	0.15–0.30
Well-treated sewage	0.12–0.23	0.05–0.10
Polluted river water	0.12–0.23	0.05–0.10

[a] Lowercase k reaction rates to the base e.
[b] Uppercase K reaction rates to the base 10.
Source: Davis and Cornwell (1991).

where k_{20} is the reaction rate constant at the standard 20 °C laboratory reference temperature, and k_T is the reaction rate at a different temperature T (expressed in °C). The most commonly used value for θ is 1.047, and although θ is somewhat temperature dependent, that single value will suffice for our purposes.

EXAMPLE 5.4 Temperature Dependence of BOD_5

In Example 5.3 the wastes had an ultimate BOD equal to 300 mg/L. At 20 °C, the five-day BOD was 200 mg/L and the reaction rate constant was 0.22/day. What would the five-day BOD of this waste be at 25 °C?

Solution First we will adjust the reaction rate constant with (5.15) using a value of θ equal to 1.047:

$$k_{25} = k_{20}\theta^{(T-20)} = 0.22 \times (1.047)^{(25-20)} = 0.277/\text{day}$$

So, from (5.12),

$$\text{BOD}_5 = L_0(1 - e^{-k5}) = 300(1 - e^{-0.277\times 5}) = 225 \text{ mg/L}$$

Notice that the five-day BOD at 25 °C is somewhat higher than the 20 °C value of 200 mg/L. The same total amount of oxygen is required at either temperature, but as temperature increases, it gets used sooner. ■

Nitrification

So far, it has been assumed that the only oxygen demand is associated with the biodegradation of the carbonaceous portion of the wastes. There is a significant additional demand, however, caused by the oxidation of nitrogen compounds that we will now briefly describe.

Nitrogen is the critical element required for protein synthesis and, hence, is essential to life. When living things die or excrete waste products, nitrogen that was tied to complex organic molecules is converted to ammonia by bacteria and fungi. Then, in aerobic environments, nitrite bacteria (*Nitrosomonas*) convert ammonia to nitrite (NO_2^-), and nitrate bacteria (*Nitrobacter*) convert nitrite to nitrate (NO_3^-). This process, called nitrification, can be represented with the following two reactions:

$$2NH_3 + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 2H^+ + 2H_2O \qquad (5.16)$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^- \qquad (5.17)$$

This conversion of ammonia to nitrate requires oxygen, so nitrification exerts its own oxygen demand. Thus, we have the combination of oxygen requirements. The oxygen needed to oxidize organic carbon to carbon dioxide is called the *carbonaceous oxygen demand* (CBOD), while the oxygen needed to convert ammonia to nitrate is called the *nitrogenous oxygen demand* (NBOD).

Nitrification is just one part of the biogeochemical cycle for nitrogen. In the atmosphere nitrogen is principally in the form of molecular nitrogen (N_2) with a small but important fraction being nitrous oxide (N_20). (Nitrous oxide is a greenhouse gas that will be considered again in Chapter 8.) Nitrogen in the form of N_2 is unusable by plants and must first be transformed into either ammonia (NH_3) or nitrate (NO_3^-) in the process called *nitrogen fixation.* Nitrogen fixation occurs during electrical storms when N_2 oxidizes, combines with water, and is rained out as HNO_3. Certain bacteria and blue-green algae are also capable of fixing nitrogen. Under anaerobic conditions, certain denitrifying bacteria are capable of reducing NO_3 back into NO_2 and N_2, completing the nitrogen cycle.

While the entire nitrogen cycle obviously is important, our concern in this section is with the nitrification process itself, in which organic-nitrogen in waste is converted to ammonia, ammonia to nitrite, and nitrite to nitrate. Figure 5.12 shows this sequential process, starting with all of the nitrogen bound up in organic form and weeks later ending with all of the nitrogen in the form of nitrate. Notice that the conversion of ammonia to nitrite does not begin right away, which means the nitrogenous biochemical oxygen demand does not begin to be exerted until a number of days have passed.

Figure 5.13 illustrates the carbonaceous and nitrogenous oxygen demands as they might be exerted for typical municipal wastes. Notice that the NBOD does not normally begin to exert itself for at least five to eight days, so most five-day tests are not affected by nitrification. In fact, the potential for nitrification to interfere with the standard measurement for CBOD was an important consideration in choosing the standard five-day period for BOD tests. To avoid further the nitrification complication, it is now an accepted practice to modify wastes in a way that will inhibit nitrification during that five-day period.

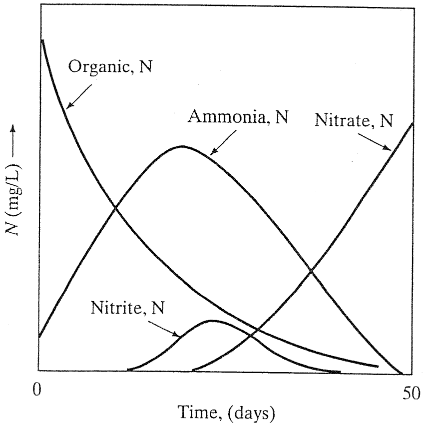


FIGURE 5.12 Changes in nitrogen forms in polluted water under aerobic conditions. (*Source:* Sawyer and McCarty, *Chemistry for Environmental Engineers*, 4th ed., © 1994. Reprinted by permission of McGraw-Hill, Inc.)

and various indus-
because they are toxic to microorganisms. The
demand, COD, is a measured quantity that does not depend either on
the ability of microorganisms to degrade the waste or on knowledge of the particular

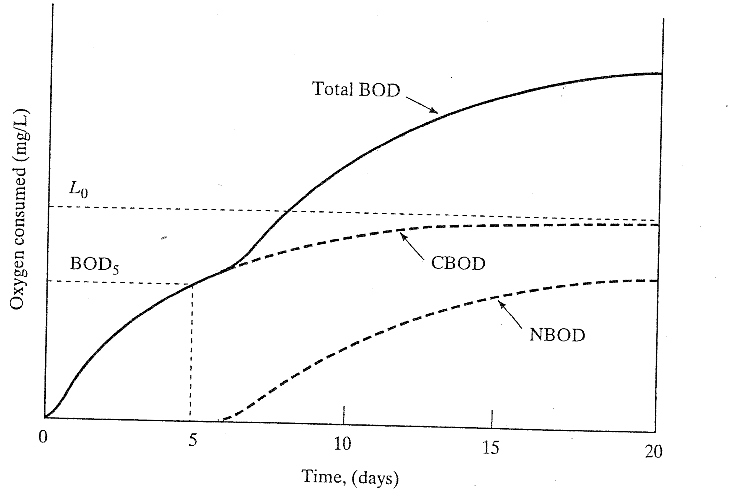


FIGURE 5.13 Illustrating the carbonaceous and nitrogenous biochemical oxygen demand. Total BOD is the sum of the two.

A stoichiometric analysis of (5.16) and (5.17) allows us to quantify the oxygen demand associated with nitrification, as the following example illustrates.

EXAMPLE 5.5 Nitrogenous Oxygen Demand

Some domestic wastewater has 30 mg/L of nitrogen either in the form of organic nitrogen or ammonia. Assuming that very few new cells of bacteria are formed during the nitrification of the waste (that is, the oxygen demand can be found from a simple stoichiometric analysis of the nitrification reactions given above), find

a. The ultimate nitrogenous oxygen demand

b. The ratio of the ultimate NBOD to the concentration of nitrogen in the waste.

Solution

a. Combining the two nitrification reactions (5.16) and (5.17) yields

$$NH_3 + 2O_2 \longrightarrow NO_3^- + H^+ + H_2O$$

The molecular weight of NH_3 is 17, and the molecular weight of O_2 is 32. The foregoing reaction indicates that one g-mol of NH_3 (17 g) requires two g-mole of O_2 ($2 \times 32 = 64$ g). Since 17 g of NH_3 contains 14 g of N, and the concentration of N is 30 mg/L, we can find the final, or ultimate, NBOD:

$$\text{NBOD} = 30\text{ mg N/L} \times \frac{17\text{g NH}_3}{14\text{ g N}} \times \frac{64\text{ g O}_2}{17\text{ g NH}_3} = 137\text{ mg O}_2\text{/L}$$

b. The oxygen demand due to nitrification divided by the concentration of nitrogen in the waste is

$$\frac{137\text{ mg O}_2\text{/L}}{30\text{ mg N/L}} = 4.57\text{ mg O}_2\text{/mg N}$$

■

The total concentration of organic and ammonia nitrogen in wastewater is known as the *total Kjeldahl nitrogen,* or TKN. As was demonstrated in the preceding example, the nitrogenous oxygen demand can be estimated by multiplying the TKN by 4.57. This is a result work noting:

$$\text{Ultimate NBOD} \approx 4.57 \times \text{TKN} \tag{5.18}$$

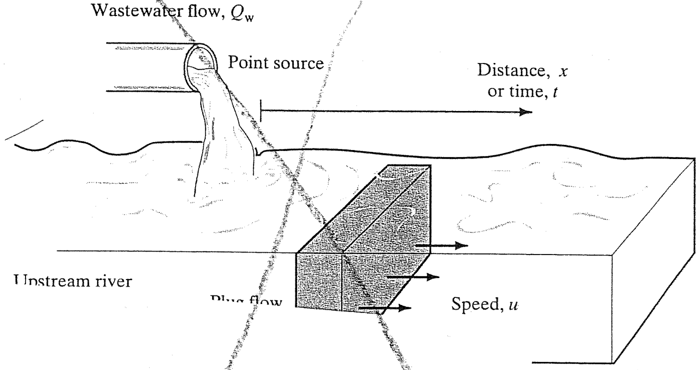
Since untreated domestic wastewaters typically contain approximately 15–50 mg/L of TKN, the oxygen demand caused by nitrification is considerable, ranging from roughly 70 to 230 mg/L. For comparison, typical raw sewage has an ultimate carbonaceous oxygen demand of 250–350 mg/L.

Other Measures of Oxygen Demand

In addition to the CBOD and NBOD measures already presented, there are two other indicators that are sometimes used to describe the oxygen demand of wastes. These are the *theoretical oxygen demand* (ThOD) and the *chemical oxygen demand* (COD).

As was described in Chapter 2, the theoretical oxygen demand is the amount of oxygen required to oxidize completely a particular organic substance, as calculated from simple stoichiometric considerations. Stoichiometric analysis, however, for both the carbonaceous and nitrogenous components, tends to overestimate the amount of oxygen actually consumed during decomposition. The explanation for this discrepancy is based on a more careful understanding of how microorganisms actually decompose waste. While there is plenty of food for bacteria, they rapidly consume waste and in the process convert some of it to cell tissue. As the amount of remaining wastes diminishes, bacteria begin to draw on their own tissue for the energy they need to survive, a process called endogenous respiration. Eventually, as bacteria die they become the food supply for other bacteria; all the while protozoa act as predators consuming both living and dead bacteria. Throughout this sequence, more and more of the original waste is consumed until finally all that remains is some organic matter, called humus, that stubbornly resists degradation. The discrepancy between theoretical and actual oxygen demands is explained by carbon still bound up in humus. The calculation of theoretical oxygen demand is of limited usefulness in practice since it presupposes a particular, single pollutant with known chemical formula, and even if that is the case, the demand is overestimated.

Some organic matter, such as cellulose, phenols, benzene, and tannic acid, resists biodegradation. Other types of organic matter, such as pesticides and various industrial chemicals, are nonbiodegradable because they are toxic to microorganisms. The chemical oxygen demand, COD, is a measured quantity that does not depend either on the ability of microorganisms to degrade the waste or on knowledge of the particular 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



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arges 1.10 m^3/s of treated effluent
flow of 8.70 m^3/s and a BOD of its
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