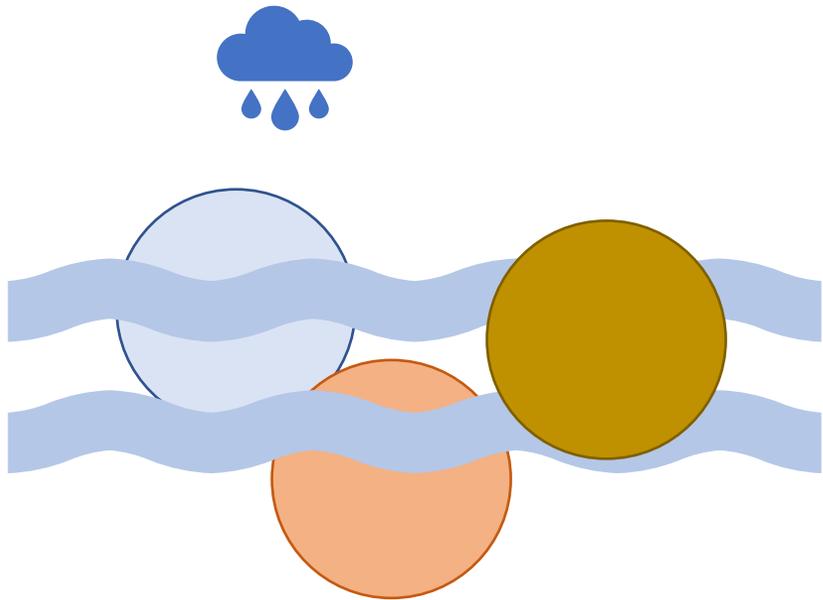
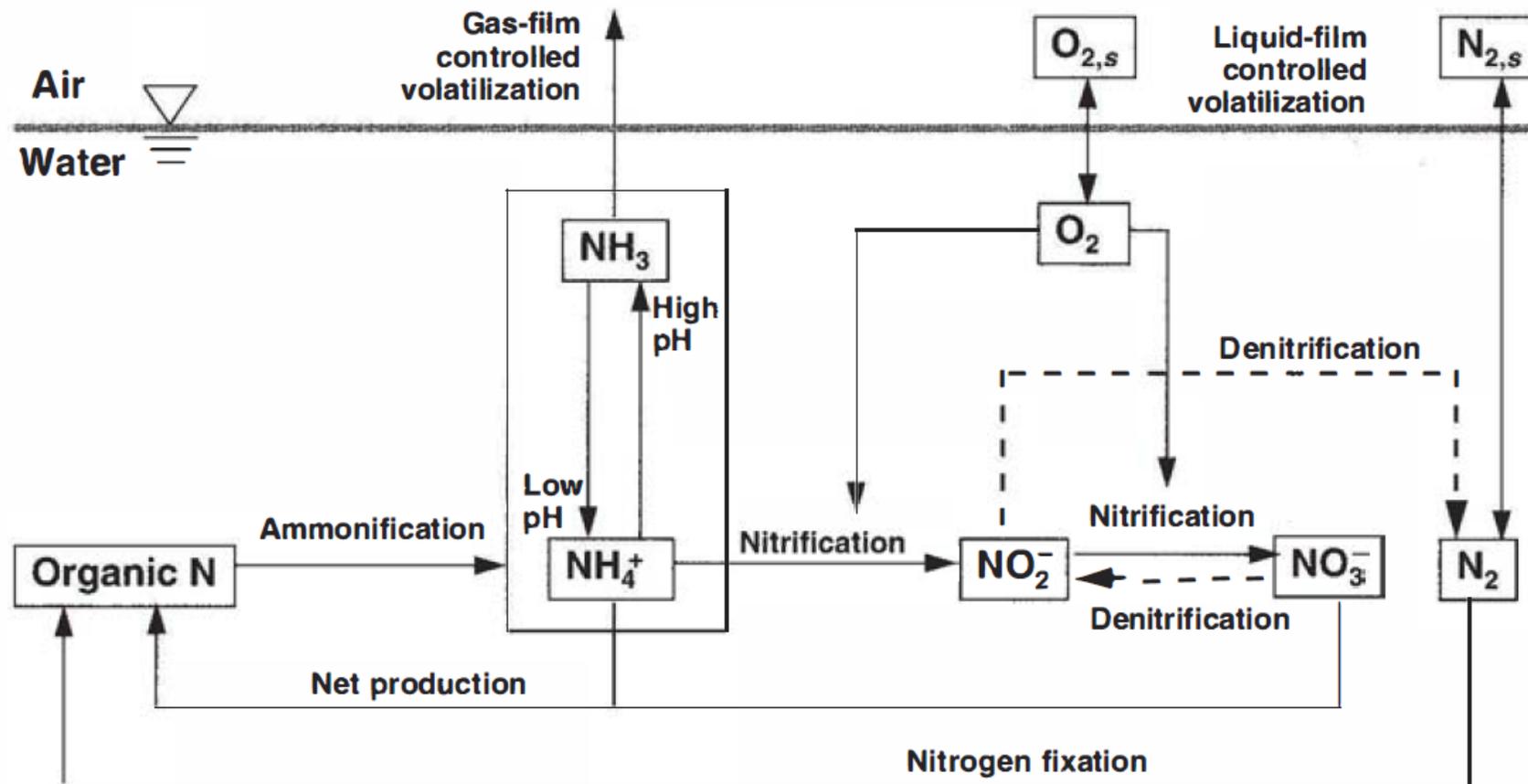


# Nitrification



**EXAMPLE 23.1. CALCULATION OF UN-IONIZED AMMONIA.** Determine the concentration of un-ionized ammonia at a point in a stream that has a total ammonia concentration of  $1 \text{ mgN L}^{-1}$ , a pH of 8.5, and a temperature of  $30^\circ\text{C}$ .



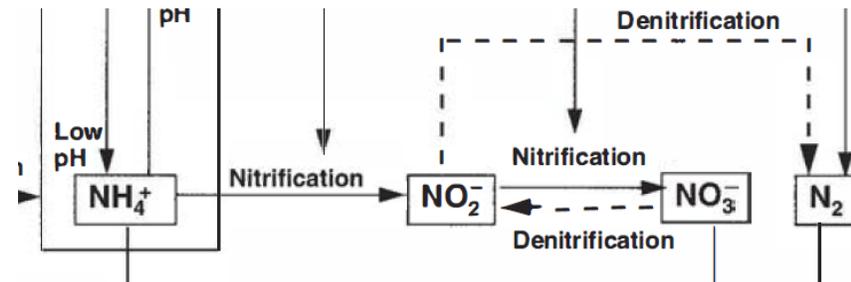
**FIGURE 23.1**

The nitrogen cycle in natural waters. The dashed arrows indicate that the denitrification reactions take place under anaerobic conditions. Note that, although it is not depicted on this diagram, the net production of organic N can have an impact on a water body's oxygen level.



# Nitrogen and Water Quality

**Nitrification/denitrification:** Ammonia is oxidized in a two-step process to form nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ). This process consumes oxygen and, thus can seriously deplete the water body's oxygen level.

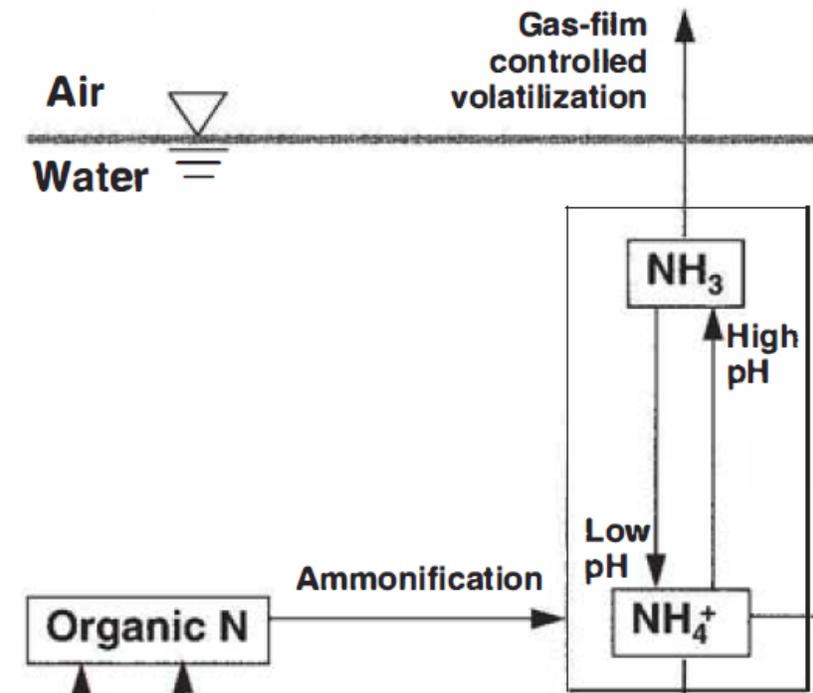


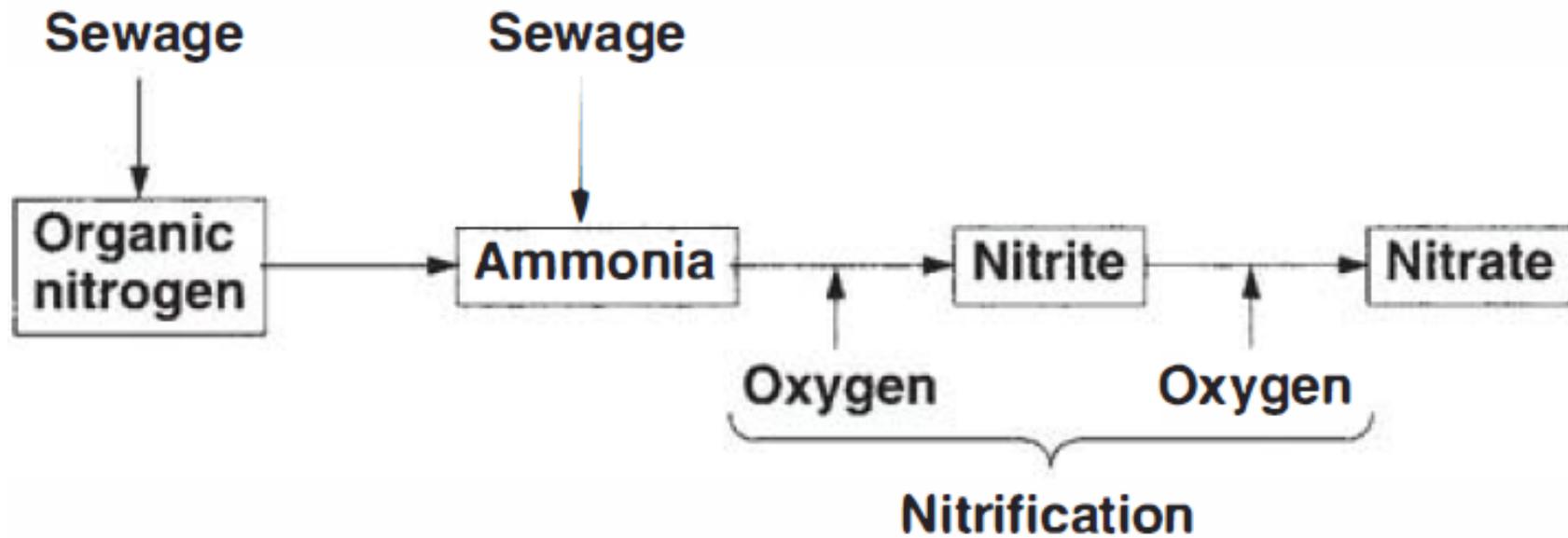
**Eutrophication:** nitrogen serves as an essential nutrient for plant growth, acting as a fertilizer for plant growth (overstimulating this growth is called eutrophication). Excess growth can impact water quality directly (scum, clogging) and also indirectly (oxygen, ammonia toxicity, etc).

# Nitrogen and Water Quality

**Nitrate pollution:** Ultimately nitrification produces nitrate ( $\text{NO}_3^-$ ), which in high concentrations can have serious (occasional) fatal effects in infants. Especially critical in agricultural regions where nonpoint sources of  $\text{NO}_3^-$  (fertilizer) supplement high levels from point sources.

**Ammonia toxicity:** Ammonia exists in two forms in natural waters: ammonium ion ( $\text{NH}_4^+$ ) and ammonia gas ( $\text{NH}_3$ ). The former is innocuous in most natural water levels, the unionized form is toxic to fish. At high pH, unionized form principally, at pH=9 (20°C), 20% in unionized form. Such conditions occur in recovery zone below sewage discharge, later inducing plant growth, depleting  $\text{CO}_2$ , inducing pH increase. Then high pH and temperature result in elevated unionized ammonia.

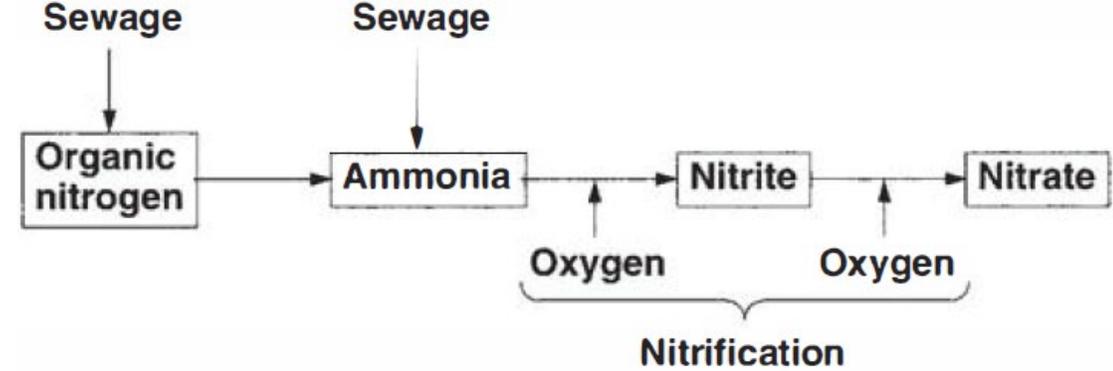




**FIGURE 23.2**

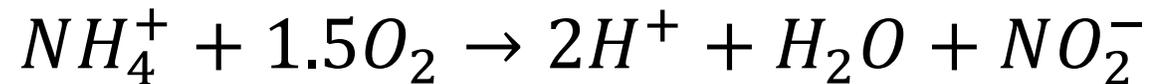
The decomposition of nitrogen compounds below a wastewater treatment plant discharge. Models have been developed to simulate this process based on a series of first-order reactions.

# Nitrification



In addition to carbonaceous BOD, nitrogen compounds in wastewater also have an impact on a river's oxygen resources.

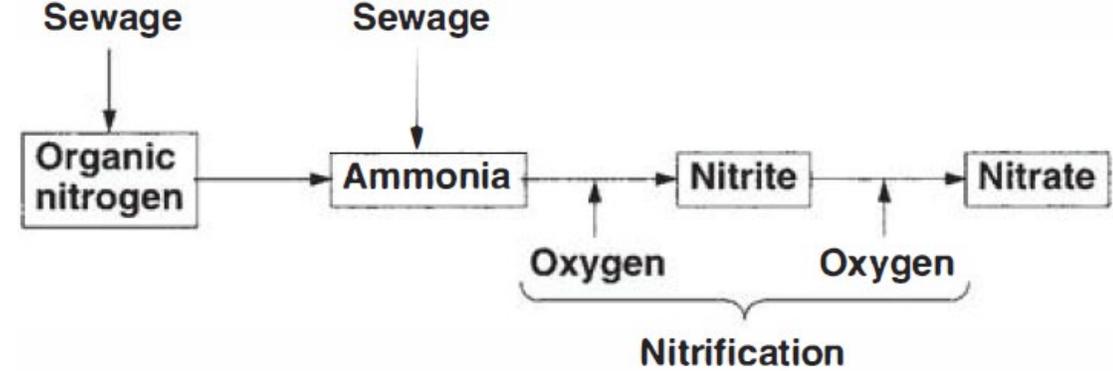
The conversion of ammonia to nitrate is collectively called **nitrification**. First, bacteria (genus *Nitrosomonas*) convert ammonium ion ( $NH_4^+$ ) to nitrite.



Second, bacteria (genus *Nitrobacter*) convert nitrite to nitrate,



# Nitrification



Both bacteria growth ( $d^{-1}$ ) are slower than heterotrophic bacteria ( $hr^{-1}$ ) and (ii)  $NO_2^-$  to  $NO_3^-$  is faster than (i)  $[NH_3]_T$  to  $NO_2^-$ .

The oxygen consumed in the two stages can be computed as:

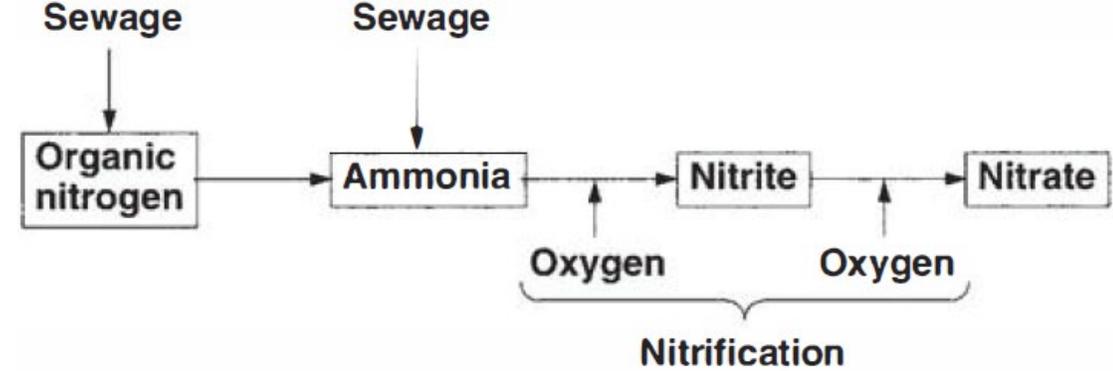
$$r_{oa} = \frac{1.5(32)}{14} = 3.43 \text{ gO gN}^{-1}$$

$$r_{oi} = \frac{0.5(32)}{14} = 1.14 \text{ gO gN}^{-1}$$

where  $r_{oa}$  and  $r_{oi}$  represent the amount of oxygen consumed due to nitrification of ammonium and nitrite, respectively. The entire process:

$$r_{on} = r_{oa} + r_{oi} = 4.57 \text{ gO gN}^{-1}$$

# Nitrification

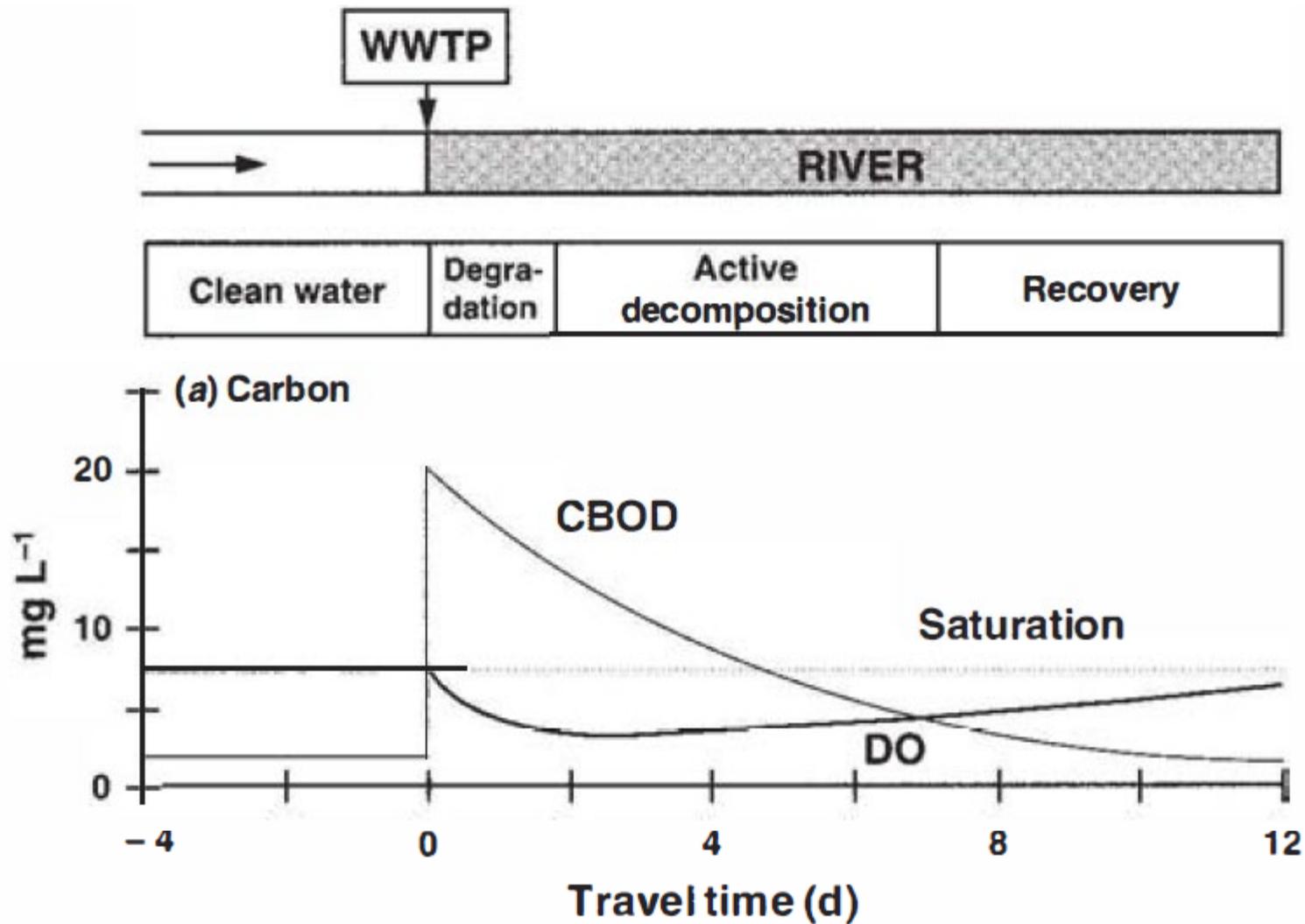


where  $r_{oa}$  and  $r_{oi}$  represent the amount of oxygen consumed due to nitrification of ammonium and nitrite, respectively. The entire process:

$$r_{on} = r_{oa} + r_{oi} = 4.57 \text{ gO gN}^{-1}$$

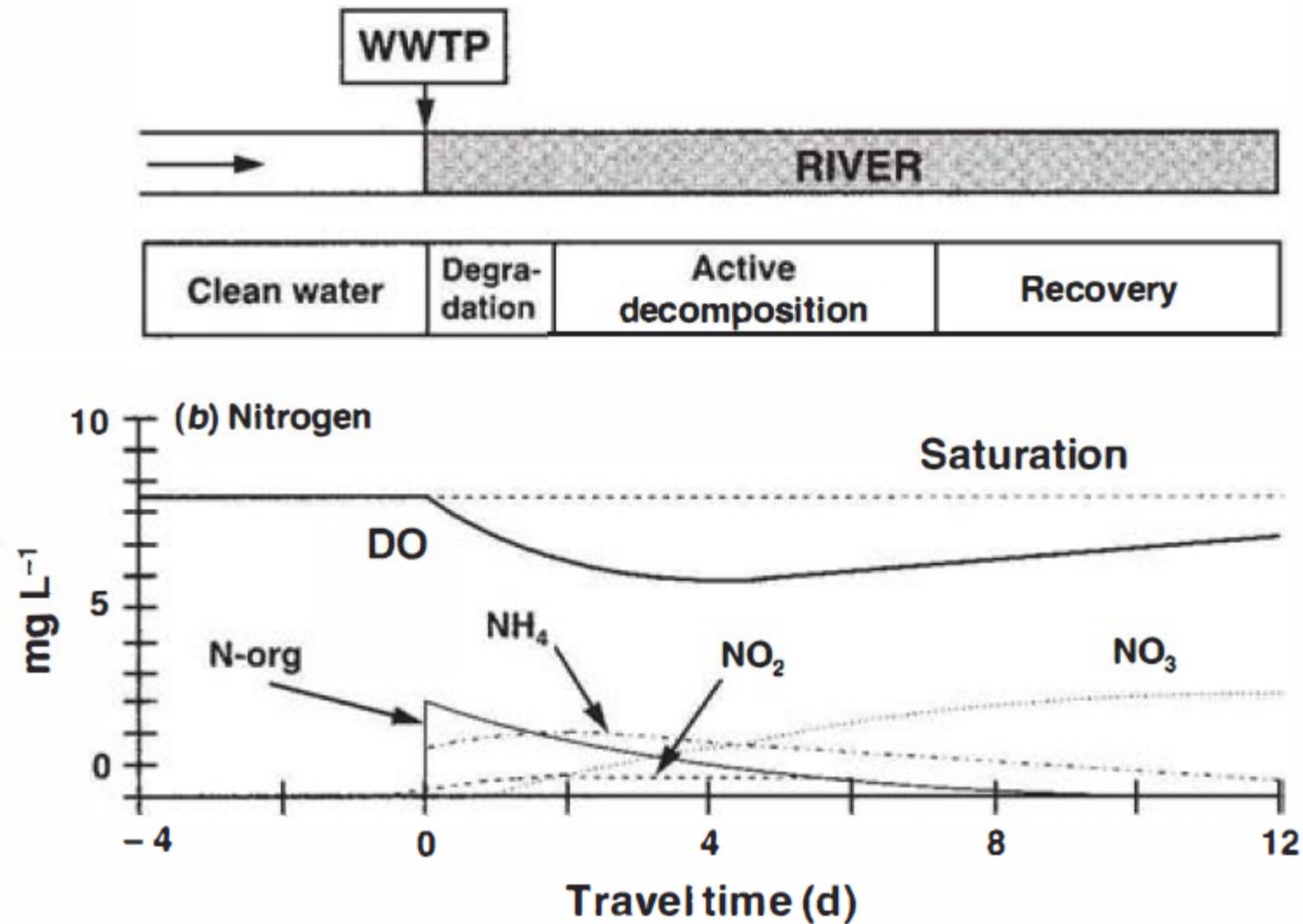
$r_{on}$  = the amount of oxygen consumed per unit mass of nitrogen oxidized in total process of nitrification. Since some of the ammonium is used for bacterial cell production, oxygen demand actually approaches **4.2 g** of oxygen per g of nitrogen oxidized.

3 factors further affect nitrification (i) presence of nitrifying bacteria/stream conditions and substrate, (ii) alkaline pH levels (about 8) neutralizing acid, (iii) sufficient oxygen (greater than  $2 \text{ mg L}^{-1}$ ). The net effect is to inhibit nitrification immediately downstream of point-source effluents.



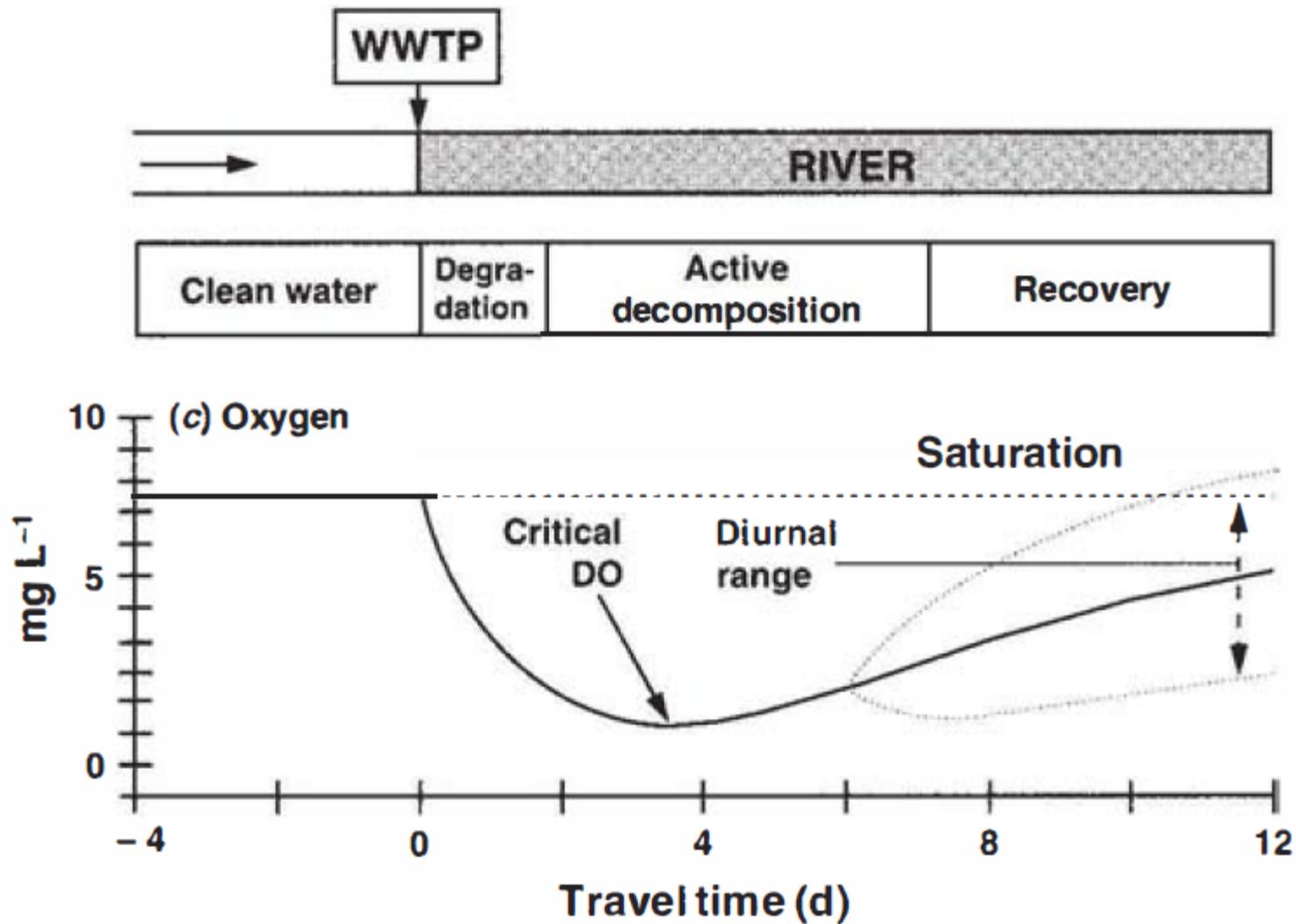
**FIGURE 23.3**

The trends of carbon, nitrogen, and oxygen below a wastewater treatment plant discharge into a river.



**FIGURE 23.3**

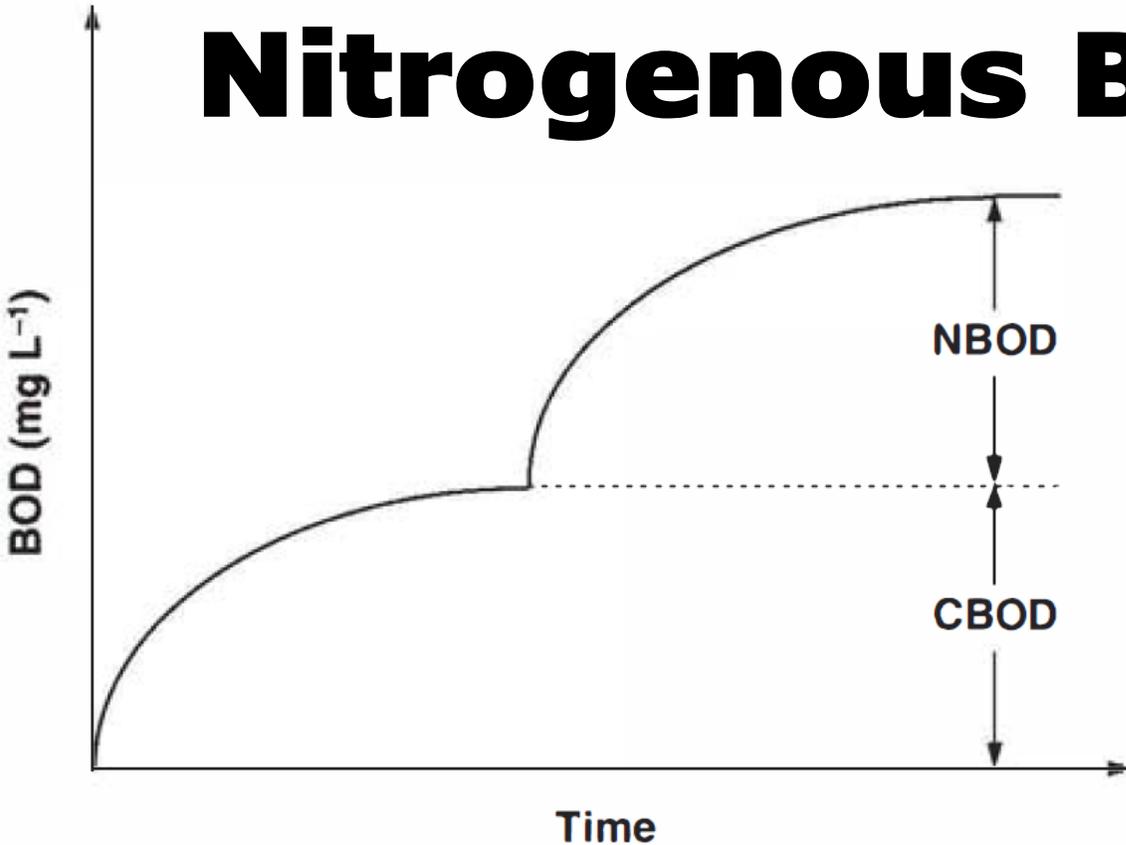
The trends of carbon, nitrogen, and oxygen below a wastewater treatment plant discharge into a river.



**FIGURE 23.3**

The trends of carbon, nitrogen, and oxygen below a wastewater treatment plant discharge into a river.

# Nitrogenous BOD Model



Initial attempts treated the additional demand due to nitrification to be treated as a nitrogenous BOD (NBOD) with mass balances written and solved for this and oxygen deficit.

NBOD could be measured from the bottle method and through indirect methods via knowledge of nitrification.

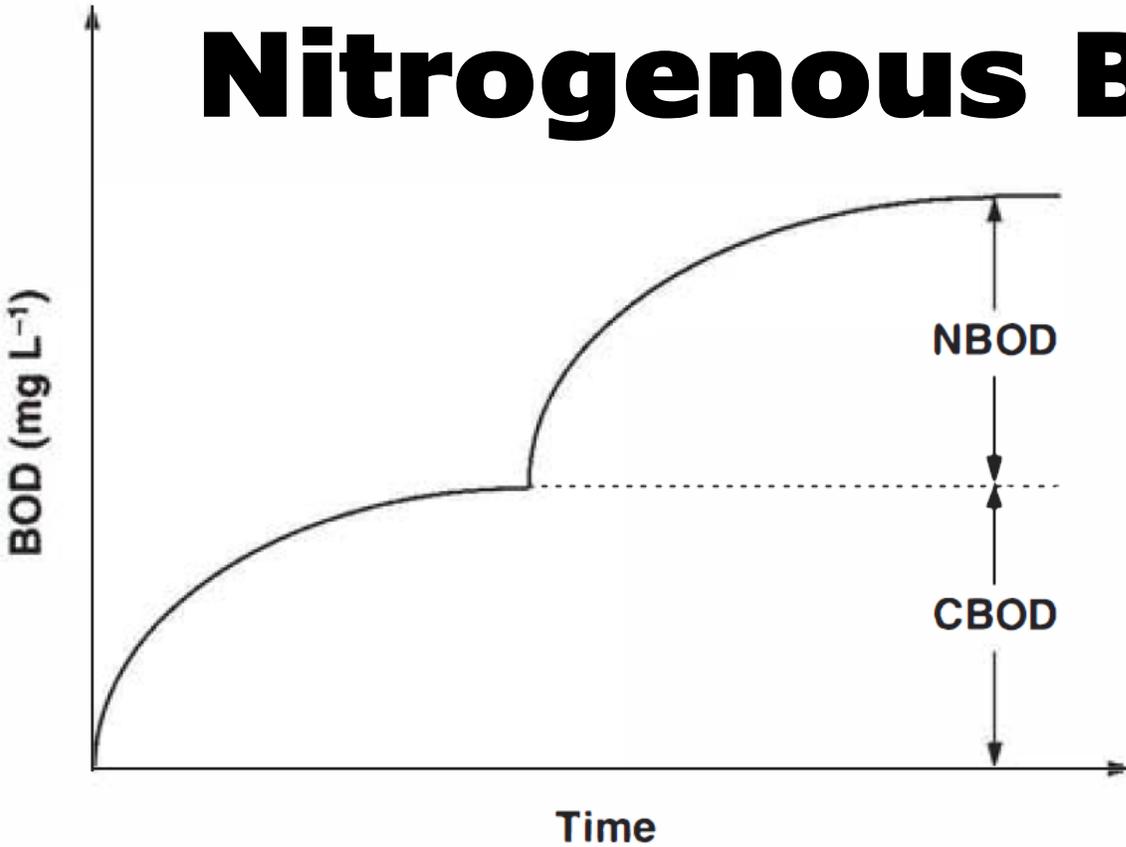
Total amount of oxidizable nitrogen is sum of organic and ammonia N (total Kjeldahl nitrogen) represents this. i.e. the NBOD could be estimate by:

$$L_N = 4.57 TKN$$

where  $L_N = \text{NBOD (mg L}^{-1}\text{)}$  and  $TKN = \text{total Kjeldahl nitrogen (mgN L}^{-1}\text{)}$ .

$$\text{(from } r_{on} = r_{oa} + r_{oi} = 4.57 \text{ gO gN}^{-1}\text{)}$$

# Nitrogenous BOD Model



Similar to mass balance for CBOD, in plug-flow system solution can be solved as below. For a point source, if  $L_N = L_{N0}$  and  $D = D_0$  at  $t = 0$ , then the equations are :

$$L_N = L_{N0} e^{-\frac{k_n x}{U}}$$

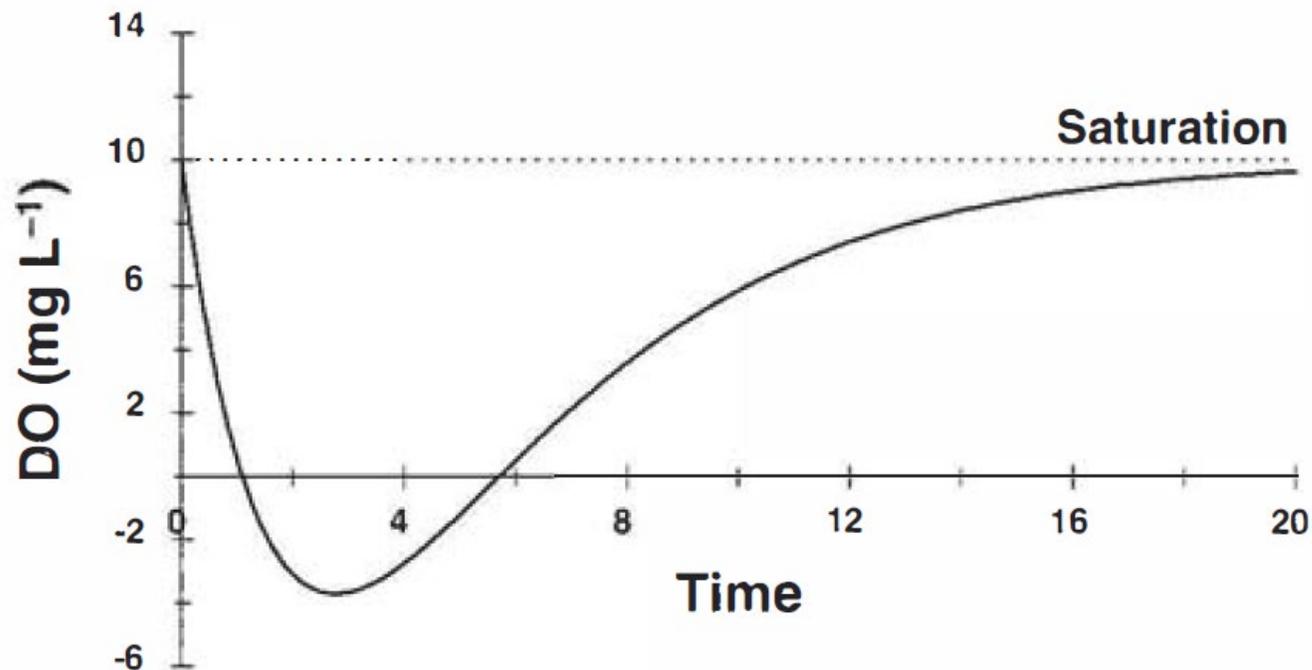
and

$$D = D_0 e^{-\frac{k_n x}{U}} + \frac{k_n L_0}{k_a - k_n} (e^{-\frac{k_n x}{U}} - e^{-\frac{k_n x}{U}})$$

where  $k_n$  = rate of NBOD oxidation (d<sup>-1</sup>), usually between 0.1-0.5 d<sup>-1</sup> for deep waters, and greater than 1d<sup>-1</sup> for shallow waters. Total CBOD and NBOD could be added in this approach.

# Nitrogenous BOD Model

**FIGURE 23.5**  
NBOD simulation.



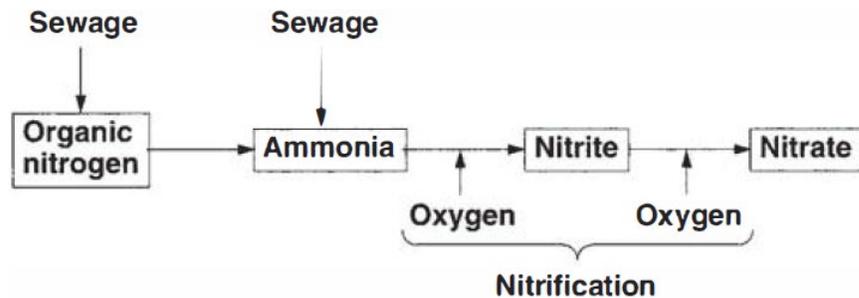
For this simulation initial conditions are 50% organic N, 50% ammonium.  $DO_0 = 10 \text{ mgL}^{-1}$ ,  $k_n = 0.25 \text{ d}^{-1}$ ,  $k_a = 0.5 \text{ d}^{-1}$ . Notice that unrealistically deficit valley is  $-3 \text{ mgL}^{-1}$  at travel time of 2.5 d.

Implicit assumptions are present:

1. If we lump, conversions ignored
2. First-order ignores 2-step nitrification
3. The NBOD perspective does not address other cofactors (presence of bacteria, pH, and oxygen)

# Modeling Nitrification

Assuming first-order kinetics, the nitrification process can be written as a series of first-order reactions,



$$\frac{dN_o}{dt} = -k_{oa}N_o$$

$$\frac{dN_a}{dt} = k_{oa}N_o - k_{ai}N_a$$

$$\frac{dN_i}{dt} = k_{ai}N_a - k_{in}N_i$$

$$\frac{dN_n}{dt} = k_{in}N_i$$

where the subscripts  $o$ ,  $a$ ,  $i$ , and  $n$  denote organic, ammonium, nitrite, and nitrate respectively. An oxygen deficit balance can be written as:

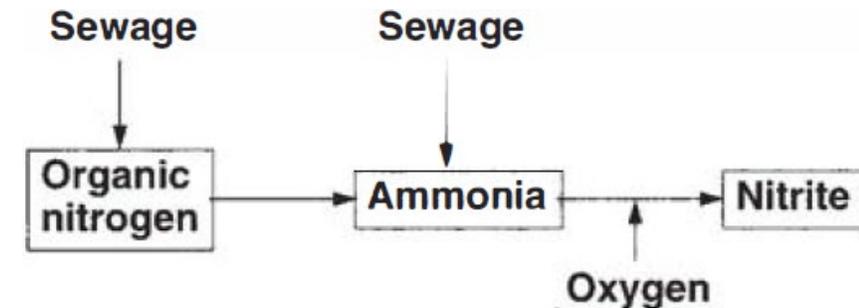
$$\frac{dD}{dt} = r_{oa}k_{ai}N_a + r_{oi}k_{in}N_i - k_aD$$

# Modeling Nitrification

Because these are sequential, they can be solved for using techniques treating them as feedforward reactors and reactions. For the case where  $N_o = N_{o0}$  at  $t = 0$ , the solutions for the nitrogen species are:

Organic N

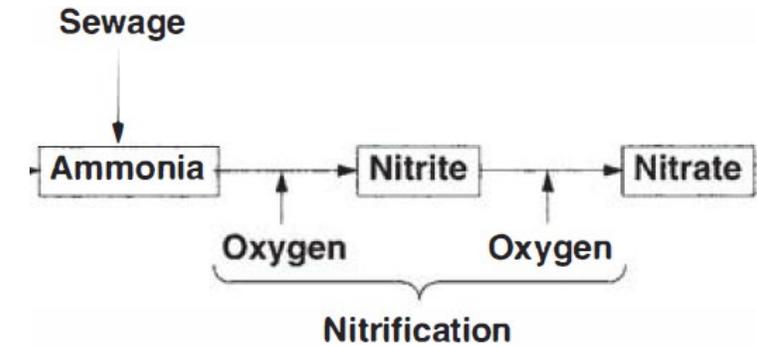
$$N_o = N_{o0}e^{-k_{oa}t}$$



Ammonia N

$$N_a = N_{a0}e^{-k_{ai}t} + \frac{k_{oa}N_{o0}}{k_{ai} - k_{oa}} (e^{-k_{oa}t} - e^{-k_{ai}t})$$

# Modeling Nitrification



Nitrite N

$$N_i = \frac{k_{ai}N_{a0}}{k_{in} - k_{ai}} (e^{-k_{ait}} - e^{-k_{int}}) + \frac{k_{ai}k_{oa}N_{a0}}{k_{ai} - k_{oa}} \left( \frac{e^{-k_{oat}} - e^{-k_{int}}}{k_{in} - k_{oa}} - \frac{e^{-k_{ait}} - e^{-k_{int}}}{k_{in} - k_{ai}} \right)$$

Nitrate N

$$N_n = N_{o0} + N_{a0} - N_{o0}e^{-k_{oat}} - N_{a0}e^{-k_{ait}} - \frac{k_{oa}N_{o0}}{k_{ai} - k_{oa}} (e^{-k_{oat}} - e^{-k_{ait}}) - \frac{k_{ai}N_{a0}}{k_{in} - k_{ai}} (e^{-k_{ait}} - e^{-k_{int}}) - \frac{k_{ai}k_{oa}N_{o0}}{k_{ai} - k_{oa}} \left( \frac{e^{-k_{oat}} - e^{-k_{int}}}{k_{in} - k_{oa}} - \frac{e^{-k_{ait}} - e^{-k_{int}}}{k_{in} - k_{ai}} \right)$$

$\left( \frac{dD}{dt} = r_{oa}k_{ai}N_a + r_{oi}k_{in}N_i - k_aD \right)$  would be solved for similarly with substitutions....

# Modeling Nitrification

$$\frac{dD}{dt} = r_{oa}k_{ai}N_a + r_{oi}k_{in}N_i - k_aD$$

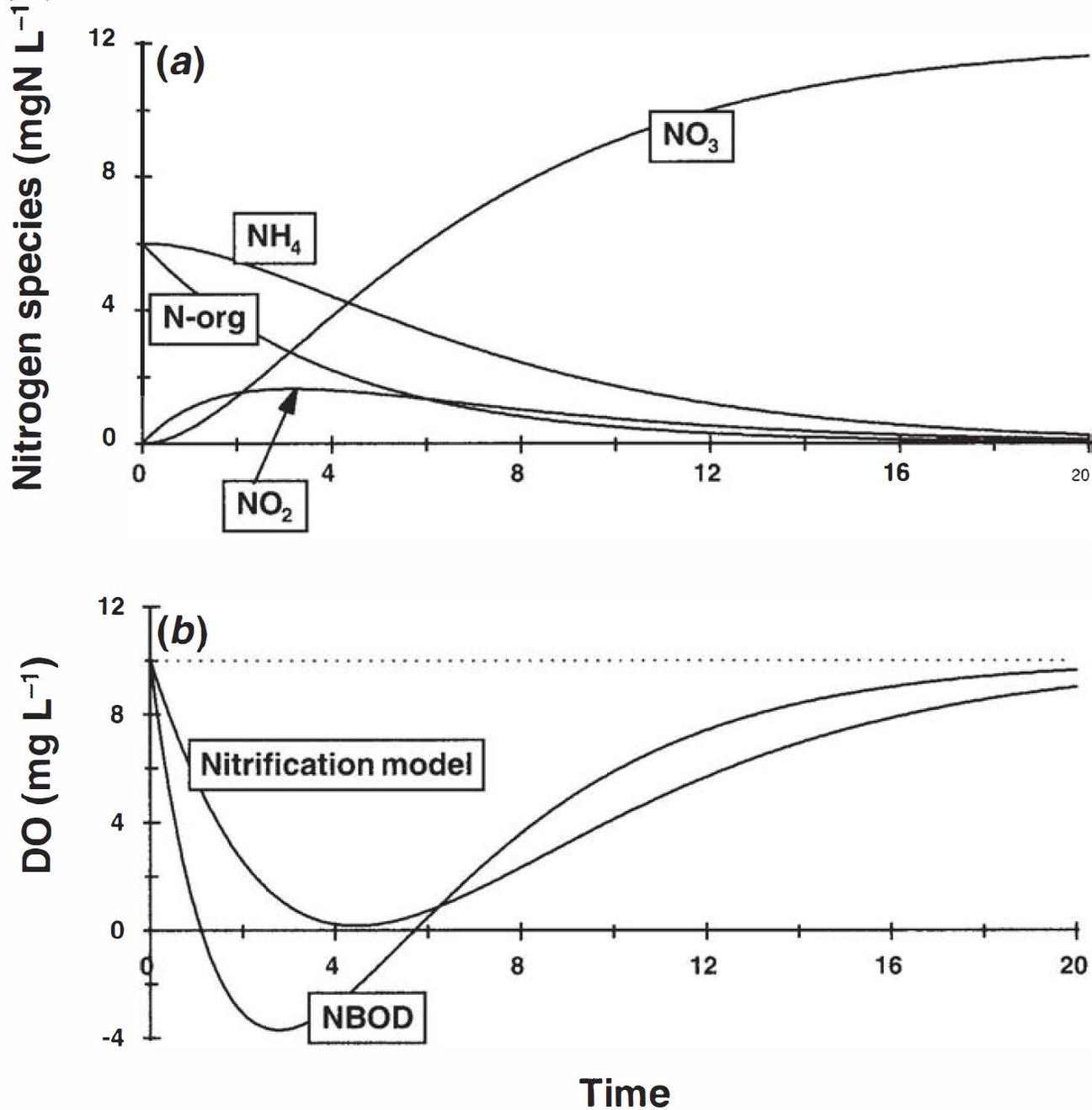
$$\frac{dD}{dt} + k_aD = r_{oa}k_{ai}N_a + r_{oi}k_{in}N_i$$

$$N_a = N_{a0}e^{-k_{ait}} + \frac{k_{oa}N_{o0}}{k_{ai} - k_{oa}} (e^{-k_{oat}} - e^{-k_{ait}})$$

$$\frac{dD}{dt} + k_aD = r_{oa}k_{ai} \left[ N_{a0}e^{-k_{ait}} + \frac{k_{oa}N_{o0}}{k_{ai} - k_{oa}} (e^{-k_{oat}} - e^{-k_{ait}}) \right] + r_{oi}k_{in}N_i$$

.....

$$c = \frac{W_e}{V(\lambda \pm \beta_e)} (e^{\pm \beta_e t} - e^{-\lambda t}) \quad [\text{eq 4.1, 4.17, 4.18}]$$



These show the results of a simulation with 50% organic N, 50% ammonium, Oxygen saturation at 10 mg L<sup>-1</sup>, all rates at 0.25 d<sup>-1</sup>, except for  $k_{in}$  (0.75 d<sup>-1</sup>), reaeration at 0.5 d<sup>-1</sup>. You can see max deficit here is 0 mg L<sup>-1</sup> at 4 d travel time.

Spread out and delayed impact.

FIGURE 23.6  
Nitrification simulation.

# Modeling Nitrification: Inhibition

The following factor is multiplied by each of the nitrification rates  $k_{ai}$  and  $k_{in}$ , in order to make up for the unaccounted-for limiting cofactors (specifically depressed oxygen levels).

$$f_{nitr} = 1 - e^{-k_{nitr}o}$$

where  $k_{nitr}$  = first-order nitrification inhibition coefficient ( $\sim 0.6 \text{ L mg}^{-1}$ ).

As oxygen approaches zero, total inhibition occurs

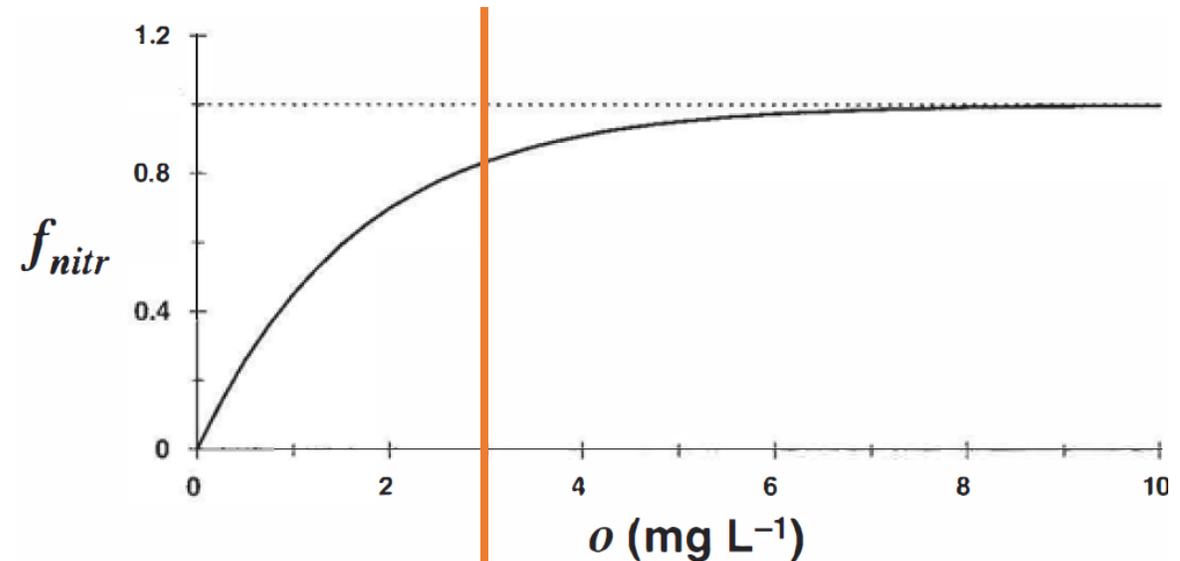


FIGURE 23.7  
Nitrification inhibition factor.

# Modeling Nitrification: Inhibition

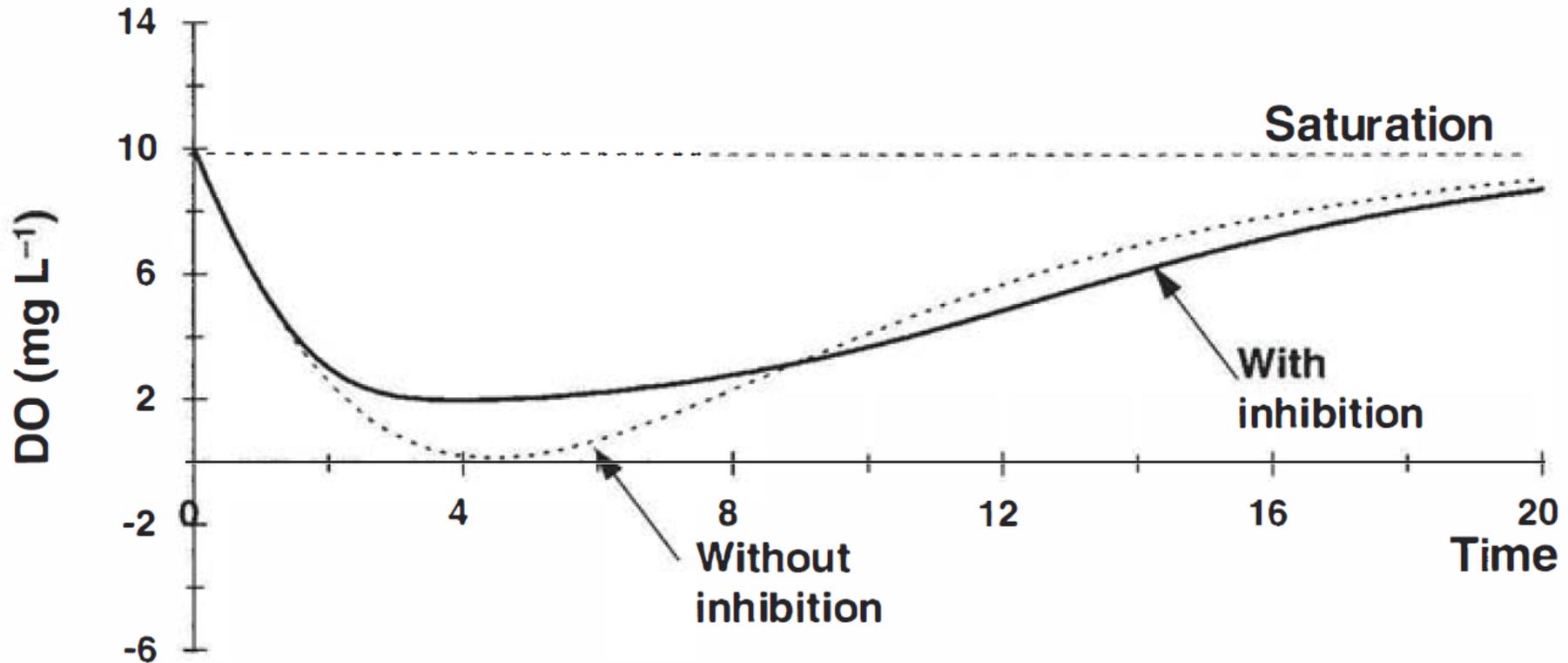
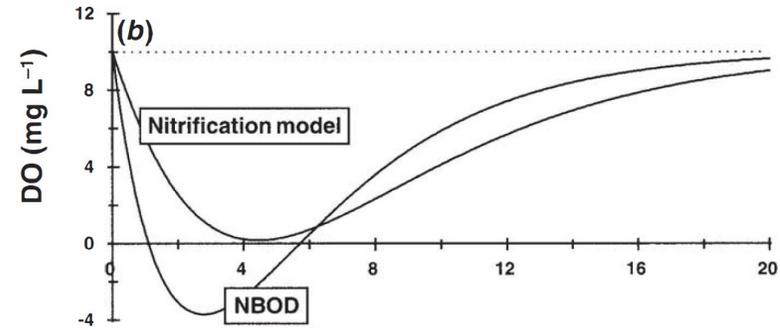


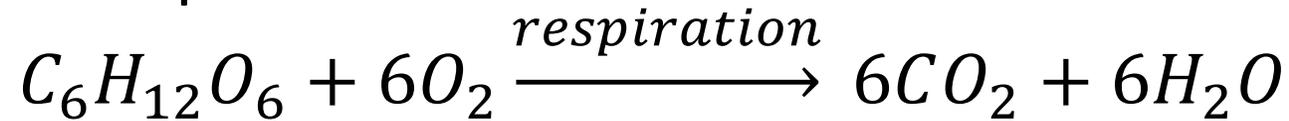
FIGURE 23.8

Nitrification simulation with inhibition at low dissolved oxygen levels.

# Nitrification and Organic Decomposition

Now we revisit the glucose (organic matter) analogy.

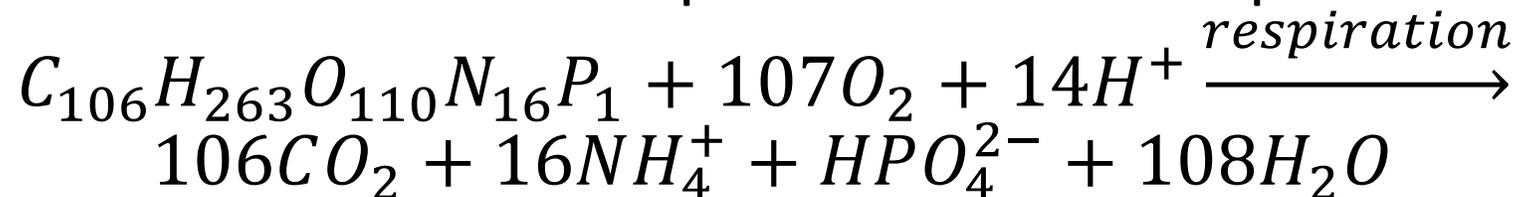
Recall we used sugar glucose,  $C_6H_{12}O_6$ , to represent organic matter using the simple decomposition representation.



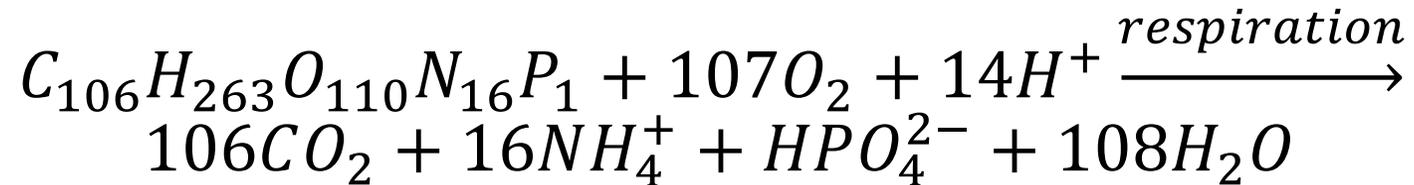
Next, we use a more detailed representation (including phosphate, ammonium)



Using the comprehensive chemical representation of respiration expressed as:



# Nitrification and Organic Decomposition



Oxygen demand per unit mass of organic carbon was obtained:

$$r_{oc} = \frac{107(32)}{106(12)} = 2.69 \text{ gO gC}^{-1}$$

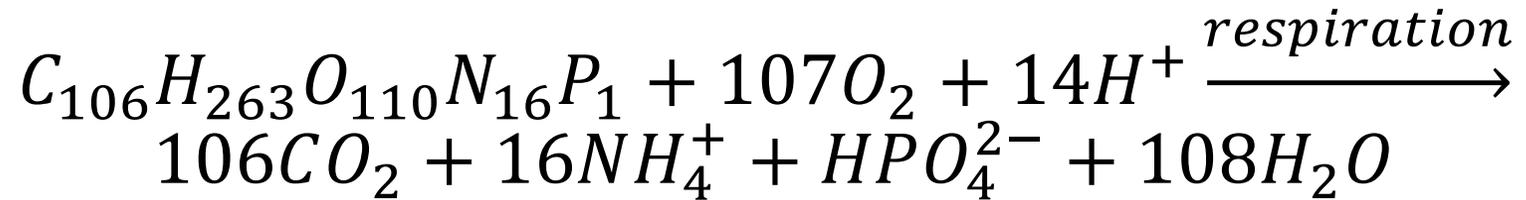
The stoichiometric yield of nitrogen from decomposition of organic carbon should be

$$a_{nc} = \frac{16(14)}{106(12)} = 0.176 \text{ gN gC}^{-1}$$

Then we compute an oxygen demand generated per gram of carbon decomposed due to nitrification

$$r_{on}a_{nc} = 4.57 \text{ gO gN}^{-1}(0.176 \text{ gN gC}^{-1}) = 0.804 \text{ gO gC}^{-1}$$

# Nitrification and Organic Decomposition



Oxygen demand per unit mass of organic carbon was obtained:

$$r_{oc} = \frac{107(32)}{106(12)} = 2.69 \text{ gO gC}^{-1}$$

Then we compute an oxygen demand generated per gram of carbon decomposed due to nitrification

$$r_{on} a_{nc} = 0.804 \text{ gO gC}^{-1}$$

Thus oxygen consumed in nitrification is 30% of oxygen consumed in carbonaceous oxidation of pure organic matter.

# **Nitrate and Ammonia Toxicity**

## **Nitrate Pollution**

The presence of high levels of nitrate in drinking water appears to be the cause of methemoglobinemia (“blue babies”), affecting infants (<6months) but also children up to 6 years. Without nitrate removal, a potential exists for nitrate problems below point sources as nitrate is the terminal point in the aerobic nitrogen cycle. More sources/sinks and conditions exist that should be used in advanced frameworks (plant intake, decay, anoxic conditions).

## **Ammonia Toxicity**

Ammonia as the un-ionized state ( $\text{NH}_3$ ) presents toxicity to organisms.

# Ammonia Toxicity

Ammonia nitrogen can exist in two states in natural waters: ammonium ion ( $\text{NH}_4^+$ ) and un-ionized ammonia ( $\text{NH}_3$ ),

$$[\text{NH}_3]_T = [\text{NH}_4^+] + [\text{NH}_3]$$

At sufficiently high levels (0.01 to 0.1 mg L<sup>-1</sup>), the un-ionized form is toxic to fish (ammonia toxicity).

Two forms can be represented by the equilibrium dissociation reaction



Where the ratio of the reactants to the products is specified by an equilibrium coefficient

$$K = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

# Ammonia Toxicity

The equilibrium coefficient (K) for the reaction is related to temperature by

$$pK = 0.09018 + \frac{2729.92}{T_a}$$

where  $T_a$  is in kelvins and  $pK = -\log_{10}(K)$

To gain insight into partitioning, we solve ( $K = \frac{[NH_3][H^+]}{[NH_4^+]}$ ) for ammonium ion and substitute

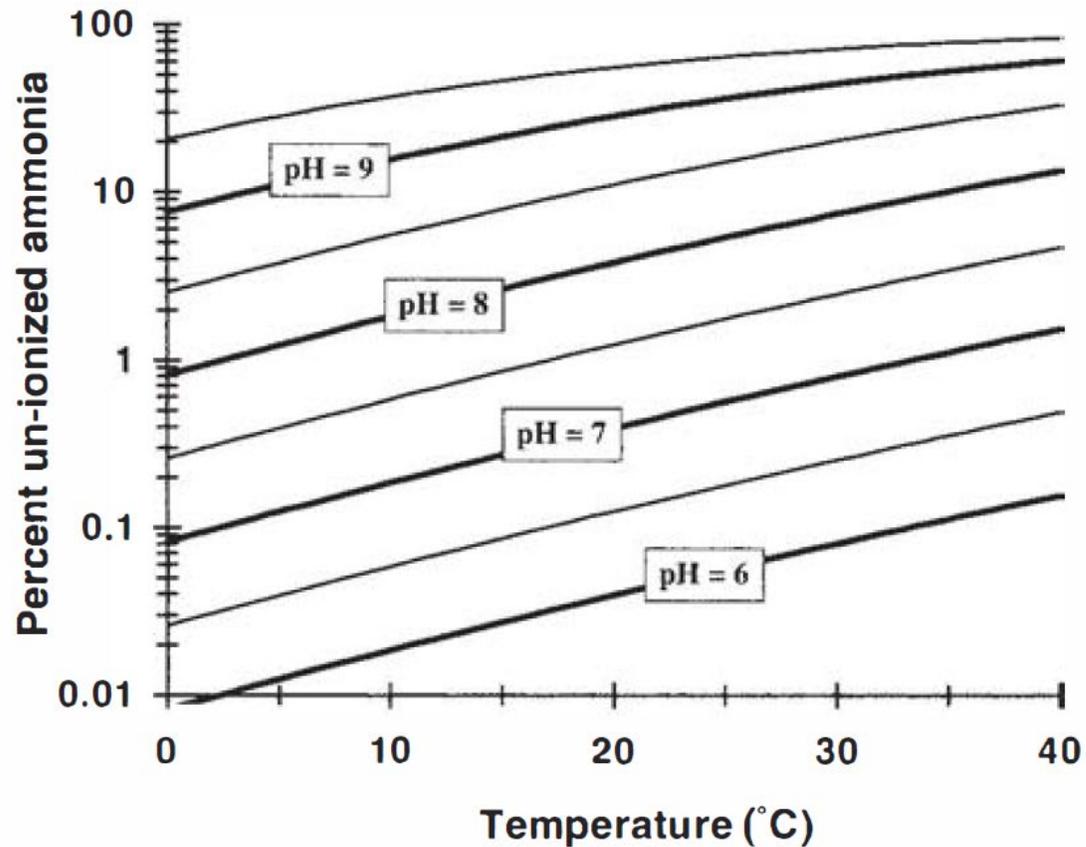
$$[NH_3] = F_u [NH_3]_T$$

where  $F_u$  = fraction of total ammonia in un-ionized form,

$$F_u = \frac{1}{1 + ([H^+]/K)}$$

**EXAMPLE 23.1. CALCULATION OF UN-IONIZED AMMONIA.** Determine the concentration of un-ionized ammonia at a point in a stream that has a total ammonia concentration of  $1 \text{ mgN L}^{-1}$ , a pH of 8.5, and a temperature of  $30^\circ\text{C}$ .

# Nitrate and Ammonia Toxicity



This figure summarizes values for percent un-ionized ammonia for a range of temperatures and pH. Systems with high pH and temperatures have highest percentage.

$$F_u = \frac{1}{1 + ([H^+]/K)}$$

**FIGURE 23.9**  
Percent un-ionized ammonia  
versus temperature for various  
levels of pH.