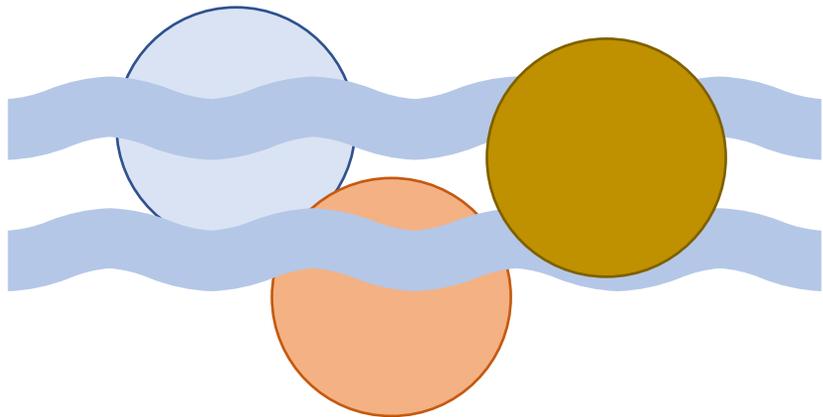


Surface Water Quality Modeling

CEE-EGIN 577

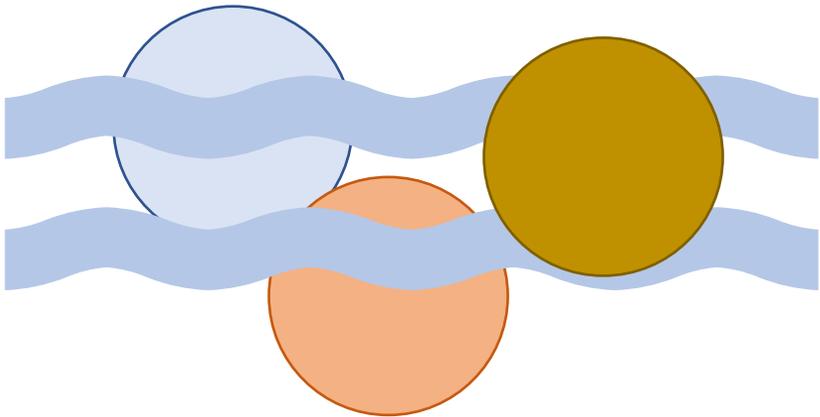


C. D. Guzman, PhD
Week 6
Monday, Feb 24,
2020



Dissolved Oxygen & Pathogens

Biological Oxygen Demand



Organic Production/ Decomposition Cycle

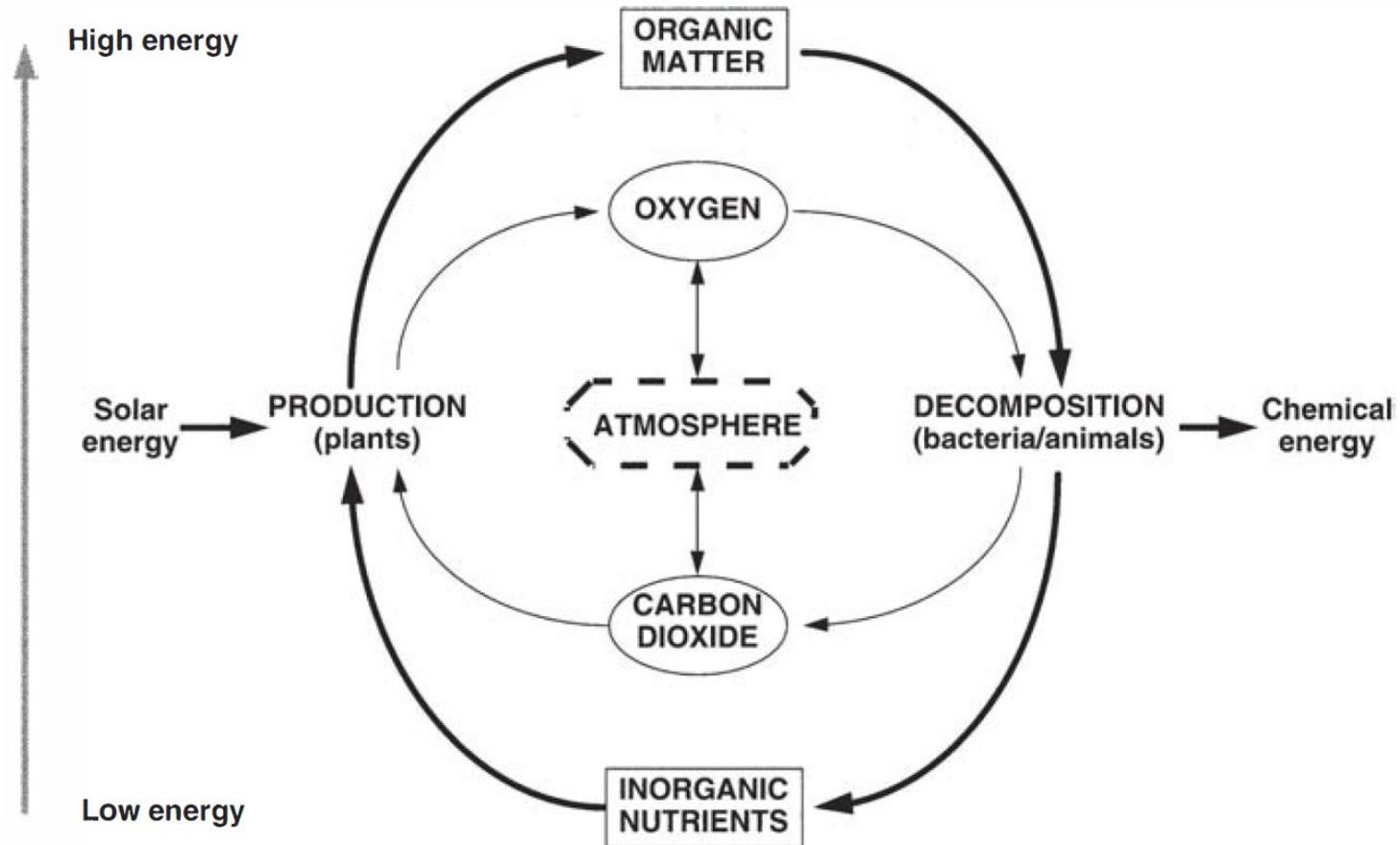


FIGURE 19.1
The natural cycle of organic production and decomposition.

Organic Production/ Decomposition Cycle

The biosphere is a cycle of life and death.

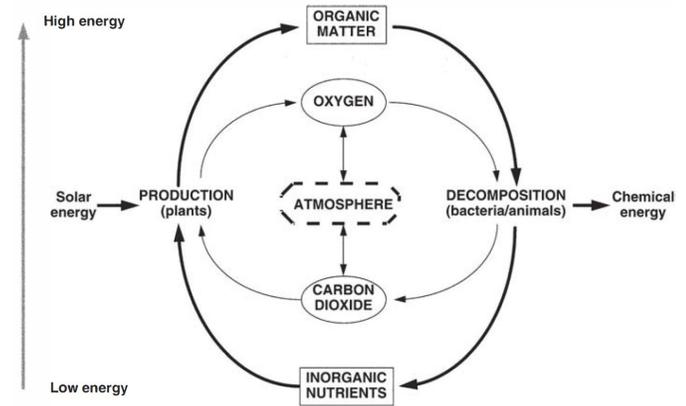


FIGURE 19.1
The natural cycle of organic production and decomposition.

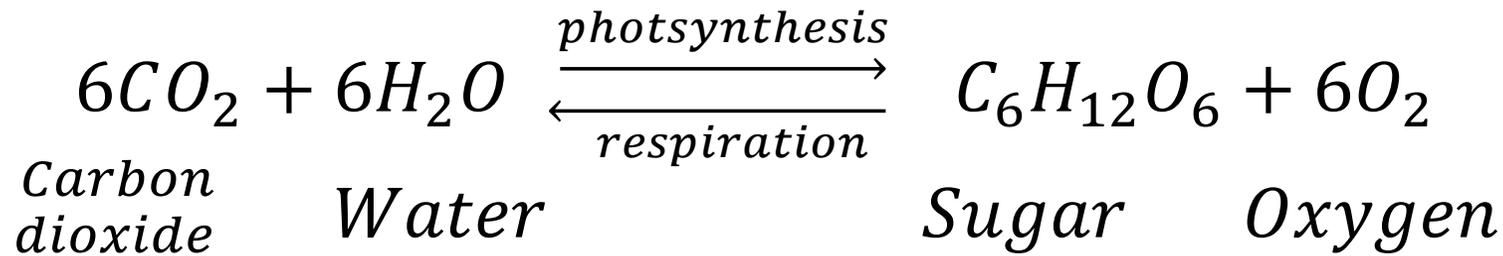
Autotrophic organism (primarily plants) convert simple organic nutrients into complex organic molecules. i.e. conversion of solar energy to chemical energy stored in organic molecules (*photosynthesis*), where CO_2 is consumed, and oxygen released.

Organic matter serves as an energy source for **heterotrophic** organism (bacteria and animals), in reverse processes of *respiration* and *decomposition*.

This returns organic matter to simpler inorganic state, consuming oxygen and releasing CO_2 .

Organic Production/ Decomposition Cycle

The cycle is represented by:



Here carbon dioxide and water are used to synthesize organic matter (sugar glucose) and to create oxygen via **photosynthesis**.

Conversely, organic matter is broken down and oxygen consumed in the reverse **respiration** and **decomposition** processes.

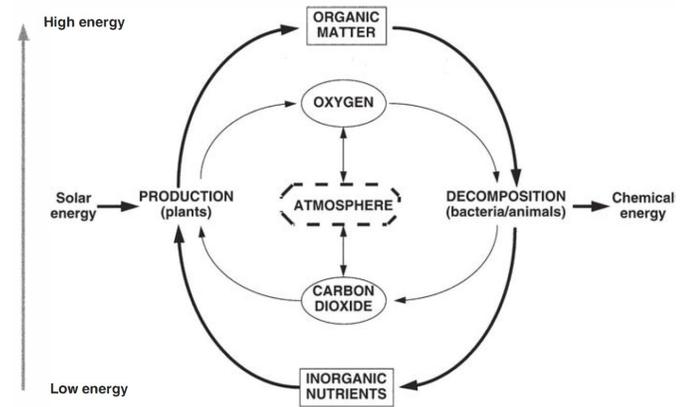


FIGURE 19.1
The natural cycle of organic production and decomposition.

The Dissolved Oxygen Sag

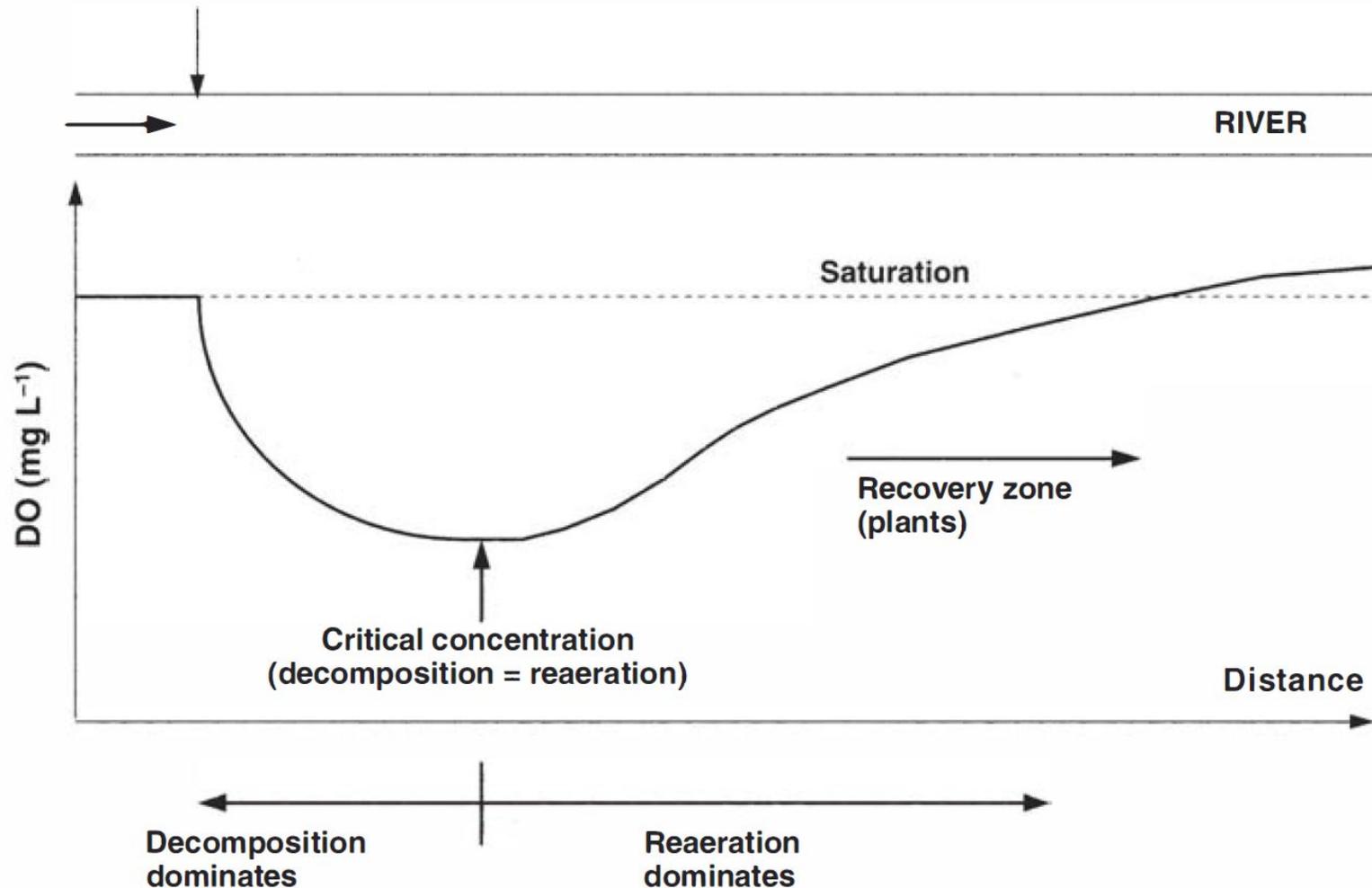


FIGURE 19.2

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

Dissolved Oxygen Sag

Now let's link this cycle to the environment of a stream below a wastewater discharge.

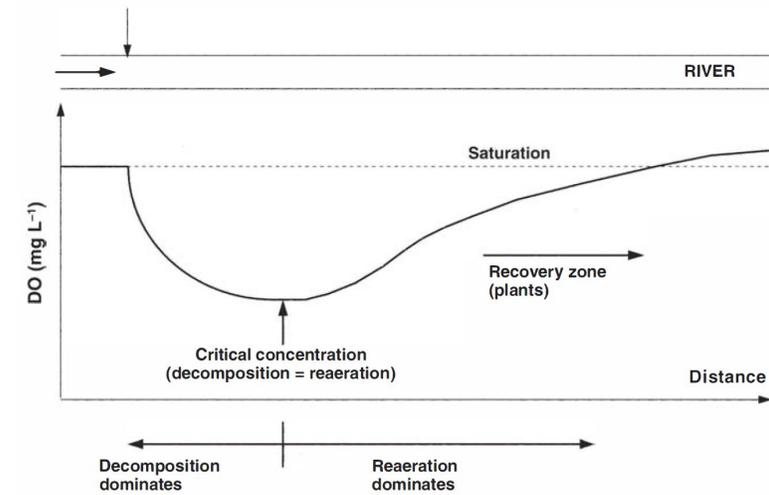


FIGURE 19.2
The dissolved oxygen "sag" that occurs below sewage discharges into streams.

The stream is initially unpolluted, with DO levels near saturation. Discharge of sewage introduces elevated levels of solids and dissolved organic matter.

Next, the solid matter makes the water turbid (inhibiting light/plant growth)

Also, OM provides food for heterotrophic organisms (depleting DO)

As oxygen levels drop, the atmosphere replenishes the concentration (reaeration). As OM is assimilated, decomposition and reaeration come to a balance at the "critical" level of oxygen. Beyond this point, recovery and clarification of water (growth of plants).

Dissolved Oxygen Sag

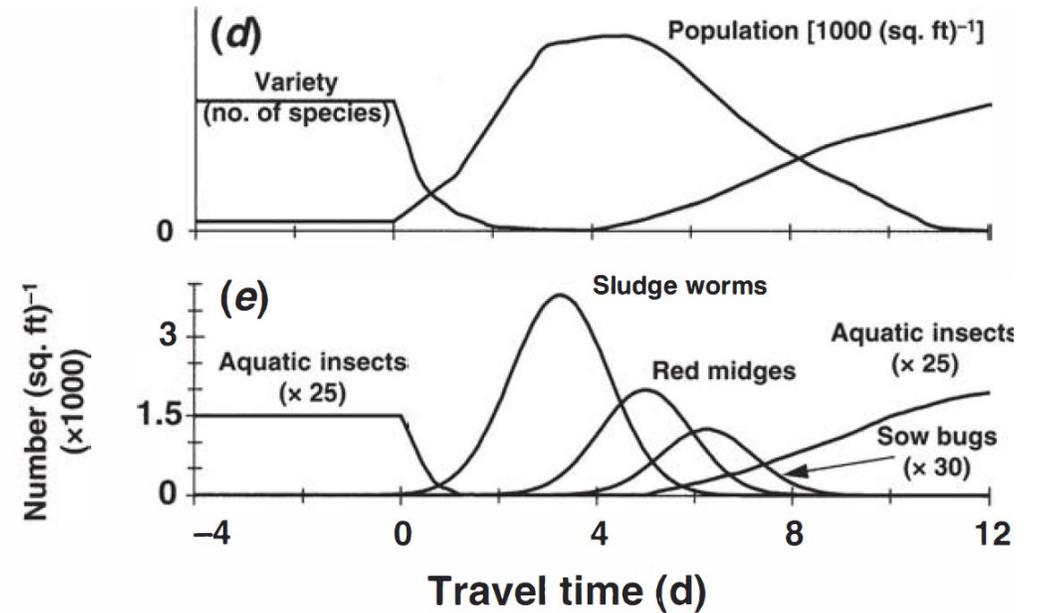
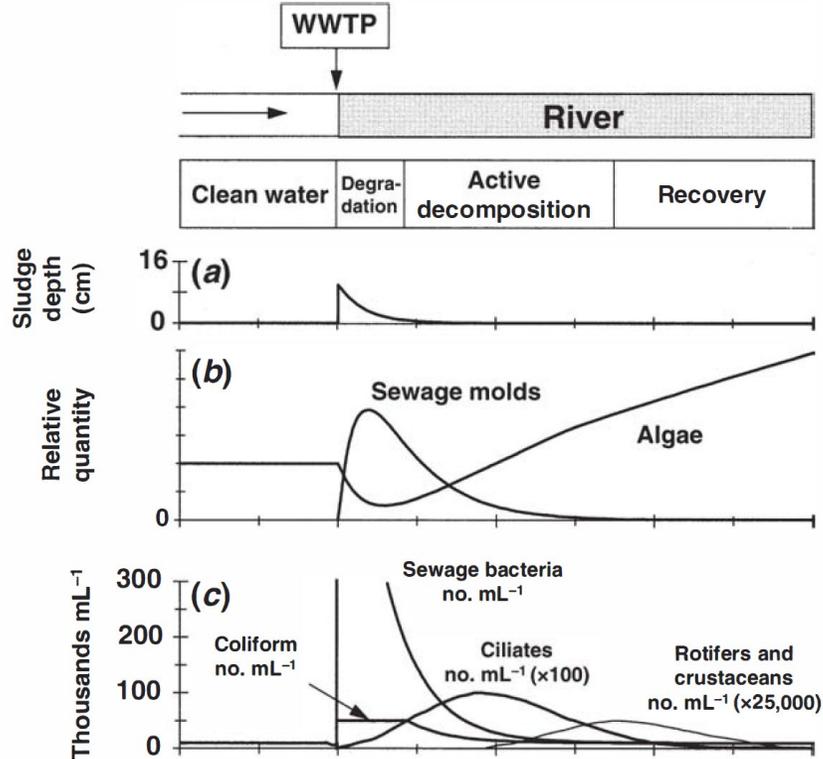


FIGURE 19.3

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

Sewage also leads to significant effects on the biota. i.e., molds and bacteria dominate near the discharge and then become a food source. Further diversity increases with higher organisms, but then decreases with recovery zones. The critical (or minimum) concentration magnitude and location depends on loading, flow, morphometry, water temperature. Next we simulate the DO sag with these factors.

Experiment: DO sag

The first step in modeling the DO sag will be to characterize the strength of the wastewater. In terms of general chemical representation, this is:



Suppose you add 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 the decomposition process is a first-order reaction, the mass balance for glucose is:

$$V \frac{dg}{dt} = -k_1 V g$$

where g = glucose concentration (mg- glucose L⁻¹) and k_1 = the decomposition rate in the bottle (d⁻¹).

Experiment: DO sag

$$V \frac{dg}{dt} = -k_1 V g$$

if the initial concentration of glucose is g_0 , then the solution for this eq is:

$$g = g_0 e^{-k_1 t}$$

Next a mass balance for oxygen is written:

$$V \frac{do}{dt} = -r_{og} k_1 V g$$

where o = oxygen concentration (mgO L^{-1}) and the r_{og} = the stoichiometric ratio of oxygen consumed to glucose decomposed ($\text{mgO mg-glucose}^{-1}$). Substituting above we get:

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

Experiment: DO sag

Substituting above we get:

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

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

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

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:

$$o \rightarrow o_0 - r_{og} g_0$$

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.

Biochemical Oxygen Demand

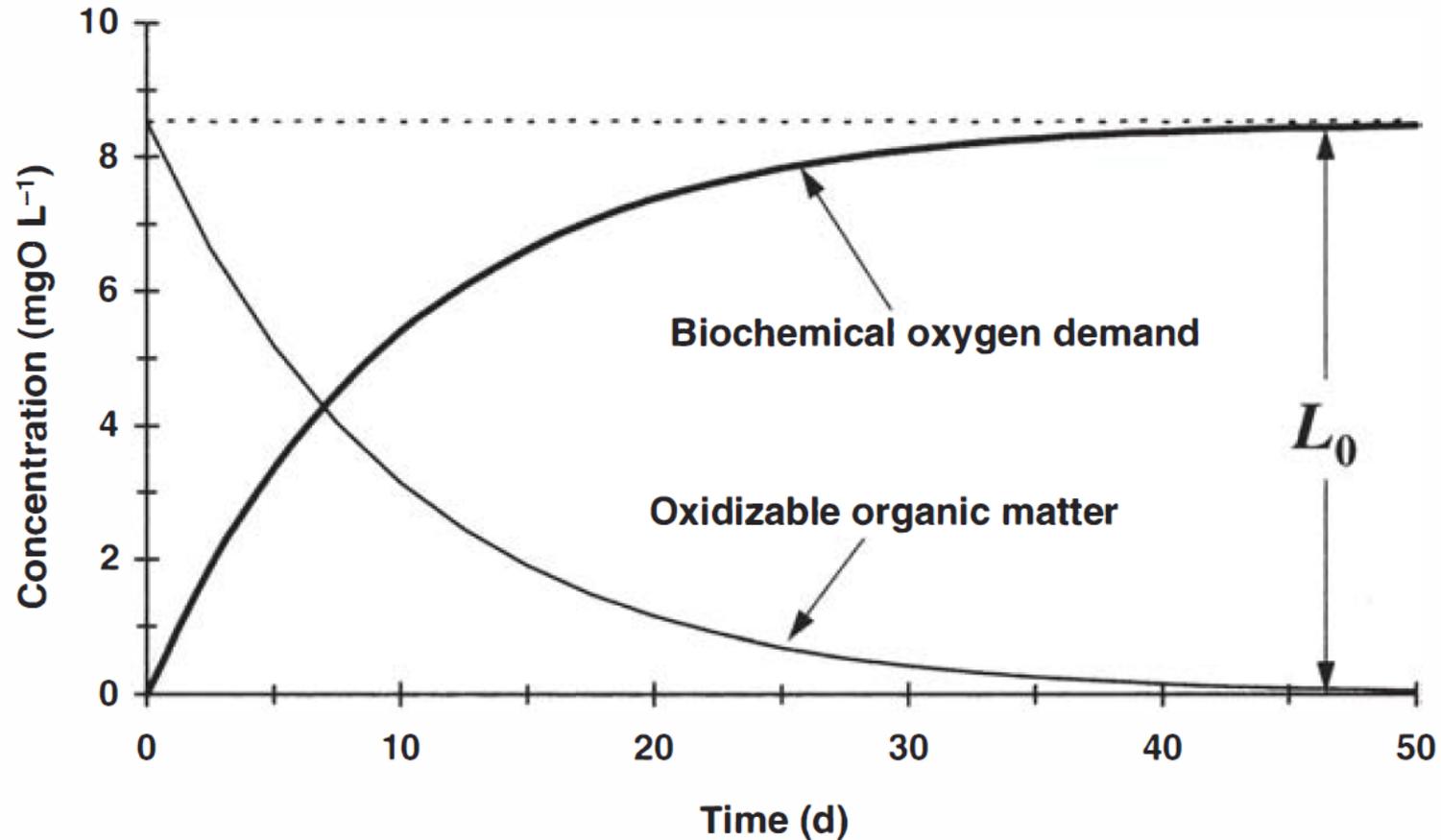


FIGURE 19.4

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

Biochemical Oxygen Demand

Outlining the previous experiment for how sewage affects oxygen levels would be intensively demanding (due to myriad organic compounds).

Early modelers used the idea of introducing some sewage into a batch reactor and measuring how much oxygen was consumed (**biochemical oxygen demand**).

For a simple model we can use a new variable L (mgO L^{-1}) to represent the amount of oxidizable organic matter remaining in the bottle expressed as oxygen equivalents.

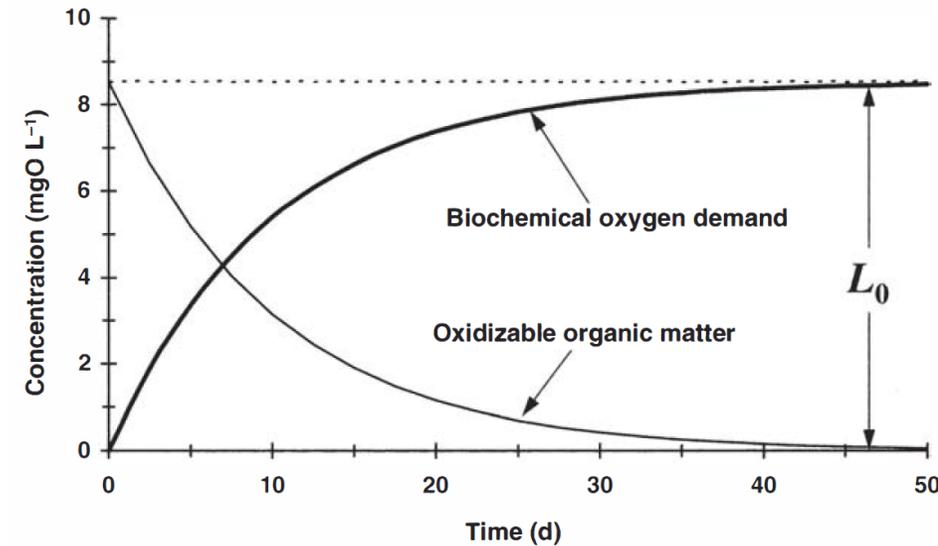


FIGURE 19.4

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

Biochemical Oxygen Demand

A mass balance for L for the batch system is:

$$V \frac{dL}{dt} = -k_1 VL$$

If the initial level is L_0 , the equation solution is:

$$L = L_0 e^{-k_1 t}$$

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

$$y = L_0 - L$$

which can be substituted:

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

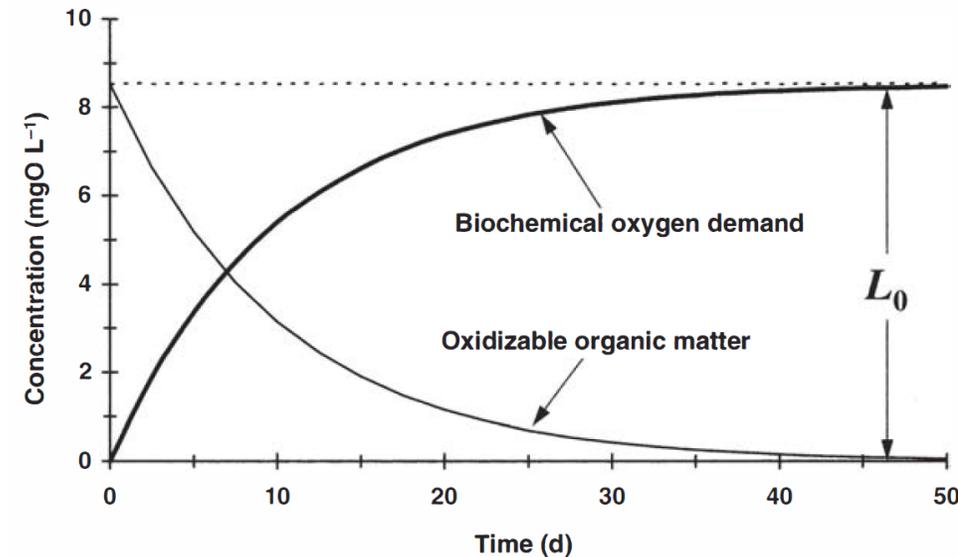


FIGURE 19.4

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

Biochemical Oxygen Demand

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

where $y = \text{BOD (mgO L}^{-1}\text{)}$ and L_0 can be defined as the initial concentration of oxidizable organic matter. Next a mass balance is written for oxygen:

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

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

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

According to the above eq, the oxygen will originally be at o_0 and then decrease exponentially to:

$$o \rightarrow o_0 - L_0$$

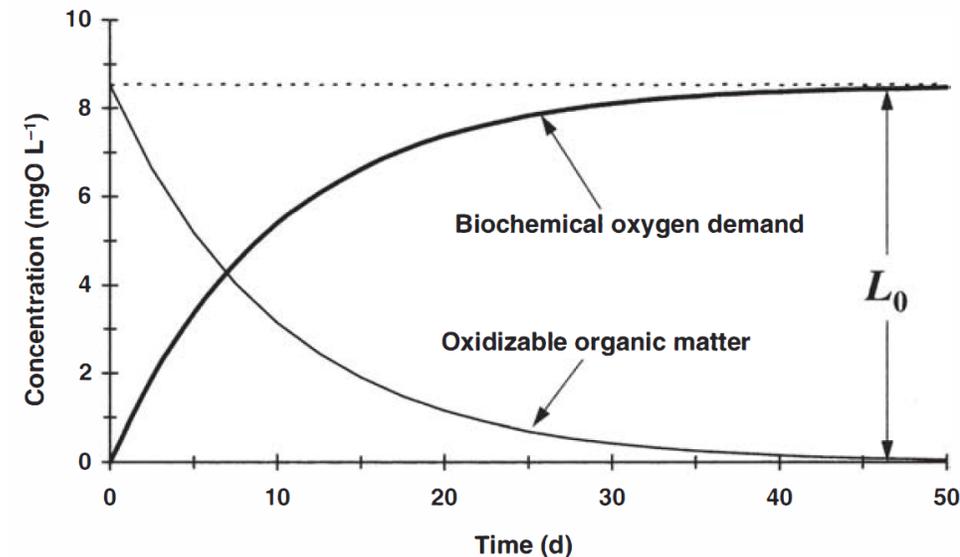


FIGURE 19.4

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

Biochemical Oxygen Demand

$$o \rightarrow o_0 - L_0$$

The organic carbon content can be measured directly and this equation can be reformulated to estimate the BOD on the basis of the organic carbon content:

$$L_0 = r_{oc} C_{org}$$

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}). Using the glucose respiration equation ($\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \xrightarrow{\text{respiration}} 6\text{CO}_2 + 6\text{H}_2\text{O}$)

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

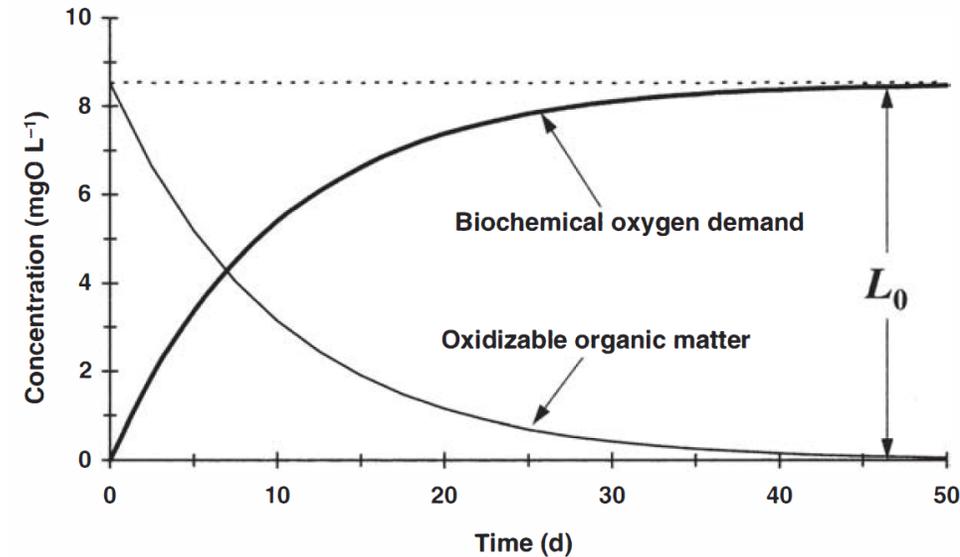


FIGURE 19.4

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

BOD Model For a Stream

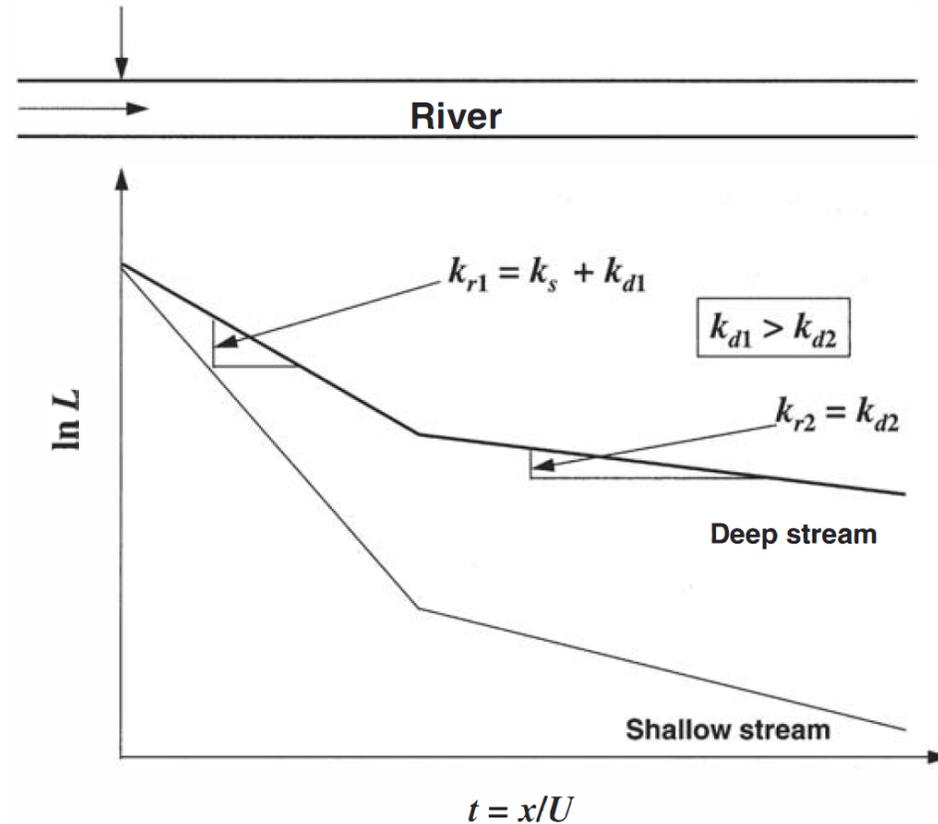
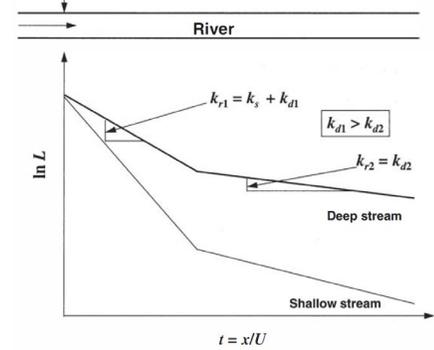


FIGURE 19.5

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.

BOD Model For a Stream



Integrating sedimentation into a mass balance, we can write a BOD mass balance for a constant-flow, constant-geometry channel:

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

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

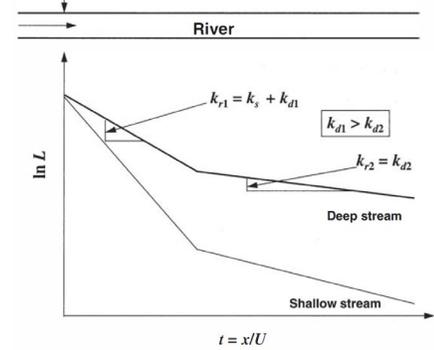
$$k_r = k_d + k_s$$

where k_d = decomposition rate in the stream (d^{-1}) and k_s = settling removal rate (d^{-1}). Note that the settling rate is related to more fundamental parameters by:

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

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

BOD Model For a Stream



Integrating sedimentation into a mass balance, we can write a BOD mass balance for a constant-flow, constant-geometry channel:

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

For steady state, this becomes:

$$0 = -U \frac{\partial L}{\partial x} - k_r L$$

if complete mixing is assumed, an initial concentration can be calculated as:

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

Using this as an initial value, the steady state solution becomes:

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

BOD Model For a Stream

Using this as an initial value, the steady state solution becomes:

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

To estimate the removal rate, take the logarithm of each side:

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

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

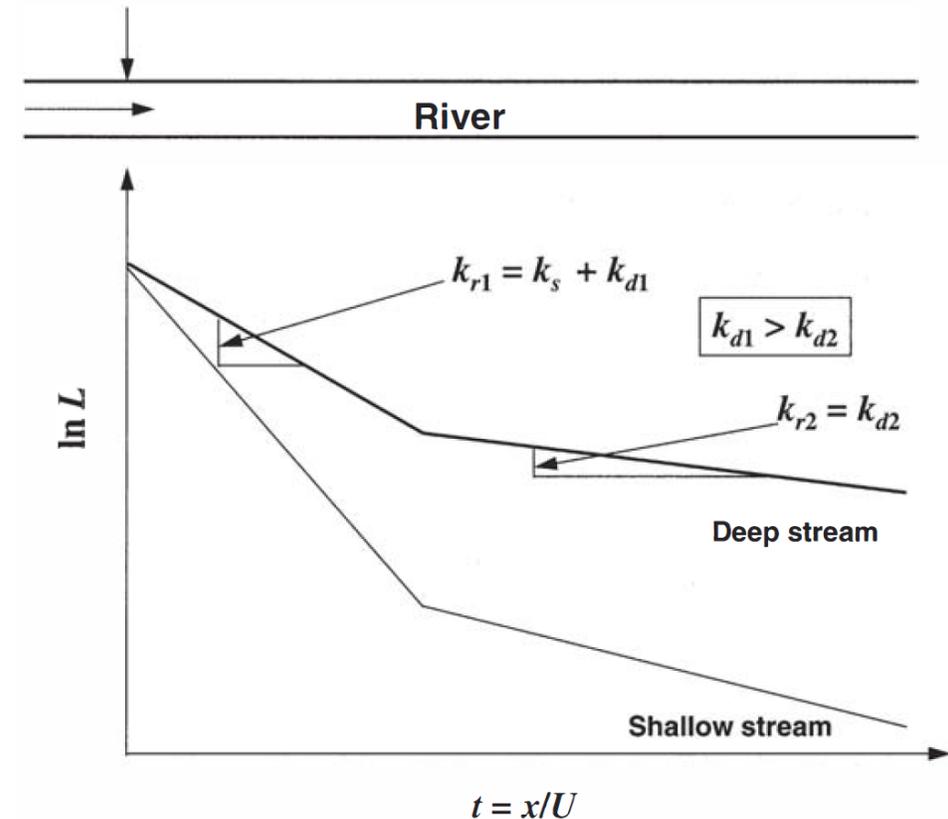


FIGURE 19.5

Plot of BOD downstream from a point source of untreated sewage into a plug-flow river having constant hydrogeomorphic 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.

BOD Loadings, Concentrations, and Rates

Now we'll review some of the parameters that relate to biochemical oxygen demand for modeling.

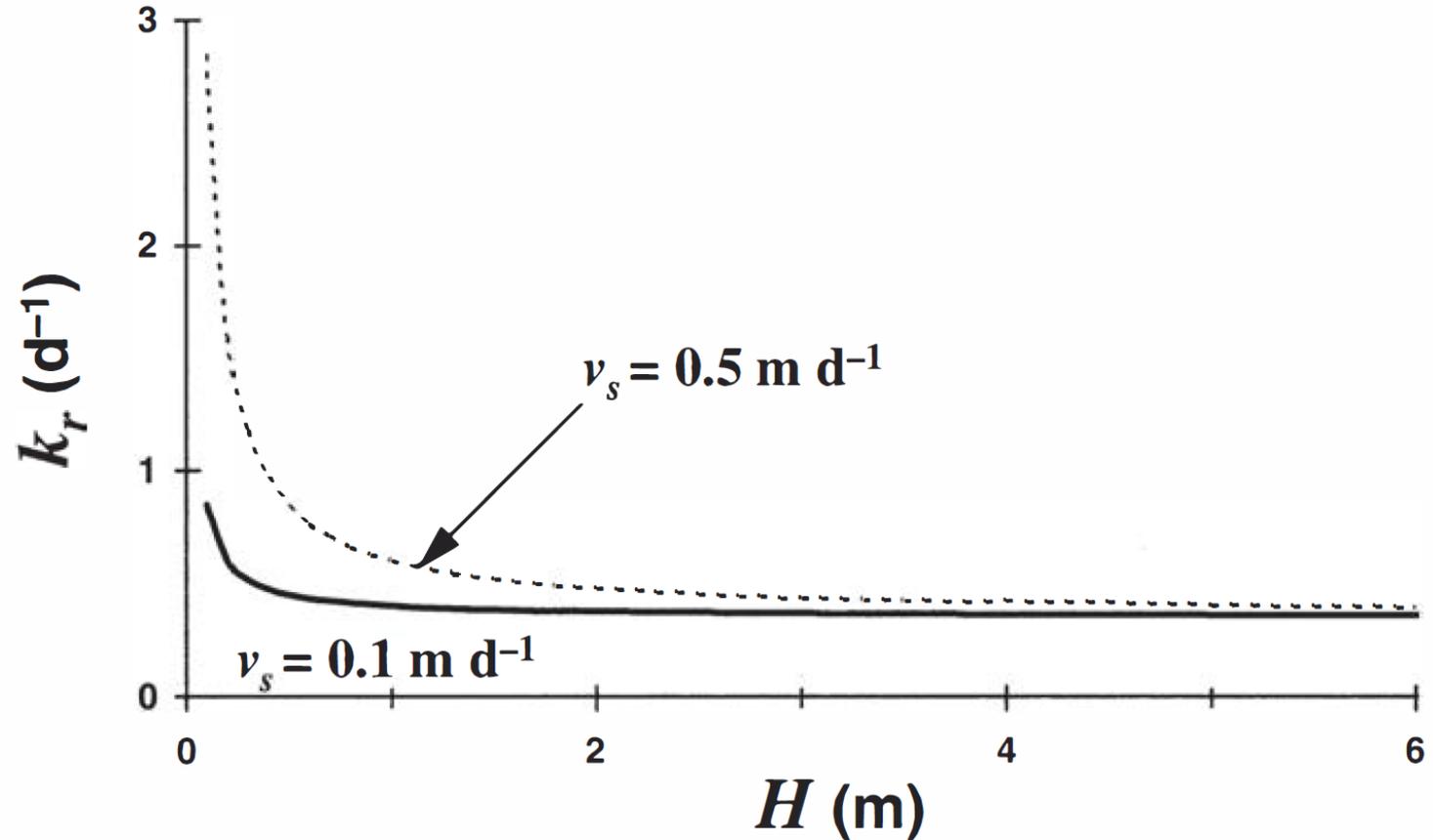


FIGURE 19.6

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.

BOD₅ (5-Day BOD)

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. Calculating a 95% response time for the bottle test yields $t_{95} = 3/0.15 = 20$ d. However, water quality analysts use a 5-day BOD test instead.

The long-term BOD, used to estimate the decay rate is :

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

where y_5 = 5-day BOD.

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	$k_1(20^\circ\text{C})$	BOD ₅ /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

BOD Loadings & Concentrations

Typical values of flow rate and BOD for raw sewage are shown below. Flow rate for the US are higher because higher water use typically accompanies higher standard of living.

Concentration is higher in developing concentration due to lower water use.

TABLE 19.2
Typical loading rates for untreated domestic sewage

	Per-capita flow rate (m ³ capita ⁻¹ d ⁻¹)	Per-capita CBOD (g 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.

BOD Removal Rates

Bottle BOD decomposition rates are rarely comparable to natural waters, but they can be a first estimate.

Raw sewage is composed of easily decomposable sugars and refractory substances, so BOD bottle rates for treated sewage are lower since it has removed the sugars.

Only in deep, slow rivers do the bottle rates and river rates coincide (settling and bed effects cause discrepancies).

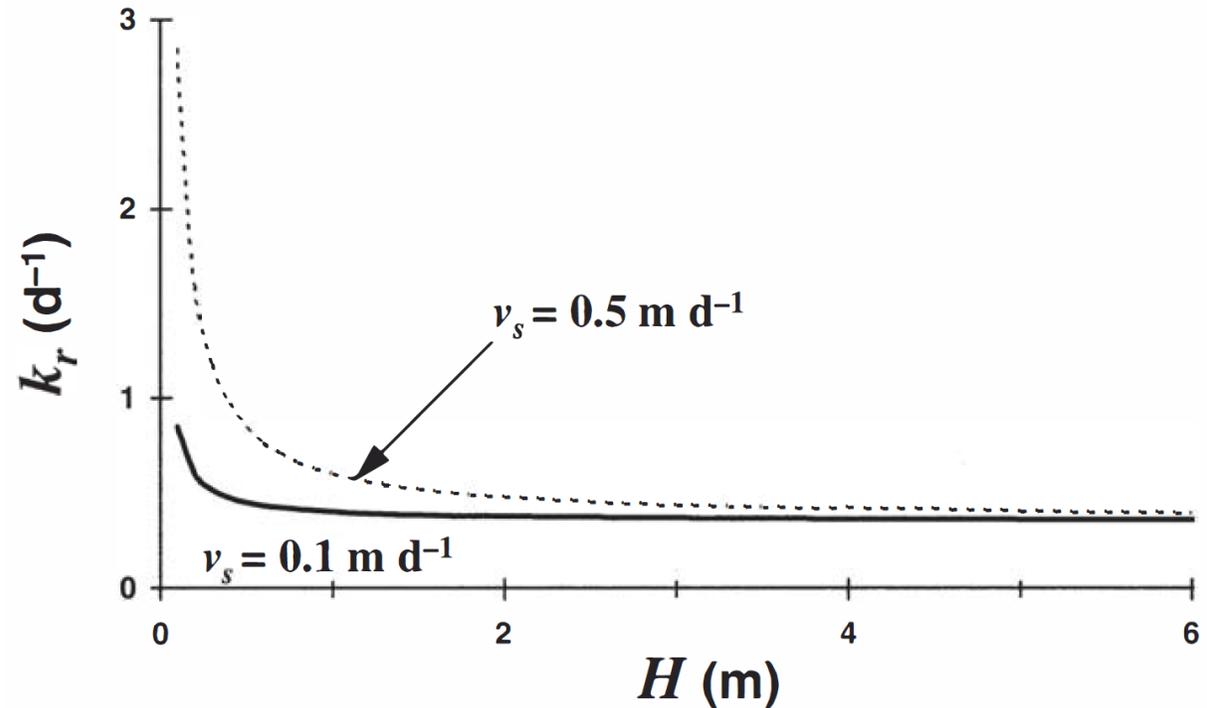


FIGURE 19.6

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.

BOD Removal Rates

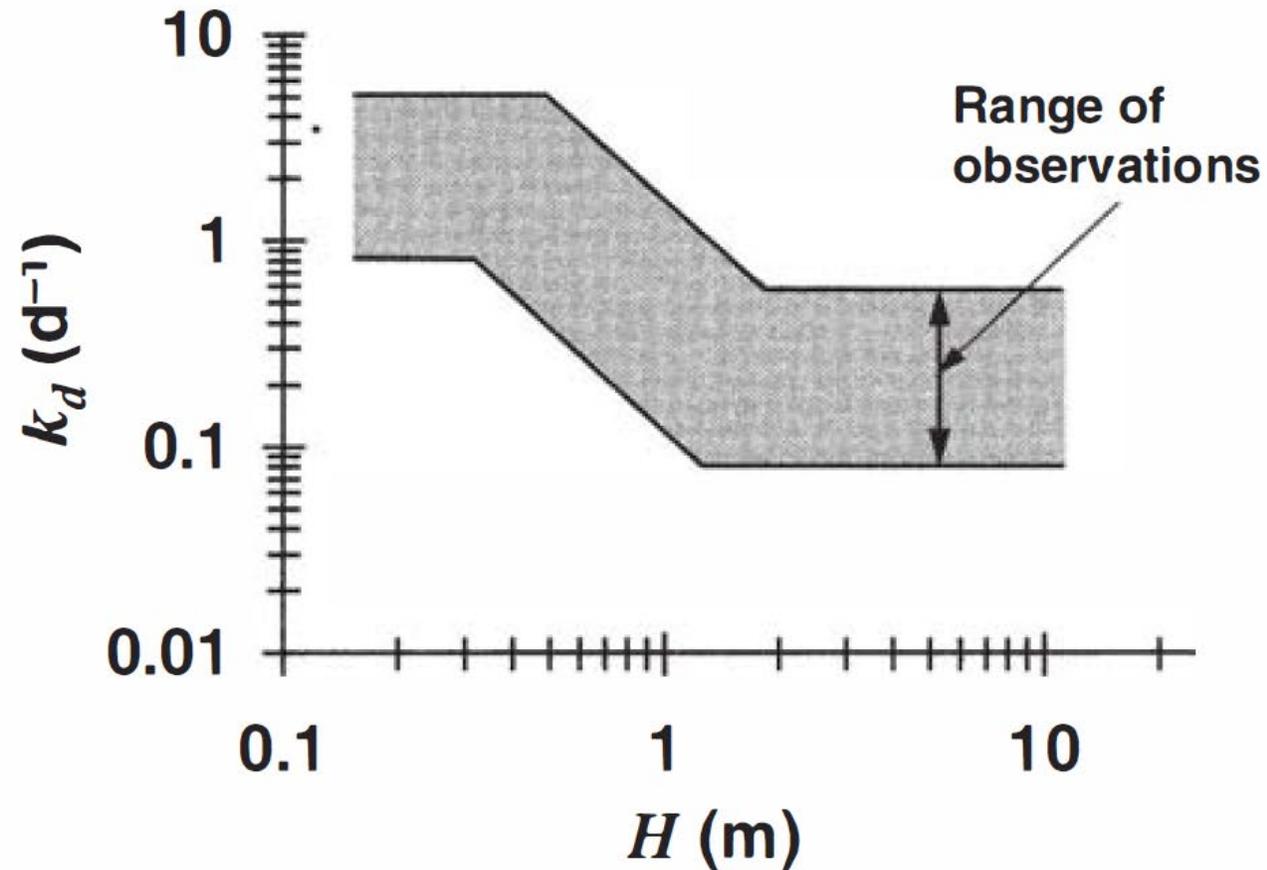


FIGURE 19.7
In-stream decomposition rate
versus depth (Bowie et al. 1985).

BOD Removal Rates

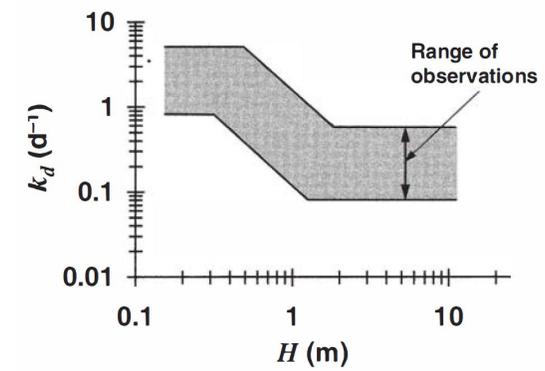


FIGURE 19.7
In-stream decomposition rate
versus depth (Bowie et al. 1985).

Settling. Settling effects relate the fact that for sewage, the removal rate will be comprised of decomposition and settling.

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

Bed effects: Bottom decomposition can be generally more effective than free-floating bacteria. Bottom decomposition becomes more pronounced in shallower systems (due to relative prominence). These trends are found by

$$k_d = 0.3 \left(\frac{H}{2.4} \right)^{-0.434} \quad 0 \leq H \leq 2.4 \text{ m}$$
$$k_d = 0.3 \quad H \geq 2.4 \text{ m}$$

BOD Removal Rates

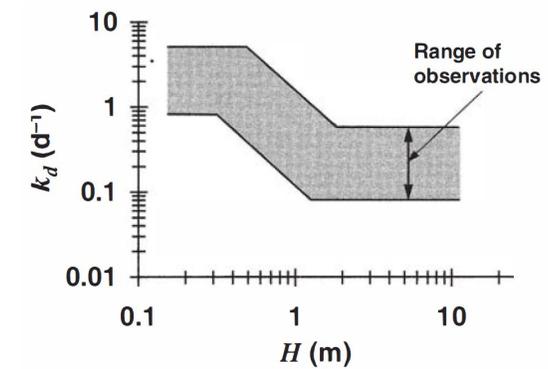


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In-stream decomposition rate
versus depth (Bowie et al. 1985).

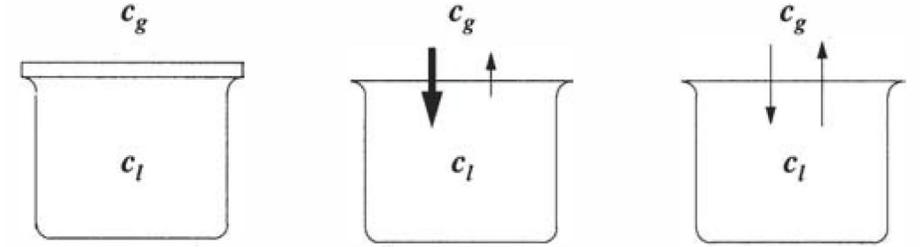
$$k_d = 0.3 \left(\frac{H}{2.4} \right)^{-0.434} \quad 0 \leq H \leq 2.4 \text{ m}$$
$$k_d = 0.3 \quad H \geq 2.4 \text{ m}$$

These BOD removal rates can be extrapolated to other temperatures:

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

In summary, BOD removal rates tend to increase with temperature and tend to be higher immediately downstream from point sources (especially in untreated wastewater). Shallower systems typically exhibit higher BOD removal rates as well due to settling and bed effects.

Henry's Law and the Ideal Gas Law



If a beaker of gas-free distilled water is opened to the atmosphere, gaseous compounds (O, CO₂, N) will cross the air-water interface and enter into solution. This process will continue until the partial pressure of the gas in the atmosphere is quantified by the concentration in the aqueous phase.

The equilibrium is quantified by:

$$H_e = \frac{p}{c}$$

where H_e = Henry's constant (atm m³ mole⁻¹)

p = partial pressure (atm)

c = water concentration (mole m⁻³)

Henry's Law and the Ideal Gas Law

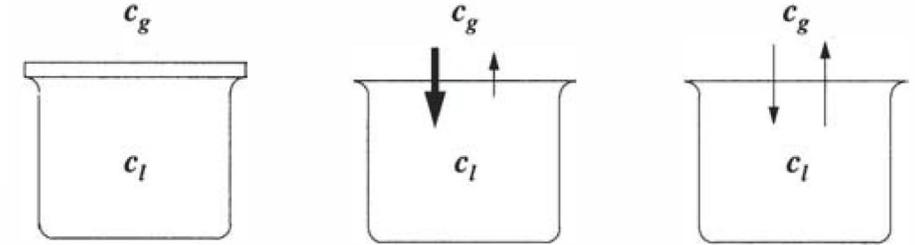
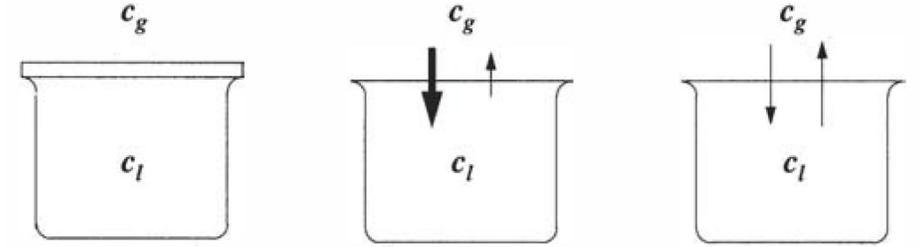


TABLE 19.3

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

Henry's Law and the Ideal Gas Law



The equilibrium is quantified by:

$$H_e = \frac{p}{c}$$

This can be also represented in dimensionless form through the ideal gas law:

$$c = \frac{p}{RT_a}$$

with R = universal gas constant [8.206×10^{-5} atm m³ (K mole)⁻¹] and T_a = absolute temperature (K). Rearranging and substituting into the first equation yields a dimensionless Henry's constant

$$H'_e = \frac{H_e}{c} = \frac{c_g}{c_l}$$

where c_g and c_l are the gas and liquid concentrations, respectively (mole m⁻³)

Henry's Law and the Ideal Gas Law

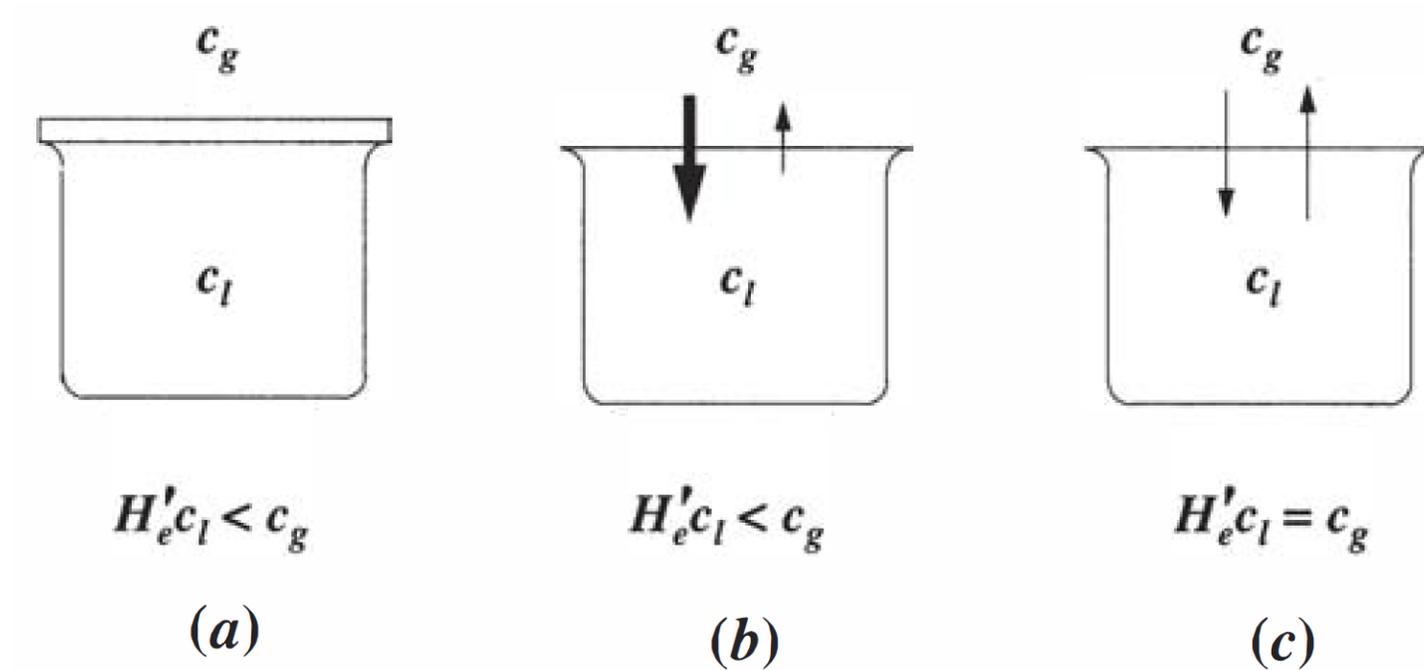


FIGURE 19.8

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.

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.

Dissolved Oxygen Saturation

The saturation concentration of oxygen in a natural water is on the order of 10 mg L^{-1} . For water quality modeling, several factors affect this value:

Temperature

Salinity

Partial Pressure variations (elevation)

Several empirically derived equations have been developed to predict these influences on saturation.

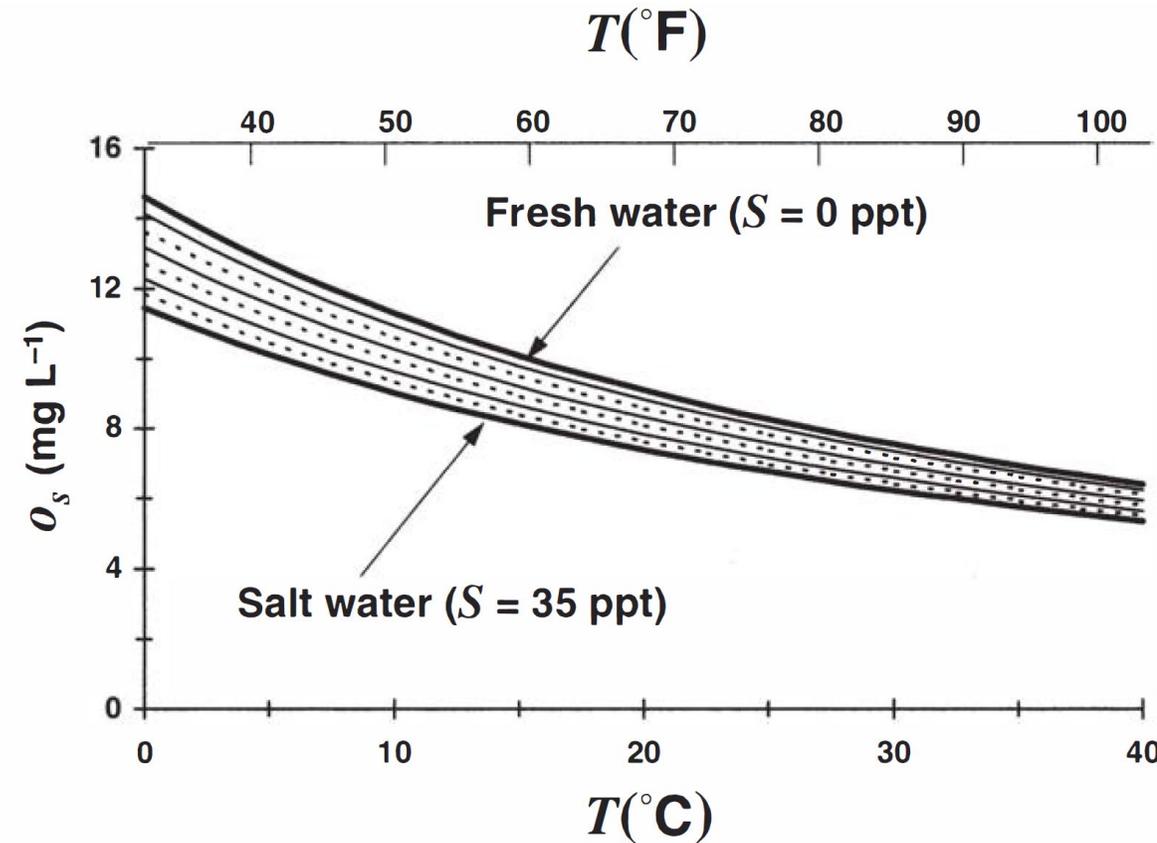


FIGURE 19.9 Relationship of oxygen saturation in water to temperature and salinity.

DO Saturation: Temperature

The following equation can be established for the dependence of oxygen saturation on temperature:

$$\begin{aligned} \ln o_{sf} &= -139.34411 + \frac{1.575701 \times 10^5}{T_a} - \frac{6.642308 \times 10^7}{T_a^2} \\ &+ \frac{1.243800 \times 10^{10}}{T_a^3} - \frac{8.621949 \times 10^{11}}{T_a^4} \end{aligned}$$

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

$$T_a = T(^{\circ}\text{C}) + 273.15$$

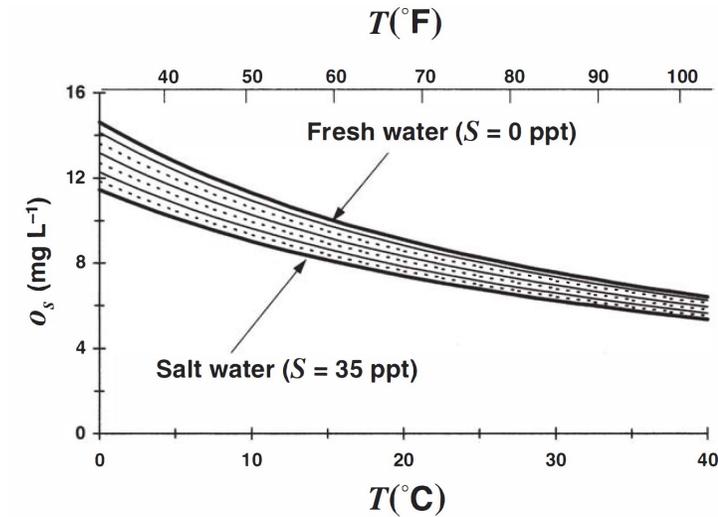


FIGURE 19.9 Relationship of oxygen saturation in water to temperature and salinity.

DO Saturation: Temperature

This equation shows that saturation decreases with increasing temperature, e.g. from 14.6 mg L^{-1} at 0°C to 7.6 mg L^{-1} at 30°C .

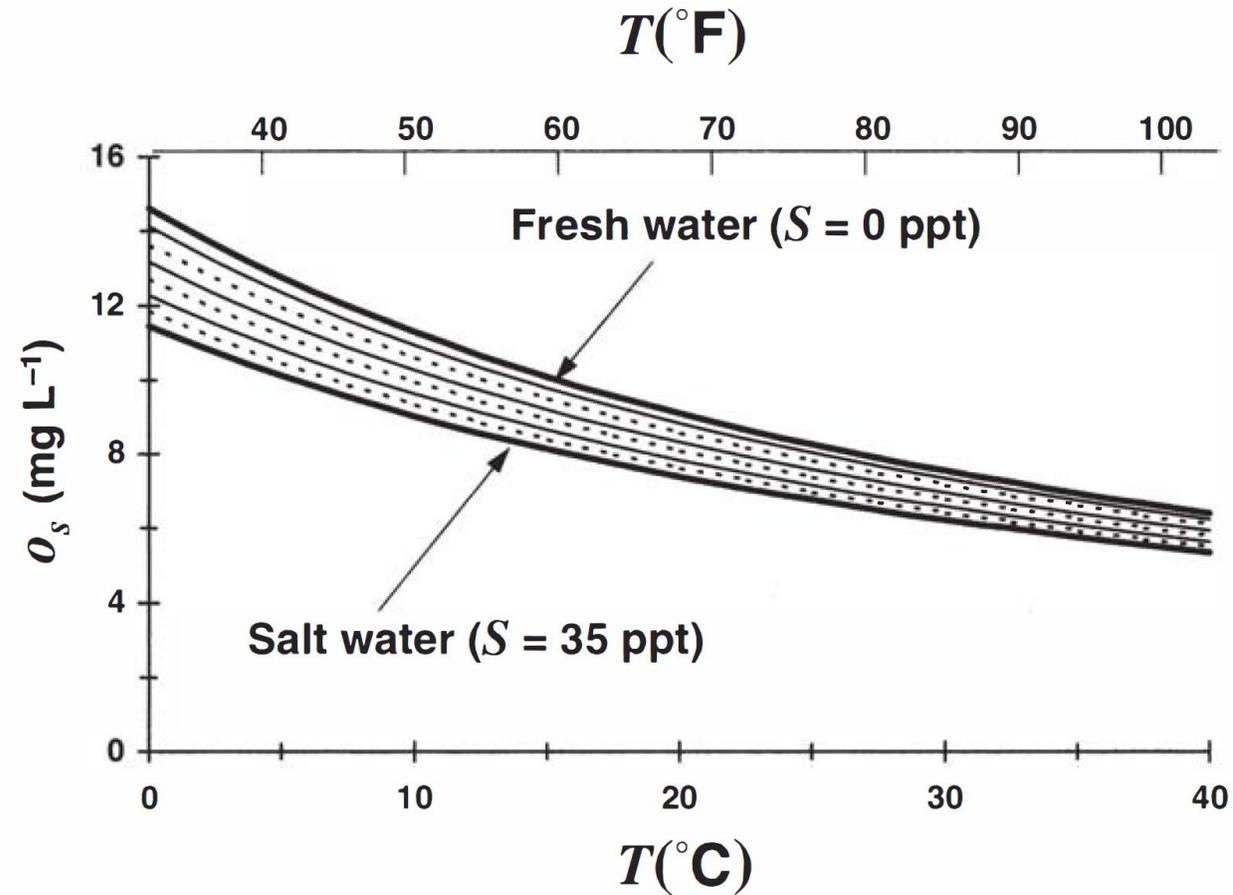


FIGURE 19.9
Relationship of oxygen saturation in water to temperature and salinity.

DO Saturation: Salinity Effect

The following equation can be used to establish dependence of saturation on salinity:

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

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:

$$S = 1.80655 \times \text{Chlor}$$

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

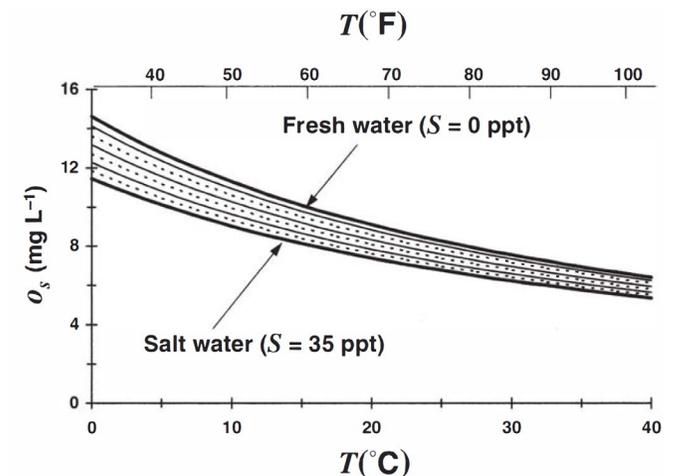


FIGURE 19.9
Relationship of oxygen saturation in water to temperature and salinity.

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.

DO Saturation: Pressure Effect

The following equation can be used to describe the dependence of saturation on pressure:

$$o_{sp} = o_{s1}p \left[\frac{\left(1 - \frac{p_{wv}}{p}\right) (1 - \theta p)}{(1 - p_{wv})(1 - \theta)} \right]$$

where p = atmospheric pressure (atm)

o_{sp} = saturation concentration of DO at p (mgL^{-1})

o_{s1} = saturation concentration of DO at 1 atm (mgL^{-1})

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

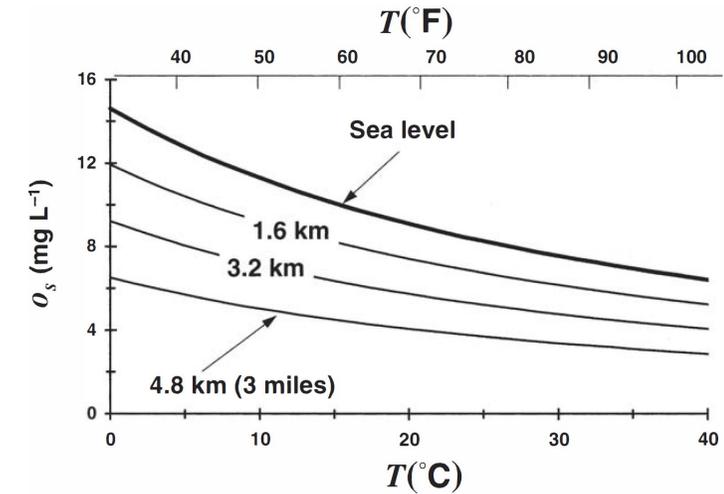


FIGURE 19.10 Relationship of oxygen saturation in water to temperature and elevation above sea level.

DO Saturation: Pressure Effect

p_{wv} = partial pressure of water vapor (atm), calculated by:

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

The parameter can be computed by

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

This formula is written in terms of $T(^{\circ}\text{C})$ rather than K.

Approximations based on elevation are:

$$o_{sp} = o_{s1} [1 - 0.1148 \times elev (km)]$$

$$o_{sp} = o_{s1} [1 - 0.000035 \times elev (ft)]$$

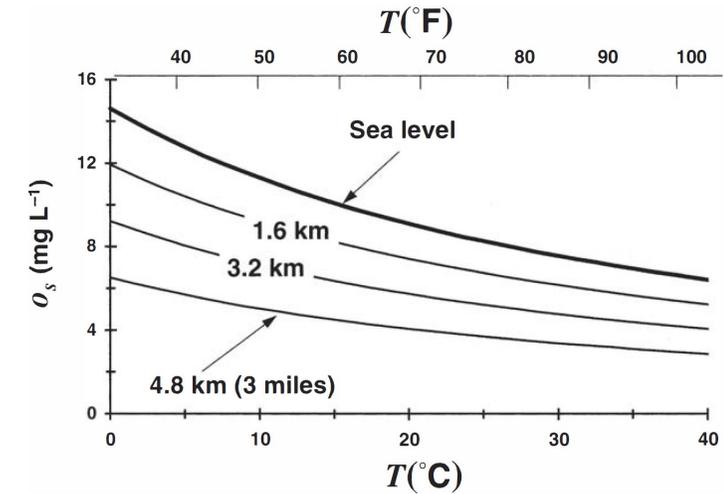


FIGURE 19.10 Relationship of oxygen saturation in water to temperature and elevation above sea level.