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ECOLOGIC MODELS

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8-1 INTRODUCTION

Ecologic models in the context of this chapter are considered to be analytical structures of broad segments of the aquatic ecosystem. Several trophic levels and chemical interactions are included. The substantial difficulty in constructing models of the ecologic system is primarily related to the lack of a basic scientific set of laws on biological behavior. This is in contrast to the state-of-the-art of modeling hydrodynamic phenomena where the basic equations governing fluid flow are known. Nevertheless, ecologic models have been constructed along several lines. These models include: (1) linear descriptions of portions of the biological setting, called *compartment models*; (2) closely related linear food-chain models of concentration of chemicals and radioactive substances, through various trophic levels; (3) detailed nonlinear models replete with complex interactions attempting to describe the details of trophic level behavior; and (4) classification models (e.g., niche analysis) coupled to sets of deterministic equations.

Nonlinear ecologic models are currently being investigated and applied in various settings. These models usually attempt to achieve higher fidelity in their representation of reality through the use of nonlinear relationships among

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the dependent variables of the problem. In particular, the kinetic behavior of the particular biological groupings is included in ways which are attempts to reproduce what laboratory or intuitive evidence is available.

Phytoplankton biomass models[1,2,3,4] have tended to be constructed along nonlinear lines since a good deal is known of the detailed phytoplankton-zooplankton nutrient interactions. In fact, many predator-prey simulations are nonlinear, since the effect of a predator on a prey appears to be specifiable as only a nonlinear interaction term. Thus, the famous Lotka-Volterra[5] equations and more modern versions are nonlinear models.

A large number of ecologic models have been constructed under the assumption of linear interactions.[6,7,8] The linearity assumption is generally made for two basic reasons. First, it is extremely difficult to specify in nonlinear detail all the complex mechanisms that may exist in a given problem context. Further, it is not necessarily clear that such a detailed specification is any better than a broad, linear interactive system. Secondly, the mathematical and computational aspects of solving large systems of interactive linear equations (perhaps with time-variable coefficients) are well understood.

Conversely, the arguments against the linear assumption also revolve about two notions: (1) even though it may not be possible to specify all details mechanistically, certain features of the problem context may be clearly nonlinear (e.g., nutrient limitation), and to ignore such an obvious well-known nonlinear structure is to invite difficulty in projecting future conditions; and (2) although linear systems may represent an adequate description of past or present conditions, the degree to which such a system can be perturbated (e.g., future changes in one compartment) is not clear.

O'Neill[9] has conducted an error analysis of ecologic models toward determining the degree to which introduction of nonlinearities results in a "better" model. The total uncertainty accompanying a model prediction was analyzed and was observed to consist of two components: (1) system uncertainty, which is generally high at the linear level, and (2) measurement uncertainty of the parameters, which tends to increase with the introduction of more complex phenomena in the nonlinear models. The degree to which these errors propagate through the system and result in an uncertain prediction may not be inituitively clear. It is interesting to note that, in a comparison of relative error between a simple three-compartment linear model and a similar nonlinear version, the linear model was calculated to be more accurate over a wide range (± 50 percent) of the equilibrium model. The nonlinear model was more accurate outside this limit.

In this chapter, specific attention is directed to a linear model of nitrification in the analysis of the dissolved oxygen in natural water systems. A nonlinear model is first presented, and a linear approximation is shown to be justified under conditions encountered in the natural systems reviewed in this chapter. The models presented here progress from relatively simple nitrogen-equivalent biochemical oxygen demand models to more complex models which incorporate feedback effects.

The broad aspects of the nitrogen cycle are reviewed, and the importance of nitrogenous discharges in the dissolved oxygen balance of natural waters is stressed. The nitrogenous compounds, which may be either organic or inorganic in nature, are found in urban and agricultural runoff, domestic waste waters, and industrial effluents. A "background" concentration of nitrogen is present in most water systems and is the result of a dynamic equilibrium of the natural sources of nitrogen in rainfall, from the land, and in the ground. Although the man-made effects are generally of greater significance in the pollution of natural waters, background nitrogen concentrations may be present in amounts that must be considered in any modeling effort.

The purpose of this chapter is to present a simplified ecologic model which has rather general application to water-quality conditions in one-dimensional natural water systems such as streams and estuaries. In order to show the significance of these models and their utility in the analysis of water pollution control programs, application may be made to the nitrification process in estuaries of the Delaware and Potomac Rivers.

Figure 8-1 schematically outlines the major features of the nitrogen cycle that are of importance in this chapter. It is appropriate to initiate the cycle at the point where organic nitrogen (amines, nitriles, proteins) and ammonia resulting from municipal and industrial waters are discharged into a water body. The organic nitrogen undergoes a hydrolytic reaction, producing ammonia as one of the end products, which in addition to the ammonia present in the waste waters, provides a food source for the nitrifying bacteria. The oxidation process proceeds sequentially from ammonia through nitrite to nitrate. The conditions under which these reactions proceed are comparatively restrictive, but if present, they provide an appropriate environment which may result in large depletions of dissolved oxygen.

The forward sequential reactions of the nitrification process often are the dominating features of the nitrogen cycle in bodies of water receiving large discharges of nitrogenous waste material. The reactions proceed in the forward direction, provided the concentration of dissolved oxygen is sufficiently high to meet the requirements of the nitrifying bacteria. However, under conditions of low concentration of dissolved oxygen, bacterial reduction of nitrate to nitrite can occur, followed by the further reduction of nitrite primarily to nitrogen gas, although a few species may reduce the nitrite to ammonia. These reactions provide a source of oxygen for the microorganisms in the stabilization of organic matter without utilizing whatever dissolved oxygen is present in the water.

In addition to the removal of nitrate by bacterial reduction, nitrate may also be used by the phytoplankton as a nutrient source, although it must be converted to ammonia by enzymatic reaction before it is assimilated. The assimilated nitrogen becomes part of the organic nitrogen in plants and, subsequently, in animals. Excretion and decay of this material releases organic nitrogen, thereby completing the cycle. Ammonia, or some form of nitrogen, is also required by the heterotrophic bacteria in the oxidation of carbonaceous mate-
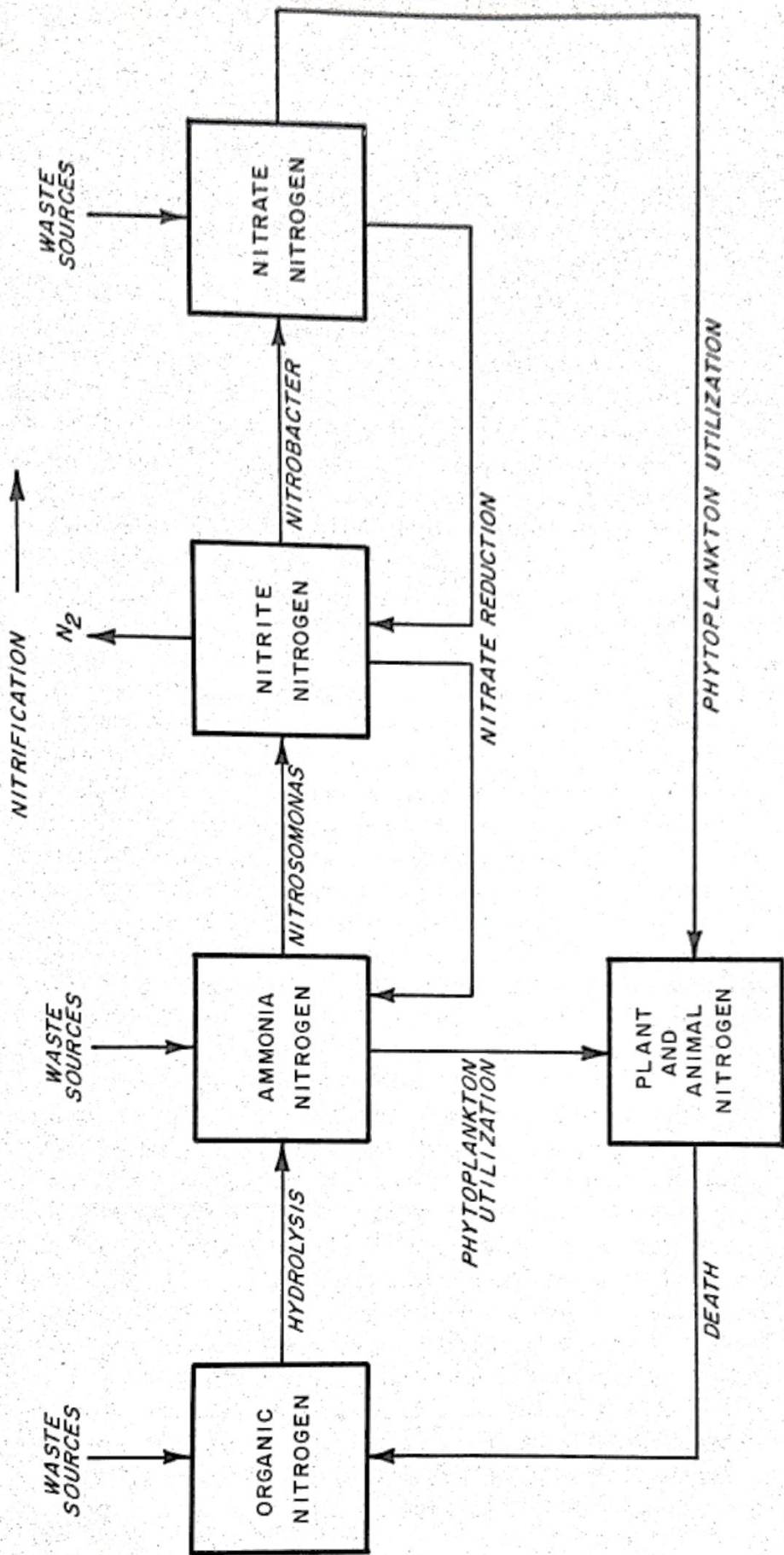
FIGURE 8-1
Major features of the nitrogen cycle.

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rial; however, this sink of nitrogen is relatively insignificant in contrast to the oxidation process or algal usage.

In summary, there are two broad areas of concern from the water-quality viewpoint with respect to the nitrogen cycle in natural waters: (1) the oxidation and possible reduction of various forms of nitrogen by bacteria and the associated utilization of oxygen, and (2) the assimilation of the inorganic nitrogen and the release of organic nitrogen by phytoplankton during growth and death, respectively. In some cases, either one or the other of these conditions dominates, the former in areas of large sources of waste water with little or partial treatment and the latter in water bodies receiving biologically treated effluents or agricultural drainage.

This report is concerned with the first of these broad areas. Its specific purpose is to present a mathematical model of the nitrification reactions in streams and estuaries. The basic theory of the nitrogen cycle is reviewed, several simplified kinetic mathematical models of portions of the cycle are constructed, and application of the simplified models to specific situations is described.

8-2 NITRIFICATION

Nitrogenous matter in waste waters consists of proteins, urea, ammonia, and, in some cases, nitrate. The intermediate decomposition products of the proteins, such as amino acids, amides, and amines, are also present in varying degrees. The proteins are broken down by hydrolysis in a series of steps into a variety of amino acids. Both exocellular and endocellular enzymes are involved in the process. Aeration and alkaline conditions favor the production of the exoenzyme. The amino acids are very soluble in water and exert a strong buffering action, the carboxyl group reacting with the hydrogen ion and the amino group reacting with the hydroxyl. The decomposition of the amino acids, which can occur in a number of different ways, is endocellular. Ammonia is released in this process of deamination, which may be a reductive, oxidative, or hydrolytic reaction, depending on the nature and structure of the amino acids. In any case, the significant end product is ammonia.

Ammonia is also released in the aerobic decomposition of proteins by heterotrophic bacteria. The ammonia, which is highly soluble, combines with the hydrogen ion to form the ammonium ion, thus tending to raise the pH. In the neutral pH zone, all the ammonia is present in this form, and at the higher pH it is evolved as a gas. The heterotrophic decomposition is the typical reaction in the first stage of the biochemical deoxygenation of natural waters. Ammonia is an end product of both this reaction and the reaction associated with the hydrolytic breakdown of proteins. The ammonia present in natural waters is thus a result of either the direct discharge of the material in waste waters or of the decomposition of organic matter in various forms.

The ammonia in turn is oxidized under aerobic conditions to nitrite by bacteria of the genus *Nitrosomonas* as follows:[10,11,12,13]

$$(NH_4) + OH^- + 0.5O_2 \xrightarrow{\text{bacteria}} H^+ + NO_2^- + 2H_2 + 59.4 \text{ kcal} \qquad (8\text{-}1)$$
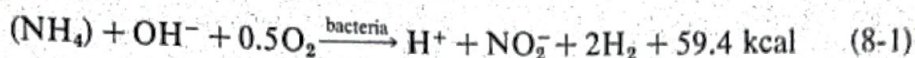
This reaction requires 3.43 g of oxygen utilization for 1 g of nitrogen oxidized to nitrite. The nitrite thus formed is subsequently oxidized to nitrate by bacteria of the genus *Nitrobacter* as follows:[11]

$$NO_2^- + 0.5O_2 \xrightarrow{\text{bacteria}} NO_3^- + 18 \text{ kcal} \qquad (8\text{-}2)$$
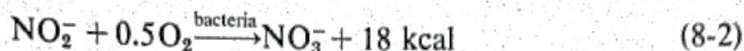
This reaction requires 1.14 g of oxygen utilization for 1 g of nitrite nitrogen oxidized to nitrate. The total oxygen utilization in the entire forward nitrification process is therefore 4.57 g of oxygen per gram of ammonia nitrogen oxidized to nitrate. The *Nitrobacter* bacteria process about three times as much substrate as the *Nitrosomonas* bacteria to derive the same amount of energy. Nitrite is therefore converted quite rapidly to nitrate.

Essential factors for nitrification are oxygen, phosphates, and an alkaline environment to neutralize the resulting acids. Nitrifying bacteria are very susceptible to action of toxic substances (e.g., manganese). These bacteria are obligate autotrophs, which derive their energy from the oxidation of simple inorganic compounds. The energy obtained from these reactions is utilized for the assimilation of carbon from either carbon dioxide or the bicarbonate ion, but not from organic carbon. However, it has been indicated that *Nitrobacter* can be grown heterotrophically on an organic substrate without losing its ability to oxidize nitrite. Acetate was assimilated as cell carbon, the optimum pH range being 8.5 to 9.5. The alkaline environment is required to neutralize the acidic end products. Below pH 6.0, which can occur in a poorly buffered system, inhibition occurs.

The presence of organic matter, particularly amino compounds in excessive concentrations, inhibits growth and respiration of the nitrifying bacteria. These excessive concentrations on the order of thousands of milligrams per liter are seldom encountered in either waste water or natural waters. However, even concentrations of organics on the order of hundreds of milligrams per liter, which may be found in practical cases, appear to retard the nitrification process. At these concentrations the heterotrophic bacteria probably predominate and assimilate the ammonia in their metabolic processes. After the death and lysis of these bacteria, nitrification takes place. The experimental evidence in this regard is not conclusive and, in fact, is somewhat contradictory. While the majority of reported work indicates some degree of inhibiting effects, other reports show minimal or no retardation. At lower concentrations of organic materials, as in natural water bodies, both heterotrophic and autotrophic reactions may occur simultaneously.

Given the appropriate conditions, the concentration of the organisms appears to be the significant factor controlling the rate of nitrification, with the concentration of the reactant having a reduced effect. However, if there is an

ample supply of organisms, the rate appears to be controlled by the concentration of the reactant (see also Sec. 8-4). The number of nitrifiers is, of course, determined by the generation time of organisms, which is on the order of 1 day, by contrast to an order of a few hours for many heterotrophic bacteria.

The common source of the nitrifying organisms is rich soil, where they are usually found in high numbers. In rivers receiving waste waters, nitrifying bacteria are probably present in varying degrees, depending on the nature and the treatment of waste waters. Their number in sewage is low (about 100/ml) but increases through biological treatment to an order of 1,000/ml. A natural habitat is in biological aggregates or on surfaces where the environment appears appropriate for optimum growth and acceleration metabolism. Surfaces such as these are found in trickling filters and activated sludge treatment plants as well as the rocky beds of shallow rivers.

8-3 DENITRIFICATION

Under conditions of low concentration of dissolved oxygen, the bacterial reduction of nitrate can occur. This reaction is to be distinguished from the utilization of nitrate and subsequent reduction by aquatic plants. A large variety of facultative bacteria can reduce nitrate. *E. coli* are cited as a common bacteria capable of reducing nitrate.[11] The reduction of nitrate by bacteria is probably all to NO_2 and then to nitrogen gas, although complete reduction to ammonia may also occur. The primary reactions seem to be:

$$C_6H_{12}O_6 + 12\ NO_3^- \xrightarrow{\text{bacteria}} 12NO_2^- + 6CO_2 + 6H_2O \qquad (8\text{-}3)$$
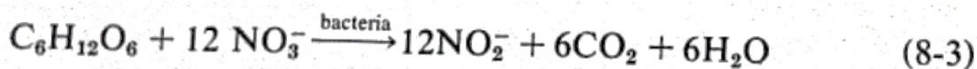
which represents the reduction of nitrate to nitrite and

$$C_6H_{12}O_6 + 8NO_2^- \xrightarrow{\text{bacteria}} 4N_2 + 2CO_2 + 4CO_3^- + 6H_2O \qquad (8\text{-}4)$$
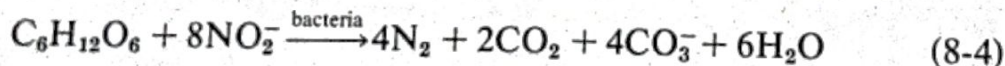
for the reduction of nitrite to nitrogen gas. It should be noted that these reactions serve to provide an oxygen source for microorganisms in the metabolic oxidation of organic compounds in a water body without drawing on the dissolved oxygen resources of the stream.

The dissolved oxygen conditions under which nitrate reduction becomes significant are subject to some differences of opinion resulting from the relatively small amount of work done in this area. Under completely anaerobic conditions, nitrification cannot occur, since the nitrifying bacteria are strictly aerobic. There is some evidence to indicate, however, that nitrate reduction is constant and is greatly accelerated under low (0 to 2 mg/l) dissolved oxygen conditions.

8-4   KINETIC MODELS

8-4.1   Monod Equation and Simplifications

The nitrification process, in which ammonia is converted through nitrite to ni-
trate, is an autotrophic biochemical reaction. The energy for the growth of the
microorganisms is obtained from the oxidation of ammonia or nitrite [see Eqs.
(8-1) and (8-2)]. In reactions of this type the rate is generally assumed to be
proportional to the concentrations of the substrate and of the microorganisms.
The substrate concentration dependency, however, may be modified by
stipulating that the rate of the reaction is independent of the concentration of
substrate at high substrate concentrations and becomes increasingly concentra-
tion-dependent as the concentration decreases. Substrate limiting kinetics
have been used in the analysis of biological waste treatment phenomena.[14,15] A
general review of the literature is given in Ref. 14. The growth equation for
the microorganisms may be written as

$$\frac{dM}{dt} = KM \tag{8-5}$$

where M = the microbial concentration
$\quad\quad K$ = microbial growth coefficient
In unlimited growth, the solution of Eq. (8-5) indicates that the microbial popu-
lation would grow at an exponential rate. If, however, a single substrate (say,
nitrogen) plays an important role in limiting the growth, one must also consider
the utilization of the substrate and consider that the growth coefficient K in Eq.
(8-5) is not a constant but depends on a substrate concentration. Thus, let

$$K = \frac{K_m c}{K_s + c} \tag{8-6}$$

where K_m is the maximum growth rate (one/day), c is the concentration of sub-
strate (milligrams per liter), and K_s (the so-called Michaelis or half-saturation
constant) is the concentration (milligrams per liter) at which the growth rate is
one-half of the saturated rate.
Substitution of Eq. (8-6) into (8-5) gives

$$\frac{dM}{dt} = \frac{K_m M c}{K_s + c} \tag{8-7}$$

This form of kinetic equation was first developed by Michaelis and Menton to
explain enzymatic reactions. It was later applied by Monod[16] to systems in-
volving growth of biological organisms. This equation can be written in terms
of microorganisms only by substituting for the substrate concentration its
equivalence in terms of microorganism; i.e., a unit increase of organisms is
equal to a unit decrease in substrate multiplied by the appropriate stochiome-

tric or yield coefficient. This is simply an expression of the conservation law, in which the total mass M is equal to the sum of the initial organisms present plus the substrate utilized to produce microbes, i. e.,

$$M = M_0 + a(c_0 - c) \qquad (8\text{-}8)$$

where a = stochiometric or yield constant (milligram bacterial mass per milligram substrate)

M_0 = initial bacterial mass

c_0 = initial substrate concentration

Substitution of Eq. (8-8) into (8-7) gives, upon integration,

$$K_m t = \frac{K_s}{M_0 + ac_0} \ln \left[\frac{c_0}{c_0 - 1/a(M - M_0)} \right]$$
$$+ \frac{aK_s + M_0 + ac_0}{M_0 + ac_0} \ln \frac{M}{M_0} \qquad (8\text{-}9)$$

A detailed dimensionless analysis of the behavior of this type of equation is given below in terms of the utilization of the substrate.

Equation (8-7) indicates that, at high concentrations of substrate ($c \gg K_s$), the rate is independent of c, and the rate expression reduces to a first-order reaction in which the growth rate is proportional to the concentration of microorganisms:

$$\frac{dM}{dt} = K_m M \qquad (8\text{-}10)$$

This equation indicates an unlimited exponential growth of organisms. At low concentration of substrate ($K_s \gg c$), the expression reduces to a second-order reaction in which the rate is proportional to the product of the concentration, as in

$$\frac{dM}{dt} = \frac{K_m M c}{K_s} \qquad (8\text{-}11)$$

This equation can also be written entirely in terms of microbial mass by considering the bacterial equivalent of the initial substrate concentration and letting M_T be the sum of the initial organisms and the substrate. Thus,

$$\frac{dM}{dt} = K_2 M (M_T - M) \qquad (8\text{-}12)$$

where $M_T = M_0 + ac_0$

$K_2 = K_m/aK_s$

Equation (8-12) is referred to as an *autocatalytic reaction* in which the rate is increased by the concentration of the end products of the reaction. It is autocatalyzed by the microorganisms which increase as substrate is oxidized.

8-4.2 Dimensionless Analysis of Growth Equations

The interacting differential equations for the substrate c and the microbial mass are given by

$$\frac{dc}{dt} = \frac{-K_m M'c}{K_s + c} \tag{8-13}$$

and

$$\frac{dM'}{dt} = \frac{K_m M'c}{K_s + c} \tag{8-14}$$

where all quantities are now expressed in terms of their equivalent substrate concentrations. Thus, $M' = M/a$, the microbial mass in substrate equivalents. Equation (8-14) is the same as Eq. (8-11), except in terms of the substrate concentration. In the interests of mathematical simplicity, the microbial loss due to endogenous respiration has been neglected in these equations. The solution to Eqs. (8-13) and (8-14) is

$$K_m t = \frac{d_s}{1 + d_M} \ln \left(\frac{1 + d_M - c/c_0}{d_M c/c_0} \right) + \ln \left(\frac{1 + d_M - c/c_0}{d_M} \right) \tag{8-15}$$

where $d_s = K_s/c_0$ a dimensionless "Michaelis number"

$d_M = M_0'/c_0$ a dimensionless microbial-substrate concentration ratio

Equation (8-15) is simply a dimensionless reexpression of Eq. (8-9). One can examine several special cases of Eqs. (8-13) and (8-14) which will provide some understanding of the behavior of these equations.

Case I: Small Michaelis constant, small initial microbial mass. The limiting value for this case is $K_s = 0$, which results in the exponential growth of microbes as given from the solution to Eq. (8-10). The substrate utilization is then

$$\frac{c}{c_0} = 1 - d_M \exp (K_M t) \tag{8-16}$$

In Eq. (8-15), the second term dominates for this case.

Case II: Large Michaelis constant, small initial microbial mass. For this case, d_s is considered large, and one obtains the logistic growth equations [Eq. (8-12)]. In terms of substrate utilization, the solution is

$$\frac{c}{c_0} = \frac{(1 + d_M) \exp [-(K_M t)(1 + d_M)/d_s]}{d_M + \exp [-K_M t (1 + d_M)/d_s]} \tag{8-17}$$

For small d_M (initial microbial mass relative to initial substrate concentration),

$$\frac{c}{c_0} = \frac{\exp (-K_M t/d_s)}{d_M + \exp (-K_M t/d_s)} = \frac{1}{1 + d_M \exp (1 - K_M t/d_s)} \tag{8-18}$$

Case III: Large initial microbial mass, large Michaelis constant. In this case, d_M is considered large; i.e., there is a large microbial mass relative to c_0 at $t = 0$. Under this condition, M' is relatively constant since the additional

microbes produced by metabolism of c_0 is small and $M' \simeq M_0'$. The appropriate dimensionless differential equation is then

$$\frac{d(c/c_0)}{d(K_M t)} = \frac{-d_M 3(c/c_0)}{d_s + c/c_0} \tag{8-19}$$

whose solution is

$$d_s \log \frac{c}{c_0} + \left(\frac{c}{c_0 - 1}\right) = K_M d_M t \tag{8-20}$$

therefore, for large d_s, i.e., small concentration of substrate relative to the Michaelis constant, the substrate decays exponentially as

$$c = c_0 \exp\left(-K_M \frac{d_M}{d_s} t\right) \tag{8-21}$$

Case IV: *Large initial microbial mass, small Michaelis constant.* On the other hand, for small d_s, i.e., $K_s \ll c_0 \ll M_0'$, the solution [Eq. (8-17)] is linear:

$$c = c_0 (1 - K_M d_M t) \tag{8-22}$$

until $\log (c/c_0) d_s \sim (c/c_0 - 1)$, where the total solution [Eq. (8-17)] indicates an exponential "tail."

Intermediate solutions can be thought of as a "linear combination" of two separate models: (1) case I, an exponential growth of microorganisms, as given by Eq. (8-10), where nutrients are not limiting [$K_s = 0$ in Eq. (8-7)], and (2) case II, logistic growth of microorganisms, as given by Eq. (8-11), where $K_s \gg c$. In terms of the substrate utilization and utilizing the dimensionless notation, these two limits can be summarized as shown in Fig. 8-2. As indicated therein for various $d_M = M_0'/c_0$, the substrate utilization varies from a linear decrease to exponential to an autocatalytic form. Under certain conditions, therefore, an appropriate exponential decrease (first-order kinetics) may be assumed in mathematical modeling under full recognition that other forms may prevail, depending on the "mix" of microbial population, the nutrient concentration, and the Michaelis constant. In the logistic growth region, for $0.1 < d_M < 1.0$, Fig. 8-2 shows that, for complex river or estuarine systems, it would be very difficult to detect departures from exponential substrate decay. Some data are available on laboratory studies to evaluate the range of M_0'. However, actual field estimates of microbial mass and substrate concentrations are not available.

As a result, laboratory studies generally use "large" initial substrate concentrations (d_s and d_M small) leading to specific nonexponential substrate utilization. Stratton and McCarty[12] obtained values for ammonia oxidation of M_0 at 20°C of 0.0033 mg bacterial mass/1. At a yield coefficient a of 0.28 mg cells/mg substrate, this is equivalent to M_0' of about 0.01 mg/1 NH_3-N. For
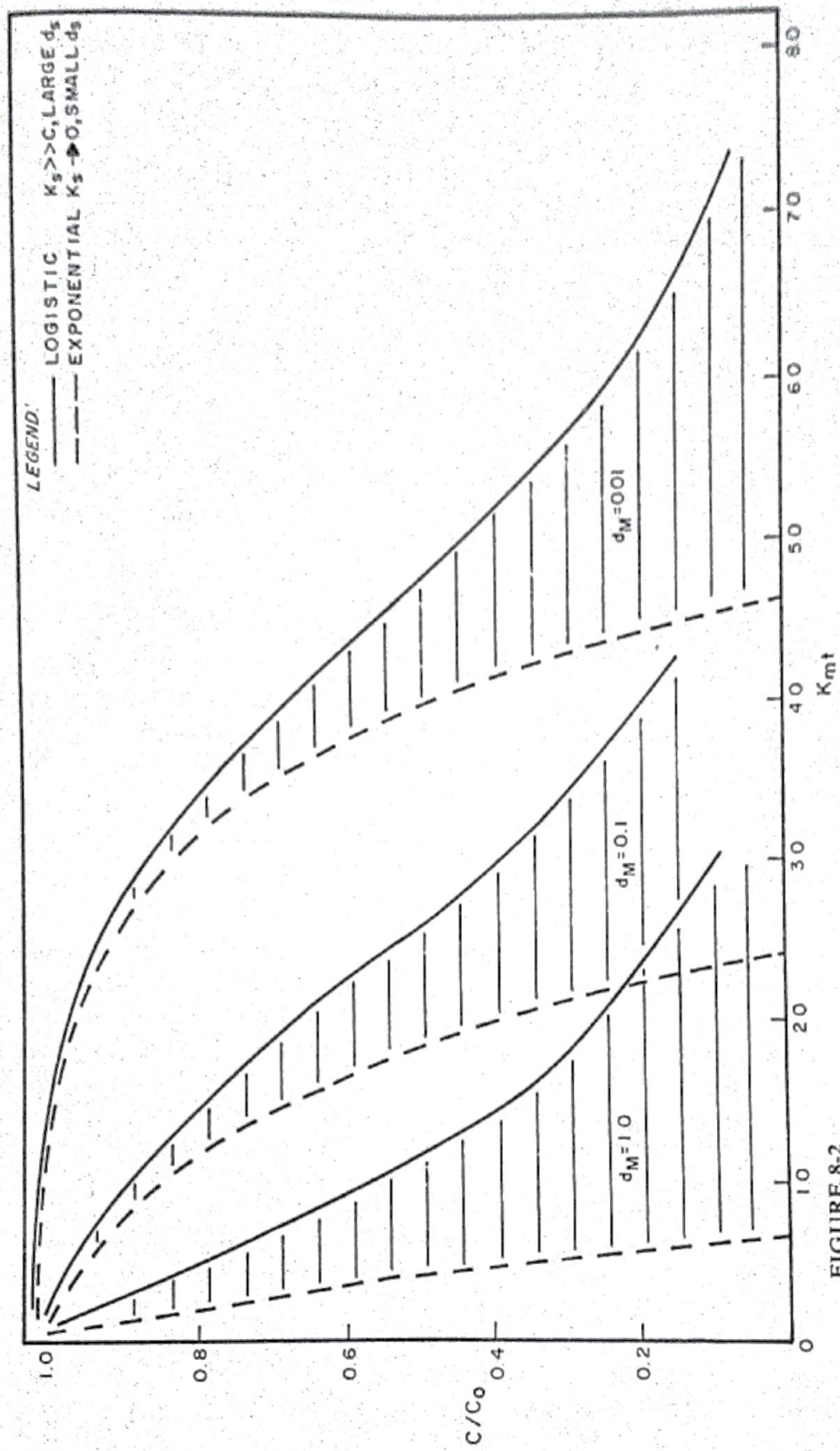
FIGURE 8-2
Logistic and exponential growth of microorganisms and accompanying nutrient
utilization.

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this case however, $K_s = 2.6$ mg/1 and $c_0 = 5.5$ mg/1 or $d_s = 0.47$. Stratton thus obtained ammonia curves similar to those shown in Fig. 8-2 for low values of d_M intermediate between exponential and logistic microbial growth. This then represents an initially low nitrifying population and a "high" initial substrate concentration. At 20°C, for $K_s \simeq 1$ to 3.0 mg/1 (Knowles et al.[17]) and normally low initial ammonia concentrations in natural waters (0.5 mg/l), d_s for ammonia could be "large." If the ratio of initial cell mass M_0' to initial concentrations is from 0.1 to 1.0, one should expect to see appropriate exponential behavior in the substrate. Therefore, for "dilute" systems, where substrate concentrations are "low," and for "well-seeded" systems, where initial nitrifying populations are high relative to initial substrate concentrations, first-order decay of substrate may be approximately justified. The actual application of these conditions must, of course, be made with care, but as a first approximation, first-order kinetics reactions for the nitrification phenomenon are a meaningful step and can aid in understanding the behavior of observed nitrogen forms in natural water systems.

8-5 FIRST-ORDER STEADY-STATE MATHEMATICAL MODEL OF STREAMS AND ESTUARIES

With an assumption of first-order kinetic reactions and steady-state conditions, several levels of mathematical models can be constructed, each of which is useful in predictions of long-term effects of nitrification on water quality. The three levels of modeling are

1. BOD equivalent models
2. Sequential reaction models
3. General feedback models

Each of the levels increases somewhat in the complexity of the equations and provides greater detail in understanding the phenomenon. The major reason for even considering several problem levels of first-order kinetic models is that all problem contexts do not necessarily require complex models for their solution. Much can be learned from the first-order models, although it is important to stress again that the actual kinetic mechanisms are more complex than those that are considered herein. If it is obvious that nonlinear kinetics apply, then one should use the models presented below only as a gross approximation, if at all. For some problem contexts, the first-order kinetics assumption may be justified on the basis of the previous analysis (Sec. 8-4). In any case, first-order kinetics simplifies the structure of the models (linearity is presumed) and provides for rapid numerical solutions.

In the following sections, the BOD equivalent models are discussed, first in the context of inputs into classical DO equations. The sequential nitrification models for streams and estuaries are discussed next, followed by the general feedback model for multidimensional systems.

8-5.1 BOD Equivalent Models

This approach is particularly appropriate when the major portion of the nitrogenous demand is present as ammonia. Either a direct measurement of the ammonia and its oxygen equivalence or the second-stage BOD measurement may be used. Either is then inputted as a sink of dissolved oxygen in a DO model. This approach becomes more approximate as the concentration of organic nitrogen becomes more significant. The organic nitrogen breaks down by hydrolysis to yield, among other products, ammonia. The oxidation of ammonia and the associate use of dissolved oxygen may therefore be delayed in accordance with the hydrolytic rate of reaction. This effect, if appreciable, is taken into account in the oxygen model by a reduction in the reaction coefficient of the nitrogenous BOD or by empirically introducing a lag in the initiation of nitrification. In spite of its simplicity, this model is quite adequate in a number of practical cases.

As indicated above, the nitrogenous oxygen demand, NBOD, is given approximately by

$$NBOD = 4.57(\text{org-N} + NH_3 - N)$$

This demand can be considered as an oxygen sink in the pair of equations describing the distribution of NBOD and DO deficit. For one-dimensional steady-state systems with constant coefficients, these equations are

$$O = E\frac{d^2L_N}{dx^2} - U\frac{dL_N}{dx} - K_NL_N + W_N(x) \tag{8-23}$$

$$O = E\frac{d^2D_N}{dx^2} - U\frac{dD_N}{dx} - K_aD_N + KL \tag{8-24}$$

where E = dispersion coefficient (usually included only for estuaries)
U = river velocity or net downstream velocity for estuaries
x = distance
L_N = nitrogenous BOD
D_N = DO deficit (due to nitrogenous BOD)
K_N = rate of oxidation of NBOD
K_a = reaeration coefficient
W_N = waste discharges of NBOD

Equations (8-23) and (8-24) can be recognized as the same set of equations that is used to describe the DO deficit due to the discharge of carbonaceous BOD (CBOD). For the constant coefficient case, the solutions to Eqs. (8-23) and (8-24) are

$$L_N = L_{N0}\exp(j_NX) \tag{8-25a}$$

$$D_N = \frac{K_NL_{N0}}{K_a - K_N}[\exp(j_NX) - \exp(j_aX)] \tag{8-25b}$$

where, for rivers where dispersive effects are small,

$$J_N = \frac{K_N}{U}$$

$$J_a = \frac{K_a}{U} \qquad (8\text{-}26)$$

$$L_{N0} = \frac{W_N}{Q}$$

and for estuaries where the tidal dispersion effect is important,

$$J_N = \frac{U}{2E}\left(1 \pm \sqrt{1 + \frac{4K_N E}{U^2}}\right)$$

$$J_a = \frac{U}{2E}\left(1 \pm \sqrt{1 + \frac{4K_a E}{U^2}}\right) \qquad (8\text{-}27)$$

$$L_{N0} = \frac{W_N}{Q\sqrt{1 + \frac{4KE}{U^2}}}$$

where for J_N and J_a the positive sign of the radical is associated with the negative x direction and the negative sign is associated with the positive x direction. The DO deficit profile due to the nitrogenous waste discharge is thus given by Eq. (8-25). The DO deficit due to the carbonaceous BOD must be added to this profile to determine the total DO deficit due to waste discharges.

The disadvantage of this simple model is that usually some judgment must be exercised in determining the spatial distribution of the reaction rate K_N. In some instances, the field data may indicate that for various reasons (organic nitrogen hydrolysis, insufficient nitrifiers) an apparent lag exists in the exertion of the NBOD. The judgmental incorporation of this effect becomes particularly significant when projections are made of expected water quality under different treatment schemes.

However, it is still somewhat surprising that even this simple model is often not considered in DO balance studies. This is especially true in the numerous analyses conducted to estimate the effects of different levels of waste treatment, where the nitrogen discharges are largely unaffected by standard high-rate biological treatment.

8-5.2 Sequential Reaction Models

This approach answers some of the disadvantages described above and especially applies when organic as well as ammonia nitrogen are present as inputs. Furthermore, when it is desirable to trace the individual components of the downstream nitrification process (organic, ammonia, nitrite, and nitrate), this approach is useful. The lag effect is incorporated into the kinetic expression by the first step of a sequence of the coupled reactions. In contrast to the

previous simplified approach, modeling with consecutive reactions is slightly more complicated analytically, requires more data, time, and experience, but provides greater understanding and increased confidence in prediction.

The sequential reaction models follow each of the nitrogen components individually. The ammonia and nitrite outputs are then converted to oxygen demands and are used as inputs into the DO deficit equation. The general constant-coefficient equations are

$$O = E \frac{d^2N_1}{dx^2} - U \frac{dN_1}{dx} - K_{11}N_1 + W_1(x) \tag{8-28}$$

$$O = E \frac{d^2N_2}{dx^2} - U \frac{dN_2}{dx} - K_{22}N_2 + K_{12}N_1 + W_2(x) \tag{8-29}$$

$$O = E \frac{d^2N_3}{dx^2} - U \frac{dN_3}{dx} - K_{33}N_3 + K_{23}N_2 + W_3(x) \tag{8-30}$$

$$O = E \frac{d^2N_4}{dx^2} - U \frac{dN_4}{dx} - K_{44}N_4 + K_{34}N_3 + W_4(x) \tag{8-31}$$

where N_1, N_2, N_3, and N_4 are organic, ammonia, nitrite, and nitrate nitrogen, respectively, K_{ii} represents the first-order decay of substance i, K_{ij} is the forward reaction coefficient, and W_i is the discharge of substance i.

Equations (8-28) to (8-31) permit the determination of the individual nitrogen components and therefore represent a more realistic description of the nitrification process than shown in Eqs. (8-23) and (8-24). The forcing functions for the DO deficit are 3.34 $K_{23}N_2$ and 1.14 $K_{34}N_3$, the first representing ammonia oxidation and the second nitrite oxidation. The entire scheme is sketched in block-diagram form in Fig. 8-3. The equation for DO deficit due to the oxidation of nitrogen forms is

$$O = E \frac{d^2D_N}{dx^2} - U \frac{dD_N}{dx} - K_a D_N + 3.43 K_{23}N_2(x) + 1.14 K_{34}N_3(x) \tag{8-32}$$

where $N_2(x)$ and $N_3(x)$ are given from solutions of Eqs. (8-28) to (8-31).

Particular utilization of Eqs. (8-28) to (8-31) again depends on the water system—either a river system where $E = 0$ or an estuarine system where tidal dispersion effects embodied in the dispersion coefficient may be significant.

The nature of the solutions to Eqs. (8-28) to (8-31) can be determined by considering the river case, where advective forces dominate and dispersion can be considered zero. Further, one can assume that $K_{ii} = K_{i,i+1} \equiv K_i$, i.e., that all material is conserved in each system and none of the forms of nitrogen are lost, for example, to the bottom sediments ($K_{ii} > K_{i,i+1}$). The rate equations for the advective stream are then

$$\frac{dN_1}{dt^*} = - K_1N_1 + W_1(x) \tag{8-33a}$$

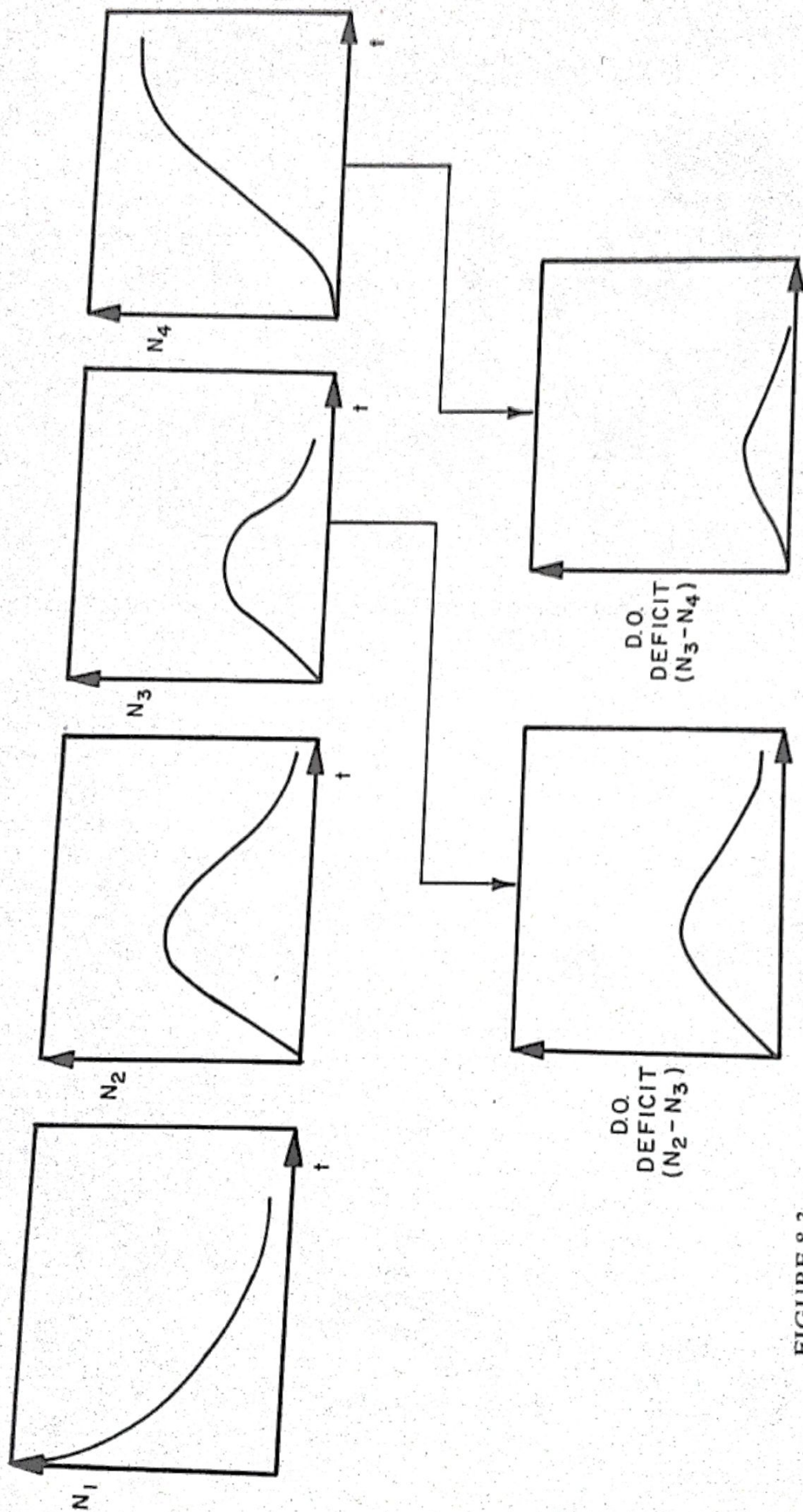$$\frac{dN_2}{dt^*} = K_1N_1 - K_2N_2 + W_2(x) \tag{8-33b}$$

FIGURE 8-3
Sequential reactions in nitrification—first-order kinetics—stream system.

$$\frac{dN_3}{dt^*} = K_2N_2 - K_3N_3 + W_2(x) \tag{8-33c}$$

$$\frac{dN_4}{dt^*} = K_3N_3 - K_4N_4 + W_4(x) \tag{8-34d}$$

where $t^* = x/u$, the time of travel.

Equations (8-33) represent a series of first-order coupled equations. The solution of Eq. (8-33a) is

$$N_1 = N_{01} \exp(-K_1 t^*)$$

where N_{01} is the initial value of N_1 at $x = 0$ given by mass balance incorporating $W_1(x)$.

Substitution of this solution into Eq. (8-33b) and integration gives the solution for ammonia, N_2, as

$$N_2 = \frac{K_1 N_{01}}{K_2 - K_1}[\exp(-K_1 t^*) - \exp(-K_2 t^*)] + N_{02}\exp(-K_2 t^*) \tag{8-34}$$

Sequential substitution and integration gives the concentrations of nitrite and nitrate. For example, for nitrite,

$$N_3 = \frac{K_1 K_2}{K_2 - K_1}\left[\frac{\exp(-K_1 t^*) - \exp(-K_3 t^*)}{K_3 - K_1} - \frac{\exp(-K_2 t^*) - \exp(-K_3 t^*)N_{01}}{K_3 - K_2}\right]$$
$$+ \frac{K_2}{K_3 - K_2}\left[\exp(-K_2 t^*) - \exp(-K_3 t^*)N_{02} + K_3 N_{03}\exp(-K_3 t^*)\right] \tag{8-35}$$

Each of the preceding inputs is reflected in this equation. In general, the total amount of end product formed by virtue of the initial sources, $C_{01} \rightarrow C_{0n}$ (for n reaction steps) is

$$C_{n0} = \sum_{i=1}^{n} C_{0i}\exp(-K_i t^*)$$

and due to the intermediate steps is

$$C_{ni} = \sum_{i=1}^{n} \frac{K_{i-1}C_{0,i-1}}{K_i - K_{i-1}}[\exp(-K_{i-1}t^*) - \exp(-K_i t^*)]$$

The sequential nature of these solutions is shown in Fig. 8-3, where the last nitrogen form, the nitrate nitrogen, is assumed conservative, i.e., $K_4 = 0$.

For estuarine situations, the solutions essentially follow the same form, except that a series of unknown coefficients is introduced by virtue of mass balances that are required. The number of coefficients is equal to the number of equations that can be written down so that explicit numerical determination of the coefficients is possible. For example, the solution to Eq. (8-28) for point-source loads is

$$N_1 = B_1\exp(S_1 x) + C_1\exp(V_1 x) + YBN \tag{8-36}$$

where $S_1 = \dfrac{U}{2E}(1 + \sqrt{1 + 4K_1 E/U^2})$

$V_1 = \dfrac{U}{2E}(1 - \sqrt{1 + 4K_{11}E/U^2})$

B_1 and C_1 = constants to be evaluated from consideration of boundary conditions

$\quad YBN$ = particular integral of sources and sinks of N_1

An equation similar to (8-36) can also be written for N_2, with the input from N_1 appearing in the particular integral. Thus,

$$N_2 = B_2 \exp(S_2 x) + C_2 \exp(V_2 x)$$

$$+ \frac{K_{12}}{K_{22} - K_{11}}[B_1 \exp(S_1 x) + C_1 \exp(V_1 x)] \quad (8\text{-}37)$$

Equation (8-37) can be compared to (8-34). This procedure is repeated for each nitrogen form resulting in four solution equations [see also Eq. (8-35)] in eight coefficients. Application of boundary conditions, mass balance, and concentration equality at each section provides the necessary equations to evaluate these coefficients. Details are given in Ref. 18, and the application of this model to the Delaware Estuary is discussed below.

Another approach that can be used to model sequential reactions is to replace the spatial derivatives with finite approximations. This results in a series of algebraic equations which can be solved simultaneously to obtain the spatial distribution of each nitrogen form. A generalization of this approach is explored in detail in the next section.

In summary, models of sequential reactions are readily structured utilizing the steady-state and first-order kinetic assumptions. For the nitrification effect, these models "track" the spatial distribution of each of a series of forms, allowing direct computation of the DO deficit due to nitrogen oxidation. For streams, the solutions can be obtained directly, while for estuaries some type of computer solution is often required.

8-5.3 Feedback Models

This approach incorporates feedback loops between any of the respective systems. In principle, this third model can include many of the features of the complete nitrogen cycle if one accepts the assumptions of linearity and first-order kinetics. Typical examples of feedback systems include denitrification and algal utilization. The denitrification phenomenon may involve two feedback loops: NO_3 to NO_2 (with attendant evolution of N_2 gas) and NO_2 to NH_3. Both of these feedback reactions occur under conditions of "low" dissolved oxygen. Actually, a more complete model of the system would include a nonlinear interaction between DO and the feedback reaction rates.

The utilization of ammonia and nitrate by phytoplankton also introduces

feedback loops. Organic nitrogen is formed as a part of the complex living matter in algae cells, which, upon death, release the organic nitrogen in dissolved form, thereby completing the cycle. This is an obvious oversimplification of the actual mechanism, which is dynamic and includes nonlinear growth-limiting terms. However, the problem here is to introduce the feedback aspect into the steady-state sequential models discussed in the previous section.

The general feedback model makes use of a finite difference approximation to Eqs. (8-28) to (8-31) and incorporates the first-order feedback reaction coefficients.

The differential equations which incorporate feedback are

$$O = E\frac{d^2N_1}{dx^2} - U\frac{dN_1}{dx} - K_{11}N_1 + K_{21}N_2 + \cdots + K_{41}N_4 + W_1(x)$$

$$O = E\frac{d^2N^2}{dx^2} - U\frac{dN_2}{dx} + K_{12}N_1 - K_{22}N_2 + K_{32}N_3 + K_{42}N_4 + W_2(x) \quad (8\text{-}38)$$

$$O = E\frac{d^2N_4}{dx^2} - U\frac{dN_4}{dx} - K_{44}N_4 + K_{14}N_1 + \cdots + K_{34}N_4 + W_4(x)$$

Equations (8-38) indicate all possible feedforward reactions K_{ij} ($j > i$) and all possible feedback reactions ($i > j$). The separate inclusion of K_{ii} allows for possible loss of material from the system due, for example, to bottom deposition. In general, to prevent creation of nitrogen it is true that

$$K_{ii} \geq \sum_j K_{ij} \quad (i \neq j)$$

If a finite difference approximation is made to these equations (or equivalently, a mass balance is constructed around a finite section), a series of n algebraic equations results, where n is the number of finite sections.[19] It should be noted that this approach is not restricted to one-dimensional systems.

A finite difference approximation to the first equation of Eqs. (8-38) is given for spatial segment k as

$$O = \sum_j [-Q_{kj}(\alpha_{kj}N_{1,k} + \beta_{kj}N_{1,j}) + E'_{kj}(N_{1,j} - N_{1,k})]$$

$$- V_k K_{11,k}N_{1,k} + V_k K_{21,k}N_{2,k} + \cdots$$

$$+ V_k K_{41,k}N_{4,k} + W_{1,k} \quad (k = 1, 2, \ldots, n) \quad (8\text{-}39)$$

where Q_{kj} is the net flow from section k to j (positive outward), V_k is the volume of the kth segment, α_{kj} is a finite difference weight $= \max(\frac{1}{2}, 1 - E'/Q)$ chosen for solution stability, $\beta_{kj} = 1 - \alpha kj$, and E_{kj} is a bulk tidal dispersion coefficient given by

$$E'_{kj} = \frac{E_{kj}A_{kj}}{L_k + L_j}$$

where A_{kj} is the interfacial cross-sectional area, L_k and L_j are segment lengths of segments k and j, and $W_{1,k}$ is the direct discharge of waste material N_1. The notation $N_{1,k}$ indicates the spatial distribution in all k segments of the water body of the first nitrogen form. If, in Eq. (8-34), all terms involving the dependent variables N_1 are grouped on the left-hand side and the input forcing function $W_{1,k}$ and other nitrogen forms N_i on the right-hand side, one obtains

$$a_{kk}N_{1,k} + \sum_j a_{kj}N_{1,j} = W_{1,k} + V_k K_{21,k}N_{2,k} + \cdots + V_k K_{41,k}N_{4,k} \quad (8\text{-}40)$$

where

$$a_{kk} = \sum_j (Q_{kj}\alpha_{kj} + E'_{kj}) + V_k K_{11,k} \quad (8\text{-}41a)$$

$$a_{kj} = Q_{kj}\beta_{kj} - E'_{kj} \quad (8\text{-}41b)$$

A total of n equations similar to Eq. (8-40) can be written for each of the spatial segments. The system of equations is then

$$a_{11}N_{1,1} + a_{12}N_{1,2} + \cdots + a_{1n}N_{1,n} = W_{1,1} + V_1 K_{21,1}N_{2,1} + \cdots + V_1 K_{41,1}N_{4,1}$$

$$a_{21}N_{1,1} + a_{22}N_{1,2} + \cdots + a_{2n}N_{1,n} = W_{1,2} + V_2 K_{21,2}N_{2,2} + \cdots + V_2 K_{41}N_{4,2}$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$a_{n1}N_1 + a_{n2}N_{1,2} + \cdots + a_{nn}N_{1,n} = W_{1,n} + V_n K_{21,n}N_{2,n} + \cdots + V_n K_{41,n}N_{4,n}$$

In matrix form, Eqs. (8-41) are

$$[A_1](N_1) = (W_1) + [VK_{21}](N_2) + [VK_{31}](N_3) + [VK_{41}](N_4) \quad (8\text{-}42)$$

where the subscripts refer to the nitrogen forms and $[VK_{ij}]$ is a diagonal matrix of the product of volumes and reaction rates. The dimensionality of the matrices and vectors represents the spatial distribution of the nitrogen species. Thus, $[A]$ is an $n \times n$ matrix and (N_k) are $n \times 1$ vectors.

The entire procedure used to obtain Eq. (8-42) for the first nitrogen form is now repeated for the second through fourth forms. The four matrix equations are then given by

$$[A_1](N_1) = (W_1) + [VK_{21}](N_2) + [VK_{31}](N_3) + [VK_{41}](N_4)$$
$$[A_2](N_2) = (W_2) + [VK_{12}](N_1) + [VK_{32}](N_3) + [VK_{42}](N_4) \quad (8\text{-}43)$$
$$[A_3](N_3) = (W_3) + [VK_{13}](N_1) + [VK_{23}](N_2) + [VK_{43}](N_4)$$
$$[A_4](N_4) = (W_4) + [VK_{14}](N_1) + [VK_{24}](N_2) + [VK_{34}](N_3)$$

It should be recalled that in Eqs. (8-43), the $[A_i]$ matrices differ only in the reaction coefficient K_{ii} on the main diagonal [see Eq. (8-41a)]. There are $4n$ algebraic equations in Eqs. (8-42) which can be solved by a variety of block decomposition and relaxation techniques. Some additional insight can be obtained by continuing the matrix analysis. The set of matrix equations (8-43)

can be written as

$$
\begin{bmatrix}
[A_1] & -[VK_{21}] & -[VK_{31}] & -[VK_{41}] \\
-[VK_{12}] & [A_2] & -[VK_{32}] & -[VK_{42}] \\
-[VK_{13}] & -[VK_{23}] & [A_3] & -[VK_{43}] \\
-[VK_{14}] & -[VK_{24}] & -[VK_{34}] & [A_4]
\end{bmatrix}
\begin{pmatrix}
(N_1) \\
(N_2) \\
(N_3) \\
(N_4)
\end{pmatrix}
=
\begin{pmatrix}
(W_1) \\
(W_2) \\
(W_3) \\
(W_4)
\end{pmatrix}
\tag{8-44}
$$

or
$$
[\bar{A}] (\bar{N}) = (\bar{W}) \tag{8-45}
$$

where $[\bar{A}]$ is a $4n \times 4n$ matrix and $(\bar{N})$ and $(\bar{W})$ are $4n \times 1$ vectors. Of course, in Eqs. (8-44) not all feedback or feedforward loops need be included. For a given sequence of loops, the solution for the four variables in all spatial segments is formally given by

$$
(\bar{N}) = [\bar{A}]^{-1} (\bar{W}) \tag{8-46}
$$

The DO deficit due to these reactions is now readily computed. If (N_2) represents ammonia and (N_3) nitrite, then a similar differencing procedure yields for the DO deficit

$$
[B] (D)_N = 3.43 [VK_{23}] (N_2) + 1.14 [VK_{34}] (N_3) \tag{8-47}
$$

where $[B]$ is an $n \times n$ matrix identical to the form of the $[A_1]$ matrices, except that the reaeration rate K_a appears on the main diagonal instead of K_{ii}, and $(D)_N$ represents the spatial distribution vector of DO deficit due to the nitrification effect. Note that, once Eqs. (8-43) have been programmed, Eq. (8-47) is a special case of that set of equations and does not require a separate computer program.

A general multidimensional, first-order kinetic, steady-state water-quality problem with any number of variables and system configuration can thus be structured by solving an MN system of equations [(Eqs. (8-44))], where M is the number of variabled forms (for nitrogen, $M = 4$).

For one-dimensional estuaries, the form of the matrices $[A_i]$ is tridiagonal, which simplifies the computations. If no feedback loops are incorporated, Eqs. (8-44) reduce to the sequential reaction models discussed in the previous section and $[\bar{A}]$ becomes upper triangular. In any case, multidimensional systems with interacting (first-order) reactions can be readily and quickly analyzed by simply solving a set of linear algebraic equations. This of course bypasses the entire issue of how one determines the K_{ij} coefficients. This is discussed in the next section.

8-6 APPLICATION OF FIRST-ORDER MODELS

8-6.1 Delaware Estuary

This estuary extends for about 86 miles from Trenton, New Jersey, to Delaware Bay. The river flows past the metropolitan Philadelphia area and enters Delaware Bay about 50 miles from the Atlantic Ocean. The estuary receives

large amounts of carbonaceous and nitrogenous wastes from municipalities and industries and is characteristic of a system where bacterial nitrification leading to oxygen depletion appears to be predominant.[18,20] The municipal and industrial nitrogenous components are indicated in Table 8-1.

A total direct load of 109,500 lb of oxidizable nitrogen per day is discharged from the municipal and industrial waste sources.

In order to incorporate the effect of local drainage along the length of the estuary, a runoff load equivalent to about 110 lb of organic nitrogen per day per mile was inputted, together with an equal amount of ammonia nitrogen.

A continuous solution model was used to represent the organic, ammonia, nitrite, and nitrate forms. Only sequential bacterial nitrification was included specifically in the model. Algal and denitrification effects were included qualitatively. The continuous solution model [see Eqs. (8-36) to (8-37)] was applied to seven reaches of the estuary, each of which included its representative geometry (area, depth) and sequential reaction coefficients.[18] This type of model, in contrast to the finite difference approximation models, results in continuous solutions. Thus, although the first segment in the Delaware Estuary nitrogen model under discussion here is 30 miles long, a continuous solution (for constant spatial parameters) is obtained throughout this length. The cross-sectional area changes in the estuary were therefore approximated by the seven segments. Major point discharges were grouped according to this segment breakdown. This is a simplification introduced to avoid numerous segment junctions at each discharge location.

The verification procedure consisted of comparing calculated profiles from the four-system model to a set of observed data representative of steady-state summer conditions. The reaction rates obtained for each of the nitrogen components were then used in the examination and verification of other profiles under different flow and temperature conditions. A consistent set of first-order reaction coefficients was therefore obtained which provides a reasonable representation of the observed phenomena.

Figure 8-4 shows the results of the first verification analysis of data collected by the Delaware Water Pollution Commission during July–August

Table 8-1   ESTIMATED MUNICIPAL AND INDUSTRIAL NITROGEN DISCHARGES TO DELAWARE ESTUARY[18] (pounds/day)

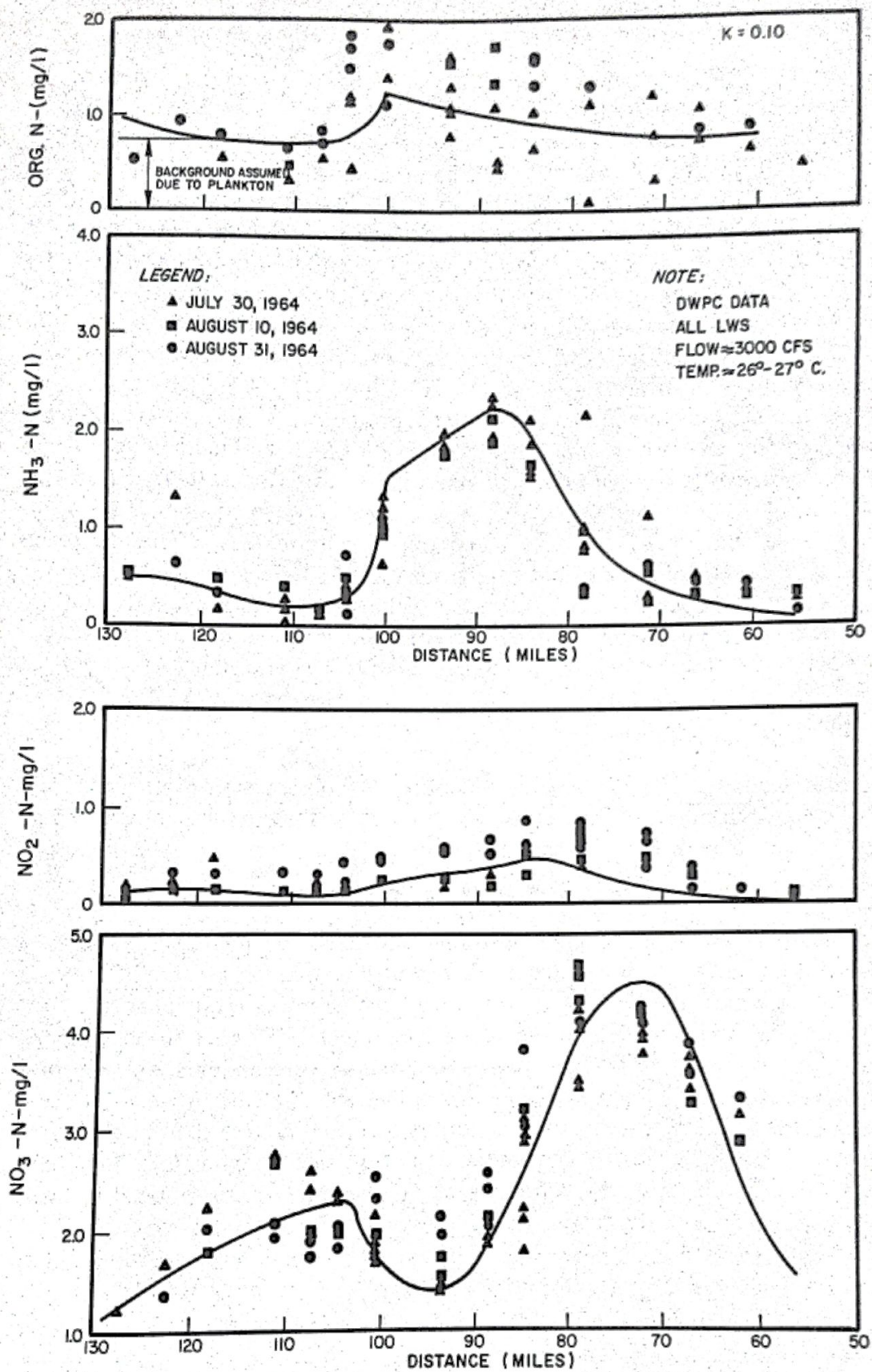|	Organic nitrogen	Ammonia nitrogen	Nitrate nitrogen
Municipal	28,500	48,500	2,000
Industrial	—	32,500	30,500
	28,500	81,000	32,500
Delaware River at Trenton (3,000 cfs)	9,000	1,000	16,000
Total	37,500	82,000	48,500

FIGURE 8-4
Observed versus computed (solid line) nitrogen profile, August 1964.[18]

1964. The reaction coefficients shown for each of the species do not constitute a unique set of rate coefficients but represent a trial-and-error fit of the observed data. The coefficients are consistent, however, with other verification analyses. This is explored further below.

Several other points should be noted in this verification analysis. The direct discharge of organic nitrogen waste loads does not alone account for the total of about 1 mg/l that was observed. It was therefore hypothesized that 0.75 mg/l of organic nitrogen was due to the presence of plankton and does not enter into subsequent nitrification reactions. This is equivalent to about 75 μg/l to 150 μg/l which is within the range of observed chlorophyll measurements for the Delaware Estuary.

It can also be noted that the ammonia profile was verified by employing a reduced reaction rate from mile 100 to mile 85. This was justified because of the low dissolved oxygen (<2 mg/l and minimums of about 0.7 mg/l) in this reach.

The nitrate analysis indicates two areas of nitrate decay. The first reach from mile 100 to 90 is attributed to denitrification. Because feedback loops were not used in this investigation, it was not possible to recycle this nitrate reduction into the system. Nitrate decay at the lower end of the estuary was assumed to be due to increased phytoplankton utilization of nitrate.

8-6.2 Temperature Effects

Experimental information on the influence of temperature on nitrification is meager. Work on the Thames estuary[21] indicated for the temperature dependence of the oxidation of ammonia,

$$K_T = K_{20}\theta^{T-20}$$

with $\theta = 1.017$. Laboratory work, however, indicated $\theta = 1.10$. Others[12,22] have estimated θ at about 1.08, while for nitrite oxidation a value of 1.06 has been determined.[12] Values of $\theta = a$ have been adopted in this analysis.

Data were available for the period November 1967 when water temperatures were 7 to 10°C and river flows at Trenton were about 8,900 cfs; 1964 loads were used. Figure 8-5 summarizes the results of the application of the model to these lower temperature data. A reaction rate of 0.025 (at temperature $= 7.5$°C) was used for the conversion of organic nitrogen, 0.01 for ammonia, 0.05 for nitrite, and 0.0 for nitrate. At these low rates, almost all forms behave as conservative variables. It was not necessary in this case to make the assumption that plankton had synthesized nitrogen into living tissue. At the low estuary temperatures, most plankton activity would be minimal. The ammonia plot in Fig. 8-5 distinctly shows the effect of reduced nitrification. This can be especially seen by comparing the November 1967 data (Fig. 8-5) to the August 1964 data (Fig. 8-4) The reduced nitrification effect at low temperatures is also evident in the nitrite and nitrate profiles. This effect will also
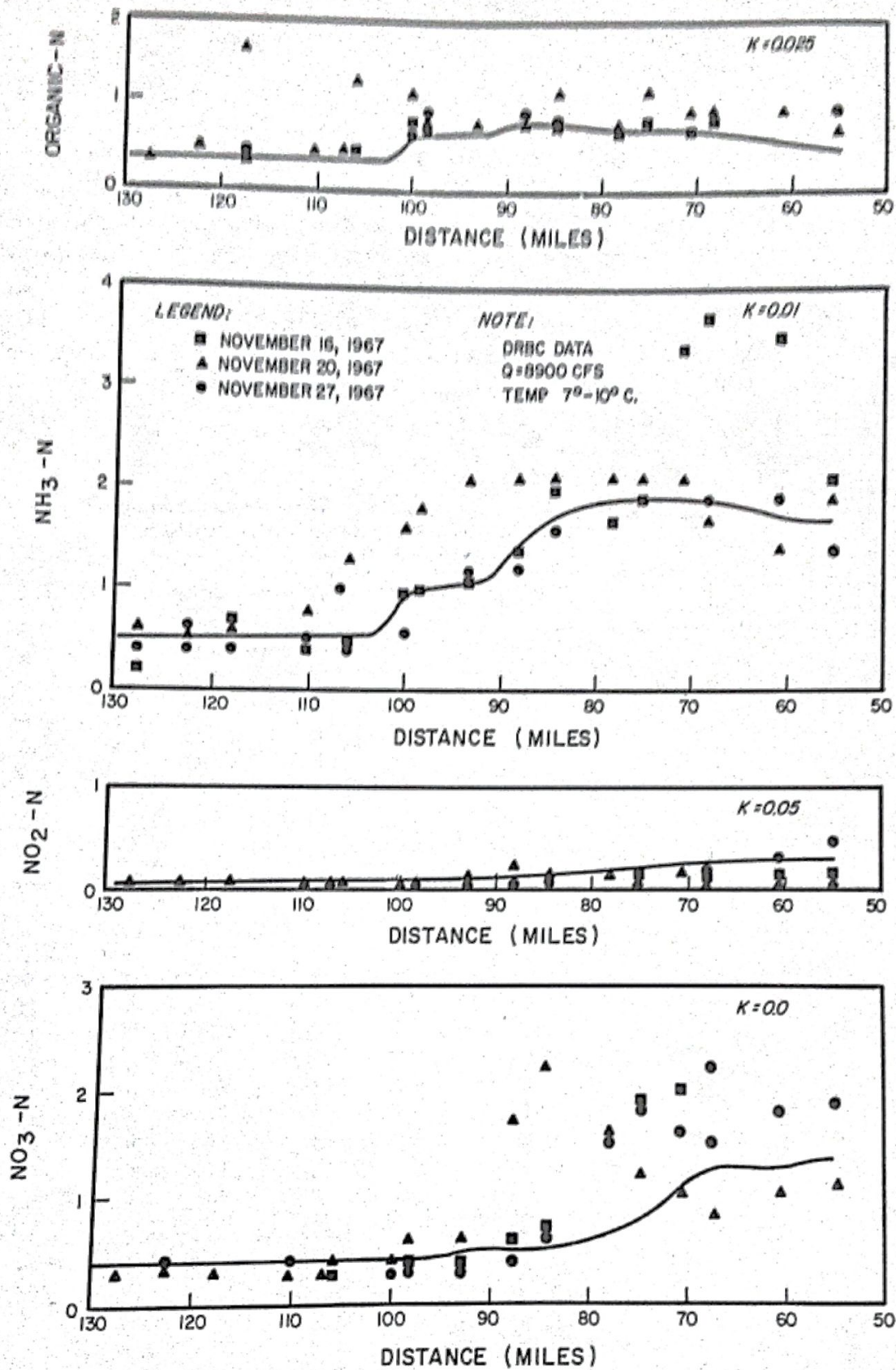
FIGURE 8-5
Observed versus computed (solid line) nitrogen profile, November 1967.[18]

be reflected in reduced oxygen utilization and has a significant impact on treatment programs that may use nitrification.

The final step in the verification analyses was to use the the temperature dependence of preceding reaction coefficients and supporting assumption to "independently" verify other profiles. Figure 8-6 is an example. As indicated, there is agreement in supporting the assumption of a consistent set of coefficients. The only change in the coefficients was to distribute the area of nitrification inhibition in accordance with low DO reaches. The additional verifications were obtained with ease, once the order of the coefficients had been established from the August 1964 and November 1967 analyses. The consistency of the reaction coefficients is illustrated in Table 8-2. While the set of coefficients is certainly not unique, Table 8-2 snows that the general

Table 8-2 SUMMARY OF REACTION COEFFICIENTS DETERMINED IN VERIFICATION OF ANALYSIS OF NITROGEN IN DELAWARE ESTUARY

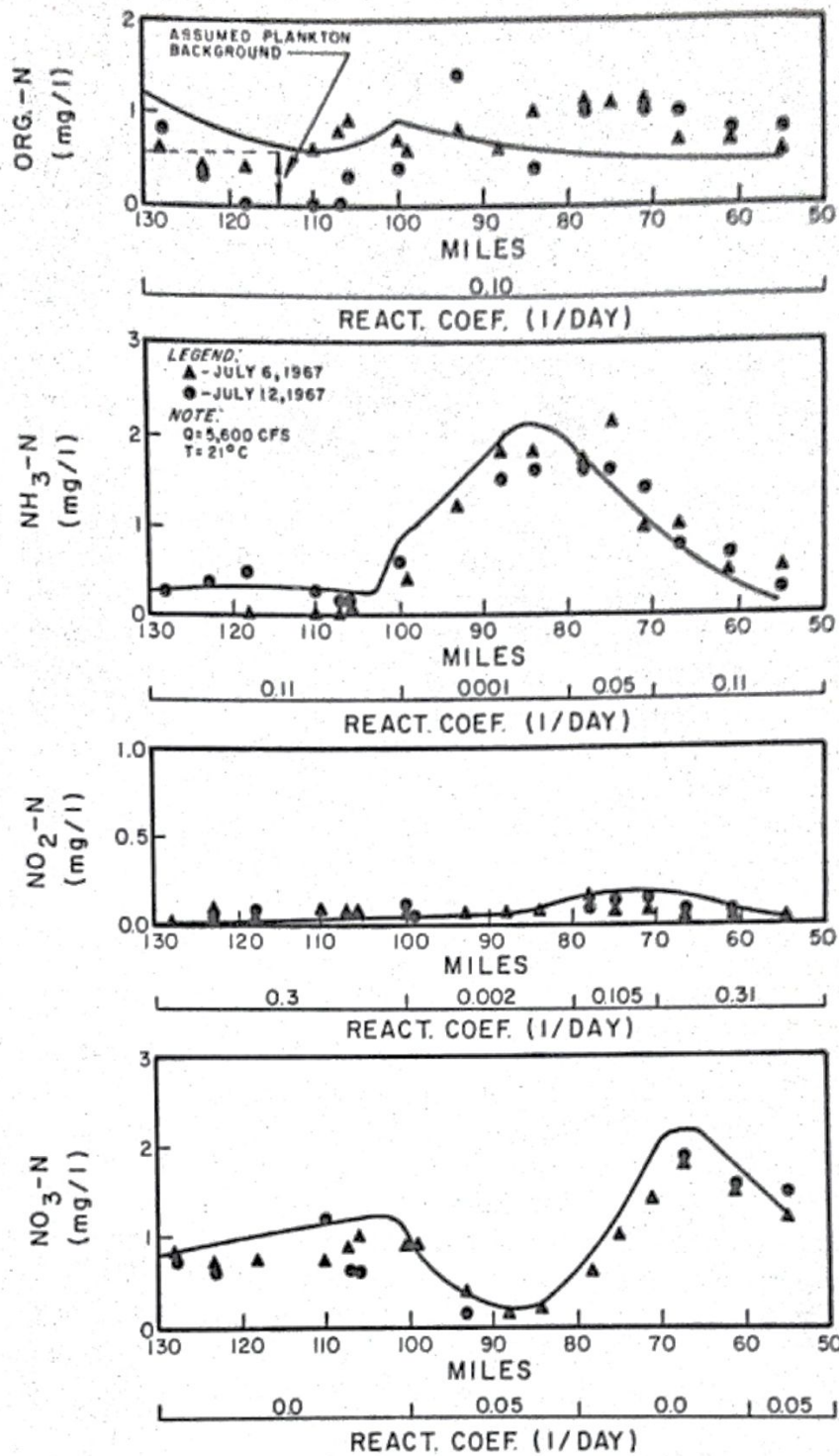| Survey	Reach No.	First-order reaction coefficient at 20°C			
		Org. to NH$_3$ (K_{12})	NH$_3$ to NO$_2$ (K_{23})	NO$_2$ to NO$_3$ (K_{34})	NO$_3$ (K_{44})
July–Aug. 1964 $Q = 3,000$ cfs $T = 26°C$	1	0.1	0.11	0.3	0.0
	2		0.001	0.002	0.05
	3		0.001	0.002	0.0
	4		0.05	0.110	0.0
	5–6		0.11	0.3	0.0
	7	0.1	0.11	0.3	0.5
June–July 1965 $Q = 2000$ cfs $T = 20°C$	1	0.1	0.11	0.3	0.0
	2		0.001	0.002	0.05
	3		0.001	0.002	0.0
	4		0.5	0.110	
	5		0.110	0.3	
	6				
	7				0.05
	8	0.1	0.110	0.3	0.05
July 1967 $Q = 5,600$ cfs $T = 21°C$	1	0.1	0.11	0.3	0.0
	2		0.001	0.002	0.05
	3		0.001	0.002	0.05
	4		0.001	0.002	0.05
	5		0.05	0.105	0.0
	6		0.11	0.3	0.0
	7	0.1	0.11	0.3	0.05
		First-order reaction coefficient at 7–10°C			
Nov. 1967 $Q = 8,900$ cfs $T = 7–10°C$	1	0.0025	0.01	0.05	0.0
	2				
	3				
	4				
	5				
	6				
	7	0.025	0.01	0.05	0.0

FIGURE 8-6
Observed versus computed (solid line) nitrogen profile, July 1967.[18]

order of magnitude of the coefficients is consistent, providing allowance is made for variable spatial distributions of the coefficients due to low dissolved oxygen values.

8-6.3   Effect on Dissolved Oxygen

The four-system model can be used to estimate the effects of the nitrification reaction on the dissolved oxygen deficit.

The organic and ammonia waste sources are inputted into the initial two systems. The output from the ammonia system is then multiplied by the reaction rate K_{23A}, which is given by $3.43 K_{23}$. This then represents the sink of dissolved oxygen due to ammonia oxidation and is inputted into the third system, which now represents the dissolved oxygen system with its accompanying reaeration rate. A total of three systems is therefore used, and the output from the third system represents the dissolved oxygen deficit due to NH_3–NO_2 oxidation. A similar procedure is followed for the NO_2–NO_3 oxidation, where $K_{34A} = 1.14 K_{34}$.

Figure 8-7 shows a typical result for the July–August 1964 condition. The reaction rates for nitrification shown in Fig. 8-4 were used in the computation, together with a constant spatial reaeration rate of 0.18/day at 20°C. The two components of the nitrification are shown. A slight shift downstream of the NO_2–NO_3 component relative to the NH_3–NO_2 component can be noted. Also, the peak in the total deficit occurs some 10 to 15 miles downstream of the major waste sources, reflecting the inhibited nitrification upstream due to low dissolved oxygen. It is also quite interesting to note a general background of 0.7 to 1.0 mg/1 dissolved oxygen deficit due to the nitrogenous discharges from tributaries and runoff, as well as municipal and industrial sources. The peak value of 2.5 mg/1 dissolved oxygen deficit is somewhat lower than previous estimates, which placed the peak at about 3.0 mg/1 but at approximately the same location.

Part of this difference is attributable to the use of the four-system model rather than an approximation through "nitrogenous BOD" with associated reduction in nitrogenous BOD decay rate or simple translation of the input of nitrogenous BOD. In general, then, Fig. 8-7 confirms previous work which recognized a downstream shift of the satisfaction of the nitrogenous oxygen demand.[20,23,24] The results indicate that this phenomenon is due to low upstream dissolved oxygen values which, together with the discharge of potentially toxic materials, have an inhibitory effect on the nitrifying bacteria. As the dissolved oxygen recovers, the nitrifying flora begins to develop and bacterial nitrification proceeds at a relatively rapid pace. This is then accompanied by an increasing utilization of oxygen.

8-6.4   Projected Effects of Nitrogen Removal Program

Nitrogen removal from waste effluents can be accomplished in several ways, including biological nitrification, air stripping, and ion exchange. Each of the methods accomplishes varying degrees of removal of nitrogenous components and at widely varying costs.

Figure 8-7 showed the estimated dissolved oxygen deficit due to nitrifica-
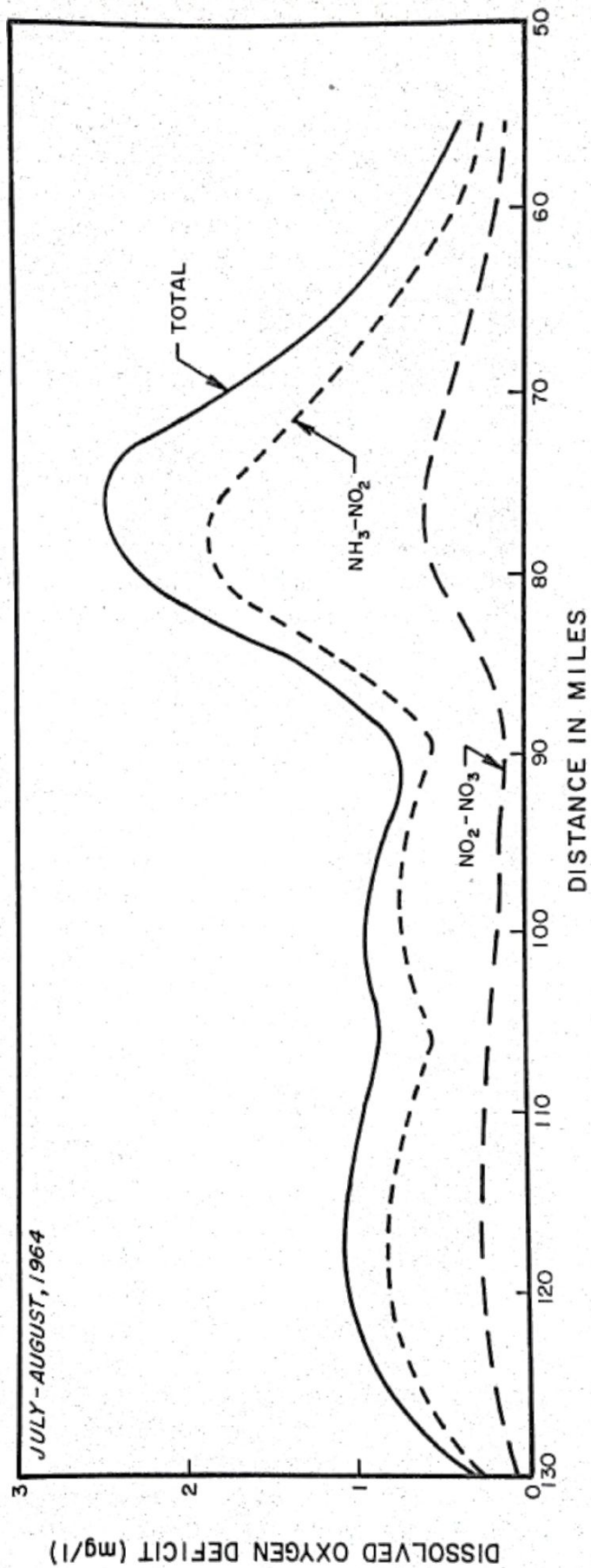
FIGURE 8-7
Estimated DO deficit due to nitrification.[18]

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tion for 1964 summer conditions. It should be recalled that the peak dissolved oxygen deficit occurred at about mile 75 because of assumed nitrification inhibition from mile 100 to 85. This inhibition was ascribed to low dissolved oxygen conditions in that reach. If, following implementation of the waste control program, dissolved oxygen conditions were at a higher level (say, greater than 2 mg/1 everywhere), it is informative to explore the resulting effect of nitrification on dissolved oxygen. Two possibilities exist under improved dissolved oxygen:

1 Ammonia oxidation will take place throughout the entire length of the estuary at a rate of approximately 0.1/day. This will result in a shift of the maximum dissolved oxygen deficit upstream.

2 Because of generally improved water quality, algal utilization of ammonia may now increase throughout the length of the estuary. Since many algal species utilize ammonia preferentially, the ammonia would be tied up in organic form and not contribute to the deficit until some time later in the year. The rate of this phenomenon is unknown.

Both effects will probably proceed simultaneously. However, in order to provide a somewhat conservative estimate, it can be assumed that all the ammonia will be oxidized and will contribute to the dissolved oxygen deficit. Under this assumption, model runs were made using ammonia oxidation rates of 0.11/day everywhere, and the dissolved oxygen deficit was computed. The results are shown in Fig. 8-8.

As shown, under favorable nitrification conditions, with ammonia oxidation proceeding uniformly, the maximum dissolved oxygen deficit shifts upstream to about mile 90. There is a decrease of about 0.2 mg/1 in the maximum and a general spreading over a larger area. At mile 90, the deficit increases from about 0.5 mg/1 to about 2.2 mg/1 under favorable nitrification conditions. On the other hand, at mile 75, the dissolved oxygen deficit decreases from about 2.2 mg/1 to about 1.4 mg/1. The difference between the downstream dissolved oxygen deficit and the upstream increase is due to the increasing cross-sectional area of the estuary in the downstream direction. If a 50 percent removal of oxidizable nitrogen were accomplished, the estimated dissolved oxygen deficit profile is as shown in Fig. 8-8. A general decrease is noted with a maximum dissolved oxygen deficit of about 1.3 mg/1 in the area of mile 90. In order to provide an overall estimate of the effect of this shift in the dissolved oxygen deficit profile and projected water-quality goals, a preliminary analysis was made of the estimated dissolved oxygen profile under existing waste removal requirements.

The estuary proper has been divided by the Delaware River Basin Commission into four zones with ultimate carbonaceous BOD removal requirements ranging from 86 to 89 percent, based on raw 1964 waste loads. These requirements will generally be met by various types of secondary treatment, including, for municipalities, biological waste reduction. It is difficult at this
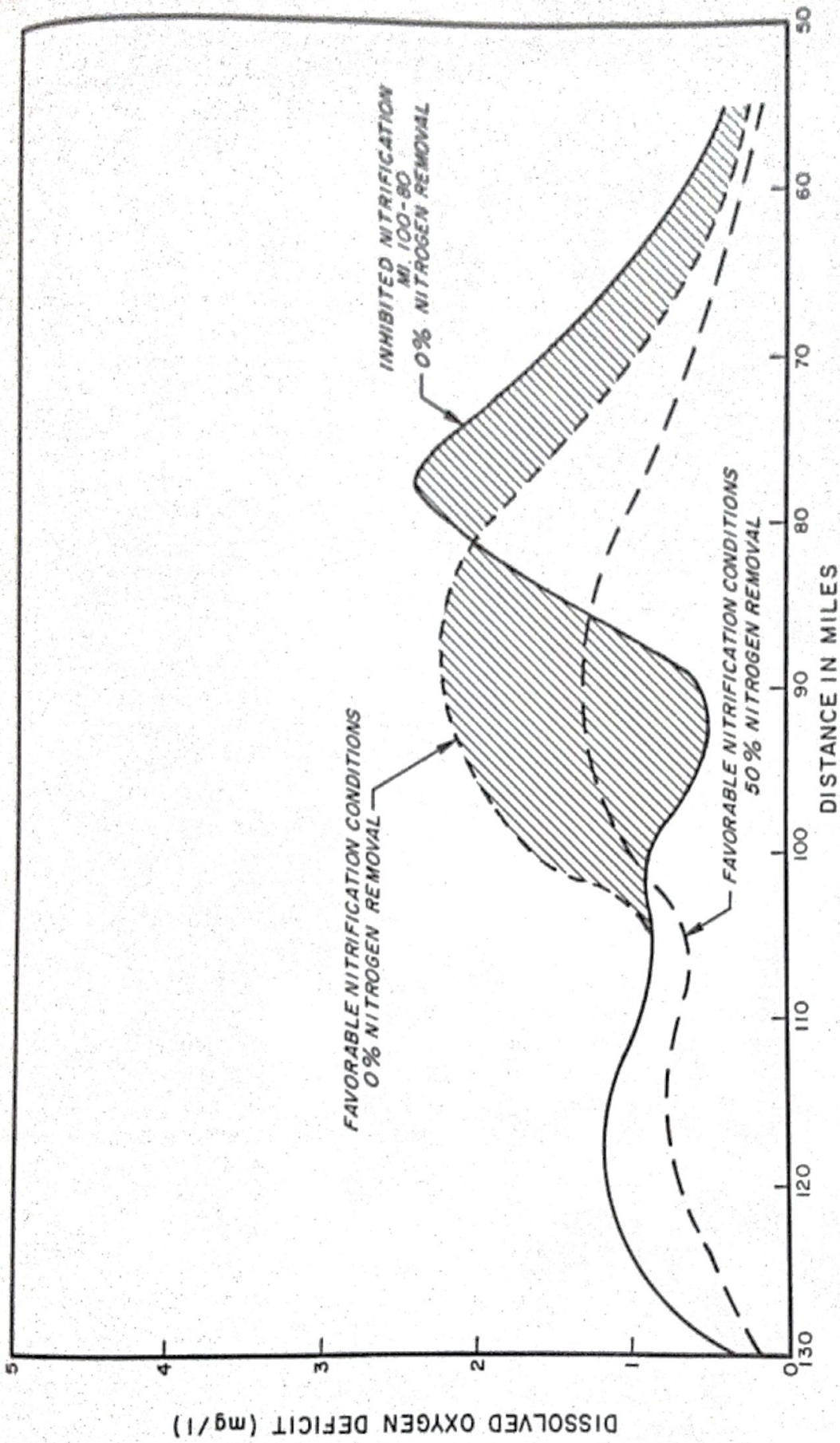
FIGURE 8-8
DO deficits under different nitrification conditions.

Labels within figure:

INHIBITED NITRIFICATION
MI. 100-80
0% NITROGEN REMOVAL

FAVORABLE NITRIFICATION CONDITIONS
0% NITROGEN REMOVAL

FAVORABLE NITRIFICATION CONDITIONS
50% NITROGEN REMOVAL

DISTANCE IN MILES

DISSOLVED OXYGEN DEFICIT (mg/l)

stage to estimate the extent of nitrogen reduction to be expected from this program. The particular design practices will govern this factor. However, for estimating purposes, a value of about 20 percent oxidizable nitrogen reduction appears reasonable.

A dissolved oxygen analysis was therefore made, using the same sectional breakdown as used in the nitrification model. The analysis indicated that, under a 20 percent nitrogen removal of 1964 loads, the dissolved oxygen goal of the DRBC will probably be met. The critical region is in the vicinity of mile 100 to 90. Under 50 percent nitrogen removal of 1964 loads, the DRBS dissolved oxygen goals will be met with a greater degree of assurance; the steady-state DO profile is estimated to be above 4.0 mg/1 everywhere.

The 20 percent removal program is equivalent to a discharge load about 95,000 lb/day of oxidizable nitrogen which would be allowable, while a 50 percent removal program is equivalent to a discharge load of about 60,000 lb/day of oxidizable nitrogen. Ultimately, therefore, waste removal programs must assign both carbonaceous BOD loads and nitrogen loads on a pounds per day basis. General unquantifiable factors that will tend to further enhance the attainment of dissolved oxygen goals include algal utilization of ammonia with subsequent reductions in the dissolved oxygen deficit due to nitrification, ammonia oxidation at a slower rate than that assumed, and specific encouragement of nitrogen removal. Factors that will tend to mitigate against achievement of the objective include a faster rate of ammonia oxidation, which will intensify and shorten the area of minimum dissolved oxygen, or carbonaceous removal designs resulting in oxidizable nitrogen removal of less than 20 percent.

The equations are

$$0 = \frac{1}{A}\frac{d}{dx}\left(EA\frac{dN_1}{dx}\right) - \frac{1}{A}\frac{d(QN_1)}{dx} - K_{11}N_1 + K_{41}N_4$$

$$0 = \frac{1}{A}\frac{d}{dx}\left(EA\frac{dN_2}{dx}\right) - \frac{1}{A}\frac{d(QN_2)}{dx} - K_{22}N_2 + K_{12}N_2$$

$$0 = \frac{1}{A}\frac{d}{dx}\left(EA\frac{dN_3}{dx}\right) - \frac{1}{A}\frac{d(QN_3)}{dx} - K_{33}N_3 + K_{23}N_2 \qquad (8\text{-}48)$$

$$0 = \frac{1}{A}\frac{d}{dx}\left(EA\frac{dN_4}{dx}\right) - \frac{1}{A}\frac{d(QN_4)}{dx} - K_{44}N_4 + K_{24}N_2 + N_{34}N_3$$

$$0 = \frac{1}{A}\frac{d}{dx}\left(EA\frac{dD}{dx}\right) - \frac{1}{A}\frac{d(QD)}{dx} - K_aD + K_{25}N_2$$

where N_1 is organic nitrogen, N_2 is ammonia nitrogen, N_3 is nitrite plus nitrate nitrogen, N_4 is algal nitrogen, D is the dissolved oxygen deficit, and $K_{21} = .57K_{32}$. As indicated previously, $K_{ii} \geq K_{ij}$ for all i. The feedback loop appears as $K_{41}N_4$, a source term in the first equation which utilizes the solution of the fourth equation.

A finite difference approximation was employed to solve Eq. (8-47) (see Sec. 8-5.3). The spatial segmentation and system parameters of other

work[25,26,27] was used. A total of 23 spatial segments was applied to the reach of the Potomac from Little Falls downstream, a distance of about 100 miles to the approximate entrance to Chesapeake Bay. In matrix form, the equations to be solved are [see also Eq. (8-44)]

$$
\begin{bmatrix}
[A_1] & 0 & 0 & -[VK_{41}] & 0 \\
-[VK_{34}] & [A_2] & 0 & 0 & 0 \\
0 & [VK_{23}] & [A_3] & 0 & 0 \\
0 & -[VK_{24}] & -[VK_{34}] & [A_4] & 0 \\
0 & -[VK_{25}] & 0 & 0 & [A_5]
\end{bmatrix}
\begin{pmatrix}
(N_1) \\
(N_2) \\
(N_3) \\
(N_4) \\
(D)
\end{pmatrix}
=
\begin{pmatrix}
(W_1) \\
(W_2) \\
0 \\
0 \\
0
\end{pmatrix}
\quad (8\text{-}49)
$$

where the $[A_i]$ are 23×23 tridiagonal matrices incorporating net advective flow and dispersion, with the K_{tt} appearing on the main diagonal. Note that $[A_5]$ has the reaeration rate K_a on the main diagonal, $[VK_{ij}]$ are 23×23 diagonal matrices, (N_i) and (D) and (W) are 23×1 vectors of the nitrogen forms, DO deficit and input nitrogen loads, respectively. The matrix equation (8-46) is therefore composed of a system of 115 algebraic equations, the simultaneous solution of which provides the steady-state distribution of the four nitrogen forms and the DO deficit in all 23 segments.

Data were available for the period July–August 1968 for verification purposes. These data included Kjeldahl nitrogen (representing the sum of organic nitrogen from waste discharges, ammonia nitrogen, and algal nitrogen), nitrite and nitrate nitrogen, and chlorophyll "a" measurement. Major input nitrogen loads are summarized in Table 8-3. Figures 8-9 and 8-10 show the results of a verification analysis of data collected during July–August 1968. The first-order reaction coefficients for the verification analyses shown in these figures are given in Table 8-4.

These coefficients represent the end result of many solutions of Eq. (8-49), which tested the effects of various interactions and levels of coefficients. It can be noted that organic nitrogen is "settled out" of the system because of the difference between the decay coefficient of organic nitrogen and the conversion of organic nitrogen to ammonia nitrogen. This was justified on the basis of bottom sampling, which indicated significant deposits in the vicinity of the Washington, D.C. outfall. Ammonia nitrogen followed two paths: (1) utilization in the algal nitrogen loop ($K = 0.02$/day), and (2) oxidation to nitrate

Table 8-3 ESTIMATED SIGNIFICANT INPUT NITROGEN LOADS POTOMAC ESTUARY, JULY–AUGUST 1968

Source	Ultimate carbonaceous BOD, lb/day	Org-N, dlb/day	NH_3-N, lb/day
Arlington, Va.	5,900	1,300	2,100
Washington, D.C.	132,000	20,000	20,000
Alexandria	11,700	1,300	2,300
Ft. Westgate	20,800	1,400	1,100

($K = 0.28$/day). This split allowed a proper spatial profile to be maintained. Nitrate was recycled to algal nitrogen, all of which was allowed to decay to organic nitrogen.

Figures 8-9 and 8-10 compare the observed data of the various nitrogen forms to computed values generated by the model with and without the feedback of ammonia and nitrate nitrogen to organic nitrogen. For Fig. 8-9, only Kjeldahl nitrogen observed data were available. The effects of the feedback loop are to increase all profiles in a nonlinear spatial manner. The relative downstream shift of the various nitrogen forms is interesting and reflects the sequential nature of these types of reactions. Steady-state analyses such as shown in Figs. 8-9 and 8-10 can provide a basis for estimating the effects of environmental changes on nitrogen distribution, in addition to the effects of nitrification on the oxygen regimes.

This latter effect is shown in Fig. 8-11, where the dissolved oxygen deficit due to nitrification is given with and without algal feedback of nitrogen. Therefore, if the nitrogen is completely stored in the algae, the dissolved oxygen deficit is lower at greater distances downstream than if the algal nitrogen is released and available for further nitrification. The peak value of 3 mg/1 DO deficit is significant from a water-quality management viewpoint and indicates the need for nitrification of the principal waste discharges.

The nitrogen algal cycle in the Potomac estuary is obviously more complex than given by this model. Nonlinear kinetics, algal growth dynamics, and environmental influences of temperature and light all affect the observed data. As a planning tool, however, the simplified model using first-order kinetics provides a rapid means for estimating order of magnitude responses and points the direction for more complex modeling efforts.

Table 8-4 FIRST-ORDER REACTION COEFFICIENTS POTOMAC ESTUARY JULY–AUGUST 1968 (Temp. $= 28$ (C)

Reaction step	Symbol	Reaction, coefficient, l/day
Decay of organic NH	K_{11}	0.2
Organic N $\rightarrow$ NH$_3$–N	K_{12}	0.1
Decay of NH$_3$–N	K_{22}	0.30
NH$_3$–N $\rightarrow$ NO$_3$–N	K_{23}	0.28
NH$_3$–N $\rightarrow$ algal N	K_{24}	0.02
Decay of NO$_3$–N	K_{33}	0.10
NO$_3$–N $\rightarrow$ algal N	K_{34}	0.10
Decay of algal N	K_{44}	0.12
Algal N $\rightarrow$ organic N	K_{41}	0.12
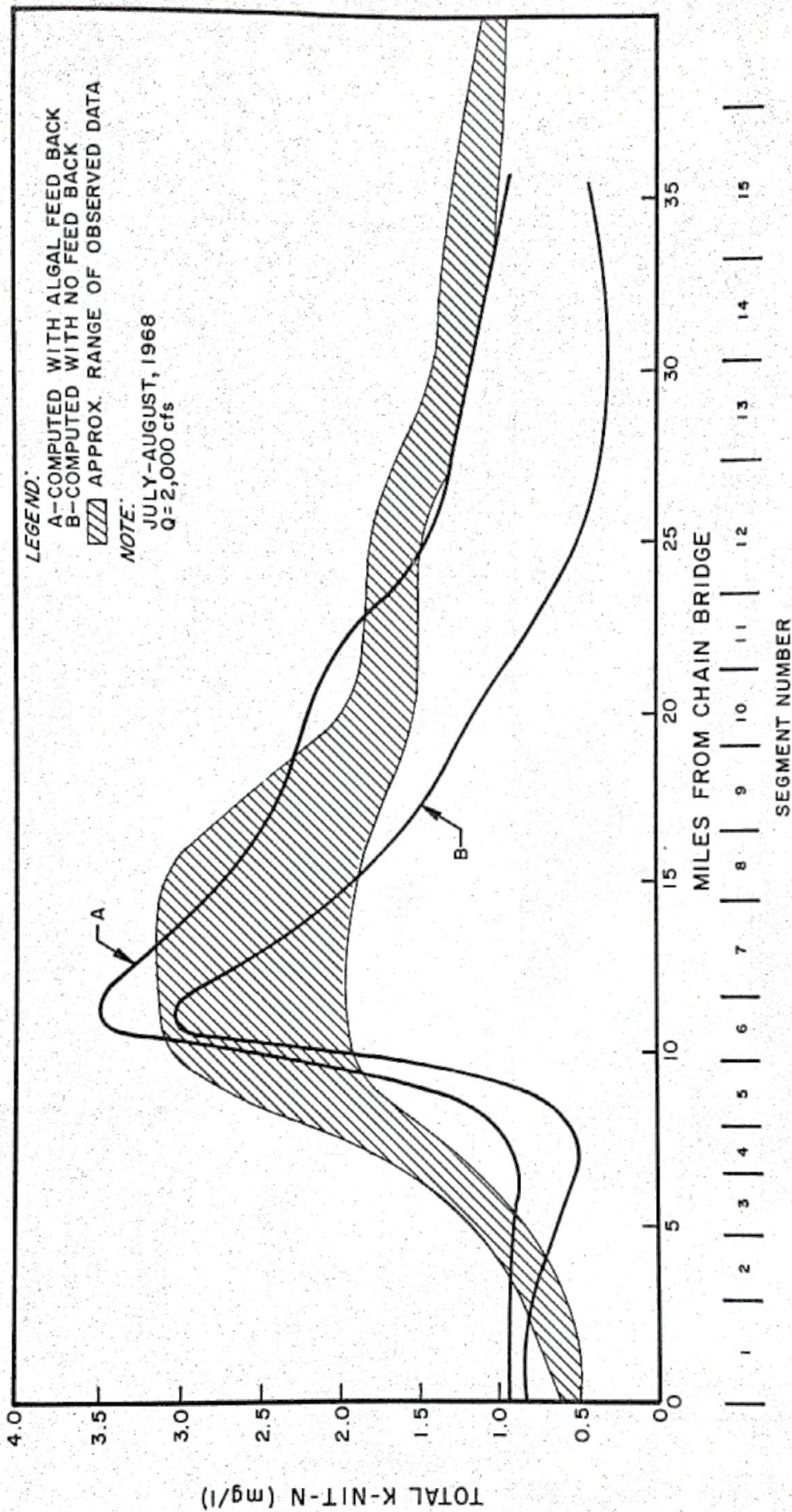
FIGURE 8-9
Verification of Kjeldahl nitrogen for the Potomac estuary.
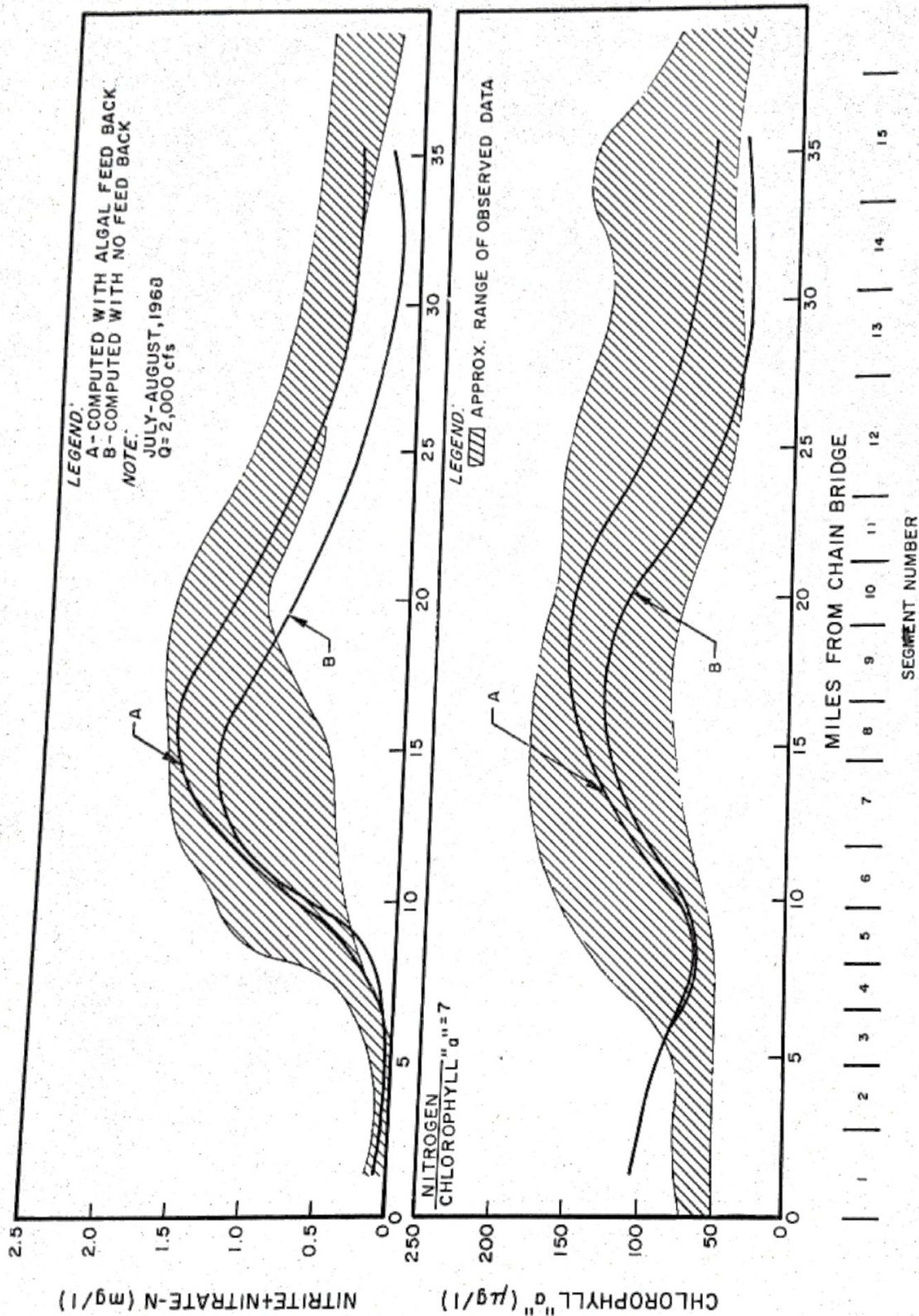
FIGURE 8-10

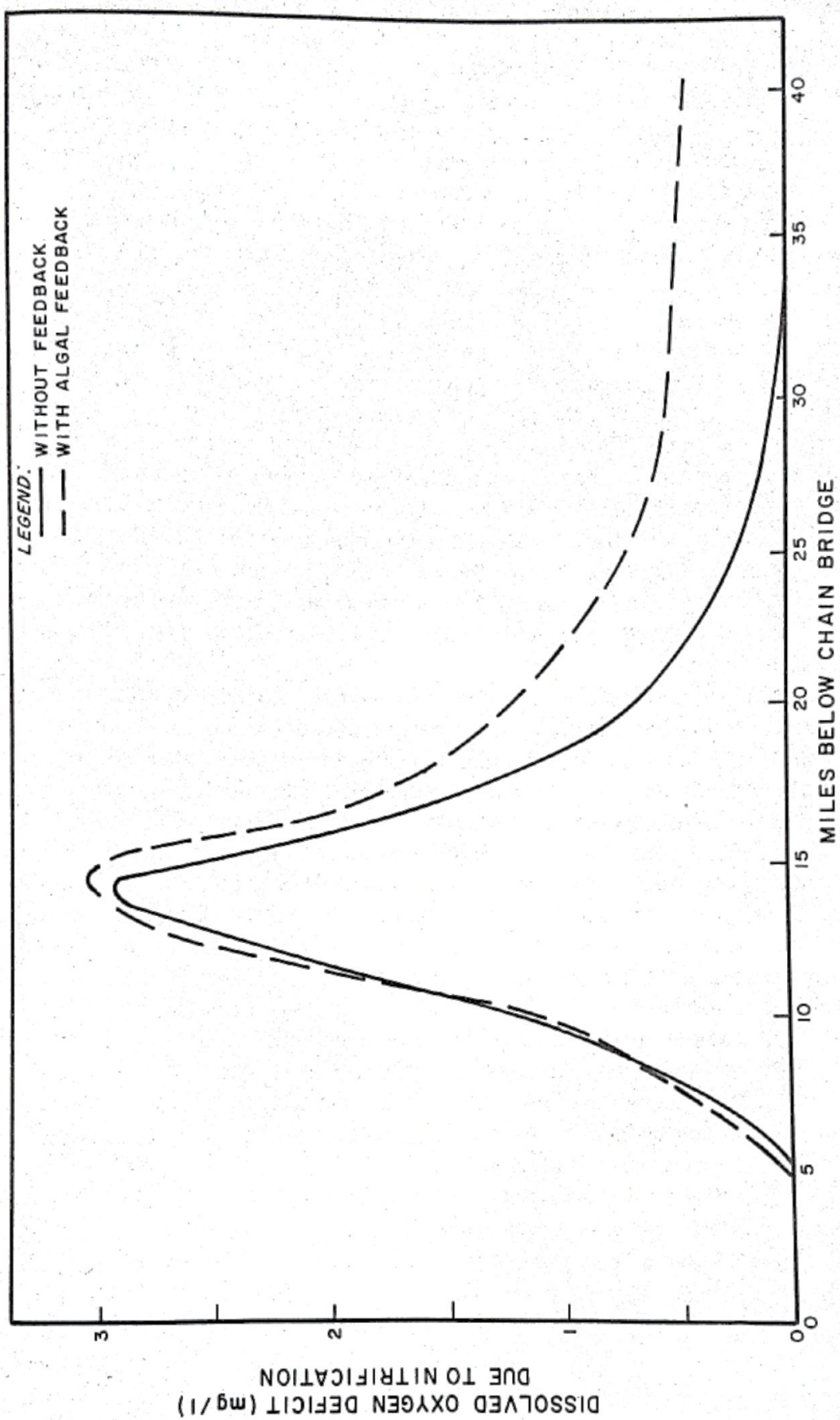Verification of nitrite and nitrate nitrogen (upper plot) and chlorophyll "a" (lower plot) for the Potomac estuary.

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FIGURE 8-11
Computed dissolved oxygen deficit due to nitrification in the Potomac estuary,
July–August 1968.

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8-7 SUMMARY AND CONCLUSIONS

The discharge of oxidizable nitrogenous waste material into streams can result in significant demands on the oxygen resources. Under complete nitrification, 1 lb of oxidizable nitrogen will require about 4.5 lb of oxygen. Organic and ammonia waste loads from municipal wastes and some industrial wastes are the primary sources of this demand, although land runoff may also contribute oxidizable nitrogen. The oxygen-demanding load due to nitrogenous compounds from some treatment plants can equal or exceed the oxygen demand due to carbonaceous compounds.

The kinetics that govern nitrification are complex and can be modeled by a nonlinear interaction between the nitrifying organisms and the substrate. Different forms of substrate utilization equations result from the nonlinear kinetics model, ranging from a linear decrease to exponential to autocatalytic variations. From dilute well-seeded systems with low substrate concentrations and relatively high nitrifying populations, a first-order kinetic assumption for substrate decay is approximately justified. For more detailed studies, where the problem context warrants it, actual nonlinear kinetics should be used if the necessary data on bacterial populations or equivalents are available. Many problems, however, can be approached on a first trial basis by assuming first-order reaction kinetics which greatly simplifies the mathematical structure and solution techniques.

The decay of organic and ammonia nitrogen and subsequent utilization of oxygen can be mathematically modeled using first-order kinetics. The simplest method of including nitrification effects in oxygen balance studies is through the nitrogenous biochemical oxygen demand. The equivalent oxygen demand of the oxidizable nitrogen is estimated and then treated as the classical BOD input into the DO equations. The disadvantages of this approach lie principally in estimating lag effects. A preferable modeling route is to preserve the integrity of the nitrogen forms and to write equations for each nitrogen compound.

The complete nitrogen models for streams are direct, and any number of consecutive reactions can be readily incorporated. For estuaries, the nitrification models must include the effects of tidal dispersion. Finite differencing of the spatial gradients under steady-state conditions leads to sets of algebraic equations to be solved simultaneously. Feedback effects can also be included. For a water body segmented into n finite sections and for m variables, a total of nm equations must be solved. Numerous computational techniques are available for solving large sets of algebraic equations.

Applications of the steady-state first-order kinetic models to the Delaware and Potomac estuaries among others indicate that the broad features of nitrification and associated oxygen demand can be approximated. For the Delaware estuary, reaction coefficients for ammonia nitrogen decay consistently were found to be in the range of 0.1/day over a variety of prototype conditions, provided that dissolved oxygen was not limiting. The application to the Delaware estuary showed the importance of the nitrification effect on the dissolved

oxygen resources, where a maximum value of greater than 2 mg/1 of deficit due to nitrification was estimated. For the Potomac estuary, a five-system feedback model was constructed and the nitrogen forms of organic, ammonia, nitrite and nitrate, and nitrogen in algae was verified for a single prototype situation. The oxygen deficit caused by oxidation of ammonia was estimated at a peak value of 3 mg/1. When algal feedback of nitrogen was included in the model, increased oxygen deficits of about 0.5 mg/1 persisted for approximately 20 miles downstream.

The models presented here are therefore of particular utility in describing the broad outlines of the effects of nitrification on dissolved oxygen. Under certain conditions of well-seeded waters, the first-order kinetic models are good approximations to the actual nonlinear kinetics. When problem context demands a complex approach, the full kinetic equations should be used. For many problems, however, the simplified models using first-order kinetics will aid substantially in describing the components of the dissolved oxygen resources.

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