VARIATIONS IN WASTE LOAD ALLOCATIONS THROUGH SENSITIVITY ANALYSIS OF THE QUAL-II WATER QUALITY MODEL ON THE SOUTH RIVER, VIRGINIA

by

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INTRODUCTION

General Problem

With the enactment of the "Federal Water Pollution Control Act Amendments of 1972" came a series of management programs designed to restore and maintain the quality of this country's water resources. One provision of this Act, Section 303e, establishes the means by which each State is to develop a "continuing planning process" for water quality management by which it may acquire the regulatory jurisdictions provided through this Law. Each State's continuing planning process must establish provisions for each of the following [1]:

1. The establishment of "effluent limitations and schedules of compliance" which are at least as stringent as the Federal requirements.

2. "The incorporation of all elements of any areawide waste management plan and basin plans."

3. The establishment of "total maximum daily loads for pollutants."

4. Development of "procedures to review the planning processes."

5. Indication of "adequate authority of intergovernmental cooperation."

6. Means for "adequate implementation, including schedules of compliance, for reviewed or new water quality standards."

7. Methods for "control of disposition of all residual waste from any water treatment processing."

8. "Establish an inventory and ranking, in order of priority, of needs for construction of waste treatment works."

The goals of this process are to provide the States with the means by which they are able to maintain local regulatory authority over the activities within their State pertaining to their respective water resources.

Basin planning is a major component of each State's planning process. It provides a means by which the other aspects of the process are brought together. Each basin plan must include [2]:

1. Detailed and major descriptions of each body of water in the basin.

2. Identification and analysis of all pollutant sources, of point and non-point origin.

3. A ranking of each segment of water in order of priority for improvement.

4. An analysis of measures to be taken to improve or maintain water quality.

5. Establishment of timetables for State actions.

6. Identification of municipalities requiring assistance under Section 201 Planning.

7. Designating areas requiring comprehensive planning and regulation through Section 208 Planning.

The objectives of each of these planning procedures (303e, 201, and

208) must remain consistent with each other, in that they will ultimately be applied to the formulation of "Level B" planning studies under Section 209. These Level B studies are to establish comprehensive and interdisciplinary water pollution control, land use, and related environmental programs for regional development on a long range scope.

In the development of the basin plans, the river system is divided into segments depending on their level of water quality. If the water quality is attaining the applicable water quality standards of that system or these standards will be achieved upon application of treatment facilities to the various point sources based upon guidelines set forth by effluent limitations, the segments are classified as "effluent limitation segments" (EL). However, if the water quality standards are not achieved upon application of this level of treatment they are classified as "water quality segments" (WQ). The effluent limitation guidelines are base level limitations consisting of best practicable control technology for industrial sources and secondary treatment for municipal sources. The level of planning involved with each river segment is dependent upon its classification. All point source discharges within effluent limitation segments are required to maintain either existing effluent quality or establish effluent quality equivalent to the effluent limitation guidelines. Those segments which are designated "water quality" will require detailed analysis to determine the most effective allocation of waste loads between all point and non-point source discharges, such that water quality standards are met. The analysis should include all parameters, chemical and biological, which are in violation of water quality standards. Each source contributing that parameter to the segment should be identified and alternative remedial measures considered. In evaluating the consequences of proposed alternative waste treatment facilities within the segment and determining the total maximum loads allowable, mathematical models which simulate the natural system are introduced. Through the use of these models, the water quality can be predicted under adjusted conditions of flow, temperature, and waste loads. Optimum use of the river's assimilative capacity can thus be achieved through the application of the best economical and technological treatment facility systems available.

Mathematical Water Quality Models

The basis for the use of mathematical models in simulating water quality conditions of a body of water is that the model is comprised of a series of mathematical expressions which represent the significant interactions that occur within the system. As the input variables, or "forcing function," are introduced, these expressions simulate the occurrences which would result in the natural system and produce a corresponding output, or "response function." The ability of the model to properly predict the interactions which occur is dependent upon the complexity of the system under study and the degree to which these complexities can be defined. Although it is important to try and account for all changes within the system, it is best to design the model on the simplest level while still maintaining an accurate simulation. This provides a means by which the most significant variables and expressions can be analyzed and tested for their reliability without interference of insignificant influxes.

With the application of a complex model composed of expressions that simulate not only the major, but also many of the minor interactions which occur, there results a variability in the degree of how these components are modeled. The actual design of the mathematical expression and how it properly represents its corresponding part in the natural system will determine its overall influence on the model's output. It is important that the model's components do not overemphasize their influence on the output and that they actually represent the degree of importance in the system.

When most models are constructed, they are not always structured around the system in which they are to be used. Instead, they are developed upon relationships which can easily be defined, and which have proven acceptable in other modeling attempts. This procedure is satisfactory in many instances, since many of the interactions which occur are similar in nature and can be represented by a generalized expression. In applying a complex model which has been designed for one system and is being applied to another, it is important to determine the degree to which the various components have influence on the output. This can be done by performing a sensitivity analysis on the variables which are used as input for the components. This analysis consists of observing the behavior of the output of the model by fluctuating only one variable and maintaining the others constant. This parameter is varied throughout the range of possible values, and at any given value of the parameter, the sensitivity of the system to the parameter is the change in output per unit change in the parameter [3]. By defining the sensitivity of each of the variables it is possible to determine if its corresponding component in the system model properly represents the system. Through this form of analysis it is also possible to determine which input parameters require the most care in defining their values, since any minor discrepancy in its measurement could result in serious error in the simulation, and its corresponding output. Since the degree in accuracy of measurement of many of these variables is difficult to ascertain, it is important to analyze the variations in output which could occur if these parameters are not properly measured. One application of the analysis of the output is that of waste load allocation determination. Once the input variables (reaction rates) have been tested for their sensitivity, they can be tested against combinations of loadings from the various sources to determine how sensitive they are in correspondence to the reaction rates. Levels of loading reductions can then be based upon a set boundary, e.g., the dissolved oxygen requirement of streams.

It is the purpose of this study to apply these various applications of sensitivity analysis to the QUAL-II water quality model utilized by the U.S. Environmental Protection Agency. The version of the model which will be used was originally designed for the Santee

River in South Carolina with the capability of application to other river systems. The main concern will be the analysis of those parameters which are either directly or indirectly related to the dissolved oxygen balance of the river.

LITERATURE REVIEW

The need for mathematical modeling of water quality is related to the predictive capability of simulating the waste assimilation capacity of a body of water. The structure of the model is dependent upon the type of natural water system under study, the complexity of that system, and the degree of accuracy which is being sought in simulation.

The two primary classifications of water which are studied are rivers and estuaries. The primary difference between these two systems are the temporal and spatial considerations of the movement of water and its corresponding loadings within them, as well as their mixing characteristics.

Spatial Dimensions

The simplest system is that of a one-dimensional flowing river where the mixing characteristics are such that the primary spatial influence is the advective current, or flow, within the river. The effect of longitudinal dispersion has been found to be insignificant in most rivers, and the maximum error induced by ignoring it has been found to be only 4% using extreme values [4]. The fundamental equation that governs the transport of material in a non-dispersive system as this is described as [5]

$$\frac{\partial c}{\partial t} = \frac{1}{A} \frac{\partial}{\partial x} (Qc) - Kc \qquad (1)$$

where,

c = water quality variable
t = time
x = distance downstream
A = cross-sectional area
Q = riverflow
K = first order decay coefficient

One assumption which is made with this type of system is that the mixing is complete such that there exists no concentration gradients in a lateral or vertical direction. As was discussed by Dougal, et al. [6], each stream has various characteristics which determine its mixing capabilities, e.g. stream turbulence, velocities gradient, flow rate, slope of channel, depth of flow, density currents, and channel roughness and configuration. These variables should all be considered to some extent when evaluating the validity of the aforementioned assumption.

Estuarine systems are different in that they may have one or two spatial dimensions (e.g. the longitudinal and vertical dimensions)[5]. A vertical distribution may exist when the fresh water flowing from the river, being less dense, remains at the surface, while the salt water having a higher density exists at lower depths. The dispersion effect in estuaries is frequently the predominant factor in determining the concentration profile in estuaries [7]. O'Connor [7] further indicates that "due to the low advective velocities associated with the fresh water flow and the high dispersion due to tidal action, a mass of pollution is retained within the estuary for long periods and usually subjected to intense mixing." Equation 1 can be redefined to include this dispersion phenomena and would become:

$$\frac{\partial c}{\partial t} = \frac{1}{A} \frac{\partial}{\partial x} (EA \frac{\partial c}{\partial x}) - \frac{1}{A} \frac{\partial}{\partial x} (Qc) - Kc \qquad (2)$$

where,

E = the dispersion coefficient

and the other variables are defined as before. In major rivers, especially around their confluences with lakes, this dispersion coefficient should be evaluated for its significance. Often under these conditions, there exists a moderate upstream diffusion of pollutant mass similar to that which occurs in an estuary. Vertical differences may also occur due to thermal stratification between the lake and river water temperatures. Therefore, the lower regions of large rivers should be studied to evaluate the predominance of one or two dimensional influence. One method proposed by Hydroscience [8] for evaluation of the dispersion coefficient in tidal rivers is through analyzing the steady-state profile of chloride concentrations or other conservative substances.

Temporal Dimensions

Another consideration to be made of the natural water system is whether its behavior follows steady state or dynamic conditions. Under steady state conditions the various inputs such as fresh water flow, effluent discharge rates, and reaction coefficients remain constant over time producing a corresponding constant output. This exact condition is seldom if ever achieved since there usually exist either random fluctuations or relatively small variations due to the nature of the system inputs, e.g. diurnal fluctuations of inflow rates from waste water treatment plants. O'Connor [9] feels, however, that "any error introduced by accepting this assumption is not significant by comparison to other variations in the physical system or approximations in the mathematical model." Conditions of steady-state are normally approached during periods of low flow in the streams when the stress on the water quality is at the extreme, thus providing a simplistic approach to its modeling.

Many natural systems do not remain in a relative steady-state condition, but have their components vary through time, thus requiring the system to respond to these fluctuations. This type of input and response is of a dynamic nature. An example of this input is with the stream flow when it is regulated by man-made structures. It is important to determine the time period with which these variations occur and evaluate their significance on the modeling being performed. Daily fluctuations in variables can be ignored if the modeling is concerned with seasonal or annual simulation exercises. Simulation of shorter periods, e.g. daily or hourly, would require the modeling to be of a dynamic nature as would occur with the cyclic flow variations which occur in estuaries.

Predictive Capabilities of Water Quality Models

There are two groups of water quality models which have varying predictive capabilities; these are the deterministic models and the stochastic models. The deterministic models are those which assume that no random or stochastic element exists within the various inputs of the model. This assumption leads to the belief that if the model components properly represent the natural system, the response can be predicted exactly [4]. This type of assumption is often made to facilitate the modeling exercise, and is satisfactory for many levels, since the random element involved may be insignificant.

When it is believed that the random variations in the forcing functions of the system are important, the use of a stochastic model is required. This incorporates the development of a probabilistic projection of how the system will respond to the lack of exact predictability of its components. Several major attempts have been made to incorporate this stochastic process and have met with varying degrees of success [10, 11, 12, 13]. Each of these models is based primarily upon principles developed through the deterministic models with varying approaches to incorporate the ability to evaluate the randomness of the system. One of the major applications with the use of a stochastic model is the ability to predict the probability and variation with which the dissolved oxygen (DO) in the system may fluctuate. This is important in that it is the extremes in the DO concentrations which can have the greatest effect on the aquatic life [14]. Deterministic models develop an estimated mean value which could occur under the varying forcing functions, but are unable to evaluate the variances which can occur.

Dissolved Oxygen Balance--Basic Equation and Components

The basic equation for the analysis of the dissolved oxygen balance of a river system follows the principles of mass conservation; that is, "the time rate of change of mass within the volume plus the net rate of mass flow in and out of the volume must equal that produced by the sources and reduced by the sinks,"[7] and follows the format of the continuity equation. Equations 1 and 2 are examples of this form, where K has been defined as a sink. This term in the equation can be positive or negative, depending on the various sources and sinks within the system. Following properties of equation 1, where the advective currents have the greatest significance and the dispersion coefficient is minimal, O'Connor [7] indicates that certain assumptions must be considered for this method of calculation to hold true. "The direction of flow is along the longitudinal axis; and there are no vertical or lateral gradients of concentration. Turbulent mixing is sufficient to produce uniform concentration over the cross-sectional area of flow, but insufficient to cause a significant spreading or distortion along the flow axis."

Streeter and Phelps [15], through their classic study on the Ohio River, redefined this general equation with further application to the dissolved oxygen balance. They assumed there was only one source and one sink of oxygen. The sink was the biochemical oxidation, or stabilization, of organic matter by bacteria within the river. Reaeration by atmospheric oxygen was considered the source. The deoxygenation reaction has been found to be a first order process, in that the reactant concentration is reduced as the reaction proceeds, and that the rate (K_1) is directly proportional to the concentration of the bacterial substrate (reactant), forming the differential equation

$$\frac{dL}{dt} = -K_1L \tag{3}$$

where,

L = oxygen demand at any time

t = time, days

K_1 = deoxygenation coefficient (the rate constant of the oxidation process), per day

Integration of the equation yields

$$L(t) = L_oe^{-K_1t} \tag{4}$$

where

L_o = the initial oxygen demand, mg/l

If the dissolved oxygen concentration is expressed in terms of the saturation deficit, that is, the difference between the saturated and the actual dissolved oxygen concentration at time, t, and temperature, °C, then

$$\frac{dD}{dt} = -\frac{dL}{dt} \tag{5}$$

The determination of the ultimate oxygen demand, L_a, can be performed through the application of the biochemical oxygen demand (BOD) test under guidelines set by the American Public Health Association [16]. Since this analysis can frequently take as long as 20 to 30 days, the incubation period can be reduced to 5 days. By applying an applicable conversion number, this 5-day BOD (BOD_5) can be converted to an ultimate oxygen demand. Velz [17] has found the ultimate BOD can be determined by dividing the BOD_5 by 0.68. Although this conversion factor has come to be fairly standard, values as low as 0.20 have been found [18].

Various methods have been proposed for the estimation of the deoxygenation coefficient, K_1. Nemerow [19] presents a fairly detailed explanation of several of the following methods. One of the earliest and most reliable techniques was devised by Theriault [10] with the application of the least squares method to a set of BOD data. This method not only determines the deoxygenation coefficient, but also calculates a theoretical ultimate BOD. The laboratory BOD_5 data is tested against the corresponding individual "time of travel" values. Since this method is highly cumbersome without the use of an advanced calculating system, other more simplistic deviations have been proposed. Thomas [21] developed a "slope" method based upon a linear relationship between the rate of change of BOD and the BOD value itself. A moments method was derived by Moore, Thomas, and Snow [22] by taking moments of the determined values about the vertical coordinate axis of the BOD versus time curve. Orford and Ingram [23] found that when the BOD is plotted against the logarithm of time, the resulting curve is approximately a straight line. They found that through several mathematical transformations of the equation of this line, the reaction coefficient can be found. Several other methods have been found to be fairly reliable within various levels of accuracy; Gaudy [24], Rhame [25], and Lee [26]. A comparison of results through the use of several of these methods has been presented by Nemerow [19]. He found that based on data for a tannery waste, the K_1 values can vary from 0.113/day to 0.210/day, with calculated ultimate BOD values ranging from 3850 to 5200 ppm. Due to this large range in predicted values, it is important that not only proper laboratory techniques be used in derivation of the baseline data, but that complimentary methods be used in calculation of the reaction coefficients.

The deoxygenation rate is a function of temperature and of the ability for bacteria to decompose the organic matter. Various authors [17, 6, 27] have agreed that the correction for temperature in this reaction is

$$K_T = K_{20°C} \times 1.047^{T-20} \qquad (6)$$

where,

K_T = deoxygenation coefficient @ temperature °C, per day

K_{20} = corresponding rate @ 20°C, per day

T = temperature, °C

The ability for bacterial oxidation of the organic matter directly affects the value of K_1. Lower values of K_1 indicate that the substrate is complex in molecular structure and difficult for bacteria to break down to utilize as a nutrient and energy source, with a corresponding relationship for high values of K_1. Early studies [15] set a typical value of K_1 for domestic waste water at 0.23 at 20°C, although moderate variations were noted. O'Connor [7] indicates that the value of K_1 for a domestic waste water is dependent on the degree of treatment and the nature of the material with typical values being

Raw: 0.35

Settled: 0.40

Treated: 0.25

and that as much as a ± 0.10 per day variance can occur. Another author

[28] found that at 20°C, K_1 could vary from 0.023 for some industrial wastes to about 0.69 per day for others which are readily oxidizable. Concerning the deoxygenation rates of river water, O'Connor [7] indicates that, "the coefficient is usually less than the coefficient of an undiluted sample. It appears that the greater the flow the lower the value of the coefficient. Furthermore, the coefficient tends to decrease in the downstream direction indicating the disappearance of the more readily oxidizable substances, the occurrence of foods, and the progressive resistance to oxidation of the more stable end products." Thomas [29] evaluated the deoxygenation rates in various types of streams and indicated that a range of from 0.06 to 0.36 could occur where there were no toxic wastes present in them.

Bennett, et al. [3] reviewed many of the discrepancies which can occur between evaluating the K_1 by means of the bottle test following techniques set by the American Public Health Association versus the K_1 which would actually be occurring in the stream. The concern was focused on the ability of a "diluted and seeded sample incubated in the dark under quiescent conditions at a constant temperature being able to simulate the behavior of a slug of water of similar size under dynamic stream flow conditions." Various studies which were used as precedents were by Owens and Edwards [30] and Gannon [31] which related the degree of turbulence with K_1 and found that K_1 increased as the agitation increased. This increase in turbulence maintains a suspension of the organic matter which enables increased bacterial oxidation. Symons [32] and Hull [33] have determined that the increase in surface to volume ratio of the BOD bottle over that in the natural system enables increased bacterial growth, thereby raising the BOD value. Another problem with the bottle technique is that it does not allow for the possible decrease in the respiration rate of organisms associated with decreased DO concentrations [30]. Owens and Edwards [30] also indicated that when the algal biomass is significant, the bottle BOD would be higher due to the respiration of the algae. In the stream, the algae would negate this effect by the photosynthetic process which would not be occurring when the bottle tests are being incubated in the dark. As previously discussed, the deoxygenation rate in the stream has been found to decrease in the downstream direction of flow. The period of these changes of K_1 is normally shorter than the 5-day incubation period of the bottle test, thus the laboratory K rate does not represent the natural system. The temperature also changes during the normal daily cycle in a stream, and this is not properly simulated by the bottle test which is kept at a constant temperature (20°C). It has been recommended by Hull [33, 34] and Camp [35] that the bottles be darkened and incubated in the stream at the point of collection to overcome this possible error.

As mentioned earlier, the only source of oxygen which Streeter and Phelps [15] considered was "the physical absorption of oxygen from the atmosphere by the flowing stream."[3] The rate of reaeration has been shown to be directly proportional to the saturation deficit

$$\frac{dD}{dt} = -K_2D \tag{7}$$

where,

D = oxygen deficit, mg/l

t = time, days

K_2 = coefficient of reaeration, per day, base e

through integration becomes

$$D = D_0 e^{-K_2 t} \tag{8}$$

where,

D_0 = initial dissolved oxygen deficit, mg/l

The dissolved oxygen balance can be determined by combining the two independent processes, represented by equations 3 and 7 to become

$$\frac{dD}{dt} = K_1 L - K_2 D \tag{9}$$

with the terms as defined previously. Equation 9 describes the DO balance as the rate of change of the dissolved oxygen deficit with "time of travel" downstream being a function of the rate of oxygen utilization by oxygen-demanding substances and the rate of oxygen replenishment from the atmosphere. By combining equations 4 and 9 and integrating,

$$D = \frac{K_1 La}{K_2 - K_1}[e^{-K_1 t} - e^{-K_2 t}] + D_a e^{-K_2 t} \tag{10}$$

with terms previously defined, thus becoming the noted Streeter-Phelps equation for determination of the dissolved oxygen deficit in streams containing oxidizable compounds.

Numerous theories have developed in recent years for predicting the coefficient of reoxygenation of natural streams. All of the theories are based around the foundation of measuring the degree of turbulence that occurs within the stream. As explained by Tsivoglou [36], "the oxygen transfer from the atmostphere into the water can take place only at the air-water interface that exists at the stream surface, and this interface is constantly and randomly changing (being replaced or renewed) due to turbulent mixing of the flowing water. Hence, for any specific degree of oxygen depletion, the rate at which oxygen can be gained by the flowing water is directly proportional to the rate at which the water surface is being replaced from below by turbulent mixing. Since the structure of turbulence is too complex for direct measurement, various approaches have been developed for making indirect calculations.

Early attempts in predicting K_2 were through indirect means by use of the Streeter-Phelps equation, wherein all of the other terms in the equation were obtained from known data, resulting in a defined enumeration of the reaeration rate that would have been required to produce the observed dissolved oxygen profile. This method of determination is open to serious error due to the fact that the values used in the other terms of the equation are not always exact, nor are all of the other influences which affect the DO profile capable of being predicted properly.

Predictive models have been developed based upon various hydraulic properties of the river system. The earliest model was by Black and Phelps [37] and was based in terms of molecular diffusion, stream depth, and a "mixing period"[36]. Since then, many approaches have been used in constructing predictive models. Several detailed summaries [38, 36, 3] have been made reviewing these concepts and procedures used in their development. Therefore, only a cursory review with supporting discussion of the major methods will be covered.

O'Connor and Dobbins [39] developed an equation based on concepts from the field of fluid turbulence and on assumed relationships defining the rate of surface renewal. Two flow categories were specified and an equation was developed for each. Those streams which were categorized by non-isotropic turbulence (Chezy C less than 17) had the equation

$$K_2 = \frac{480\ D_L{}^{1/2} S^{1/4}}{H^{5/4}} \times 2.31 \qquad (11)$$

where,

D_L = the coefficient of molecular diffusity, sq. ft/day

S = slope of the stream channel, ft/ft

H = average depth, ft

Camp [28] estimated D_L for oxygen at 20°C to be approximately 2.03×10^{-5} cm^2/sec. These types of streams show a pronounced vertical velocity gradient. For a Chezy C greater than 17; isotropic turbulence is assumed to exist, as in deep channels, and is represented by

$$K_2 = \frac{D_L{}^{1/2} V^{1/2}}{2.31\ H^{3/2}} \times 2.31 \qquad (12)$$

where

V = the mean velocity of flow

Two reaeration models have been suggested based on considerations of the difference between the rate of entry and the rate of loss of gas (oxygen) molecules from a surface layer of liquid (water)[40, 41].

Tsivoglou [41] concluded that the ratio of the mass-transfer coefficients for the simultaneous transfer of two gases is directly proportional to the first power of the ratio of their molecular diffusities [3]. He stated further that the ratio of gas transfer coefficients was a constant within the limits of experimental error for the range of temperatures and turbulence conditions which were studied. Application was made of this theory for the determination of the reaeration rate. The two gases to be monitored are oxygen which will be transferred from the air to the liquid phase, and krypton-85. Upon determination of the gas-transfer coefficients for these two gases, calculation of the natural reaeration can be made even in the presence of pollution and photosynthetic effects. This method was field tested and developed through several studies; Tsivoglou, O'Connell, Walter, Godsil, and Logsdon [43], Tsivoglou, Cohen, Shearer, and Godsil [42], Tsivoglou [41], and Tsivoglou and Wallace [36].

As describbed by Bennett, et al. [3], "the technique uses an instantaneous injection of three tracers at a point upstream from the reach over which the reaeration coefficient is to be measured. The tracers used are: 1) a fluorescent dye, the purpose of which is to enable field personnel to follow the movement of the other tracers; 2) tritiated water, which is used as a conservative dispersion tracer; and 3) the radioactive tracer gas, krypton-85, which is used to measure the gas transfer capacity of the flow. The transfer capacity of the flow for the tracer gas is obtained from the relative concentrations of the gas and tritiated water tracers at the two ends of the reach."

The tracer gas transfer coefficient is found by

$$\frac{\left(\frac{C_G}{G_L}\right)_b}{\left(\frac{C_G}{C_L}\right)_a} = e^{-K_2^G t} \tag{13}$$

where C is concentration, t is flow time, G and L are subscripts referring to the krypton and tritium tracers respectively, "b" and "a" are subscripts for respective downstream and upstream monitoring stations, and K_2^G is the gas-transfer coefficient of the tracer gas. The reaeration rate, K_2, can be obtained through conversion

$$K_2 = \frac{K_2^G}{0.83} \tag{14}$$

The value 0.83 was found by Tsivoglou [41] to be the gas-transfer ratio between krypton and oxygen. This ratio must be assumed to be a constant; independent of temperature, flow conditions, and the presence of pollutants.

Most of the other major studies concerned with means by which the reaeration coefficient can be determined are based on semi-empirical or empirical equations based on relationships between the mass-transfer rate and various hydraulic properties. Several of these prediction equations were based on studies done in artificial flumes. An example is given by Thackston [44] whose data yielded through regression analysis

$$K_2 = 0.000125\ (1 + F^{0.5})\frac{U}{H} \times 2.31 \tag{15}$$

where,

F = Froude number

U = shear velocity, fps

H = depth, feet

The Froude number is characteristic of the flow regime in the river. The importance of the inclusion of this variable is questionable, therefore it has frequently been removed yielding

$$K_2 = 0.000125 \frac{U}{H} \times 2.31 \tag{16}$$

Variations in depth during the study were simulated from 0.05 to 0.23 feet.

Isaacs and Gaudy [45] utilized a circular tank with rotating walls to simulate streamflow. Simulation studies covering velocities from 0.55 to 1.63 fps, and depths from 0.50 to 1.50 feet were made yielding

$$K_2 = 3.053 \frac{U}{H^{3/2}} \times 2.31 \tag{17}$$

with terms as defined previously. A similar study by Negulescu and Rojanski [46] performed in a recirculating flume resulted in

$$K_2 = 1.423\, D_x \left(\frac{U}{H}\right)^{1.63} \times 2.31 \tag{18}$$

where,

D_x = longitudinal dispersion coefficient, ft^2/day

and the other terms are defined as before. Their study covered ranges in depth from 0.164 feet to 0.492 feet, and velocities from 0.656 to 1.903 fps.

A study done in England by Owens et al. [47] used the disturbed-equilibrium method for determination of K_2 by deaerating the streams with the addition of sodium sulfite and a cobalt catalyst. Their studies were performed on six different streams with flows, velocities, and depths ranging from 1.50 to 36.2 cfs, from 0.13 to 1.83 feet per second, and 0.34 to 2.44 feet, respectively. Multiple regression analysis of their data yielded

$$K_2 = 9.41 \frac{U^{0.69}}{H^{1.85}} \times 2.31 \qquad (19)$$

with terms as defined earlier.

As Tsivoglou [36] relates, the most comprehensive empirical field study was performed by Churchill et al. [48]. Their studies were carried out below dams where the dissolved oxygen level of the outfall was reduced due to thermal stratification in the dam impoundments. Variables included in the regression analysis were flow, velocity, mean depth, energy slope, resistance coefficient, fluid density, fluid viscosity, surface tension, molecular diffusion coefficient, and a vertical diffusion coefficient. The flow conditions which existed ranged in discharge from 952 to 17,270 cfs, mean depth from 2.12 to 11.41 feet, and velocity from 1.85 to 5.00 fps. The equation that the authors recommend to use based on their data is

$$K_x = 5.026 \frac{U^{0.969}}{H^{1.673}} \times 2.31 \qquad (20)$$

with terms as defined before.

Langbein and Durum [49] combined the data from several previous studies to determine their predictive equation

$$K_2 = 3.3 \frac{U}{H^{1.32}} \times 2.31 \qquad (21)$$

with the same defined terms.

The previously discussed equations are based upon a temperature of 20°C and must be converted to the ambient conditions of the natural system. This conversion is expressed as follows

$$K_T = K_{20} \times \theta^{T-20} \qquad (22)$$

where,

K_T= reaeration coefficient @ T°C

K_{20}= reaeration coefficient @ 20°C

θ = 1.0241 (1.016 to 1.04)

The value of θ is generally defined as 1.0241 by Elmore and West [50], but has been found to vary by others.

As these predictive models have shown, the reaeration coefficients vary depending on the hydraulic properties of the stream which determine the rate of mixing and the rate of renewal of the gas-liquid interface. It has been found that depth has a greater significance on the coefficient than does velocity [49] as can be seen in Table 1. In larger streams, as the depth increases it overshadows any minor increase in velocity, thus lowering the reaeration rate.

The presence of various pollutants has been shown to reduce the reaeration capacity of that system. Tsivoglou [36] found reduction in the coefficient, K_2, to increase as the concentration of the detergent surfactant linear alkylate sulfonate (LAS) increased, and that at a constant concentration, the reaeration rate decreased as the turbulence

Table 1. Variations of the Reaeration Coefficient with Size of Stream[1]

Stream Order	Average Discharge cfs	Average Depth, ft	Average Velocity fps	Computed Coefficient K_2, per day
1	0.6	---	---	---
2	2.8	---	---	---
3	14	0.55	1.2	9.3
4	65	0.95	1.6	5.5
5	310	1.8	1.8	2.6
6	1500	2.7	2.0	1.8
7	7,000	5.0	2.5	1.0
8	33,000	12.0	3.0	0.37
9	160,000	25.0	4.0	0.19
10	700,000	45.0	5.0	0.10

[1] Source: Langbein and Durum [49] as reported by Dougal et al. [6].

increased, where it would be the most beneficial. His studies also indicated that the reaeration capacity was adversely influenced in stream reaches which received discharges from municipal waste treatment facilities.

Dissolved Oxygen Balance--Advanced Systems Equation

As previously discussed, the Streeter-Phelps theory is based on the assumption that there are only two major processes occurring within the dissolved oxygen balance of a stream; these are the stabilization of organic matter by bacterial oxidation and the replenishment of oxygen into the system through surface reaeration. This description of a natural river system's dissolved oxygen balance has been expanded with the work of Dobbins [51] and others. This work has indicated that there are several other factors which can affect the BOD-DO relationship in a stream. These are:

1. The removal of BOD by sedimentation and absorption.

2. The addition of BOD along the reach by the scour of bottom deposits or by the diffusion of partly decomposed organic products from the benthal layer into the water above.

3. The addition of BOD by diffuse source runoff.

4. The removal of oxygen from the water by diffusion into the benthal layer to satisfy the oxygen demand in the aerobic zone of this layer.

5. The removal of oxygen from the water by the purging action of gases rising from the benthal layer.

6. The addition of oxygen by photosynthetic action of phytoplankton, periphyton, and fixed aquatic vascular plants.

7. The removal of oxygen by the respiration of plankton, periphyton, and attached plants.

8. The continuous redistribution of both BOD and DO by longitudinal dispersion.

Along with these influences listed by Dobbins [51], several other relationships have been brought out. The importance of nitrogenous oxygen demand (NOD) has been reviewed by Wezernak and Gannon [52, 53], Gannon [31], and DeMarco et al. [57]. Velz and Gannon [58] have shown the relationship of biological extraction to the DO balance. Many of these aforementioned reactions are coupled, that is, the output from one system component is the input for another. By combining these various elements of the river system and relating all to a single variable, the DO deficit, gives the following equation

$$D = D_0 \exp[-(K_2 \tfrac{X}{U})] \qquad (23)\ \text{a}$$

$$+ [\frac{K_1}{K_2 - K_c} (\exp[-(K_c \tfrac{X}{U})] - \exp[-(K_2 \tfrac{X}{U})])]_{L_o} \qquad \text{b}$$

$$+ [\frac{K_n}{K_L - K_n} (\exp[-(K_n \tfrac{X}{U})] - \exp[-(K_2 \tfrac{X}{U})])]_{L_o^n} \qquad \text{c}$$

$$+ \frac{K_1}{K_2 K_c} (1-\exp[-(K_2 \tfrac{X}{U})])$$

$$-[\frac{K_1}{(K_2 - K_c) K_c} (\exp[-(K_c \tfrac{X}{U})]- \exp[-(K_2 \tfrac{X}{U})])_{L_{RD}} \qquad \text{d}$$

$$- (1-\mathrm{exp}[-(K_L \frac{X}{U})]) \frac{P}{K_2} \qquad e$$

$$+ (1-\mathrm{exp}[-(K_2 \frac{X}{U})]) \frac{R}{K_2} \qquad f$$

$$+ (1-\mathrm{exp}[-(K_2 \frac{X}{U})]) \frac{S_B}{K_2} \qquad g$$

where all of the terms have been defined previously except

x = distance

K_c = first order carbonaceous BOD decay coefficient

K_n = first order nitrogenous BOD decay coefficient

L_o^n = initial nitrogenous BOD

L_{RD} = total distributed carbonaceous BOD source

P = gross DO production by photosynthesis

R = DO utilization by plant respiration

S_B = DO sink due to benthal demand

The various terms of the solution are interpreted as

a. initial value of DO deficit

b. deficit due to point source of carbonaceous BOD

c. deficit due to point source of nitrogenous oxygen deman

d. diffuse source addition of BOD along the reach

e. reduction of the deficit due to photosynthesis

f. deficit due to algae and plant respiration

g. distributed benthal demand effect

Equation 23 is representative of the predominant factors encountered in one-dimensional rivers, with exclusion of diffused source input of nitrogenous oxygen demand and the addition of deficits along the stream. Any of the variables on the right-hand side of the equation could predominate, and the others dropped without serious error. Each of the variables fluctuates in significance in the overall expression dependent upon the properties and behavior of the natural system. The importance of nitrification, benthal influences on the DO balance, and the effect of algal communities on the river system are reviewed in the following sections.

Nitrifiction

The role of nitrification in the aquatic system is only one part of the influence nitrogen compounds have, with others being the affect of ammonia reacting with residual chlorine and producing chloramines, and the utilization of ammonia and nitrates by algae and aquatic vascular plants as a nutrient source. However, focus has been centered around the nitrification process due to its direct influence on the dissolved oxygen balance.

Municipal and industrial waste treatment facilities are responsible for the discharging of various forms of nitrogen compounds; e.g. organic nitrogen (proteins, amines, urea), ammonia, nitrite, and nitrate. The quantity of each of these forms is dependent on the process which occurs within the industrial or municipal boundaries, and the form of treatment which is utilized. The organic nitrogen compounds are broken down through hydrolytic and microbial reactions yielding ammonia and simpler organic nitrogen forms. Painter [59] summarized three pathways in which organic nitrogen is broken down to ammonia: 1) from extracellular organic nitrogen containing compounds, chemically or biochemically; 2) from living bacterial cells during endogenous respiration; and 3) from dead and lysed cells. It is possible for the simpler organic nitrogen forms to be directly incorporated into the metabolic pathways of bacteria and plants, both algal and vascular [60]. Many of the organic nitrogen compounds from municipal waste water treatment plants are fragments of proteins (amino acids) and can be readily utilized by bacteria. Whereas, many of the organic nitrogen compounds from industrial sources are of a more complex structure and are not readily incorporated.

The actual nitrification process is associated with the stepwise oxidation of ammonia to nitrates with nitrites being an intermediary compound. This biochemical reaction is performed by bacteria of the family Nitrobacteriaceae of the order Pseudomonadales. The two genera normally isolated are Nitrosomonas and Nitrobacter, the former containing ammonium oxidizers and the latter nitrite oxidizers. These bacteria are obligate autotrophs in that they derive their energy solely by the oxidation of their respective inorganic nitrogen compounds. The Nitrobacter bacteria convert approximately three times as much substrate as Nitrosomonas, thereby having the latter form being the controlling factor in the overall process. This also accounts for the fact that nitrite is normally low in concentration, since it is rapidly oxidized to the nitrate form. On a stoichimetric basis, when all the nitrogen forms are expressed as N- nitrogen, the conversion of ammonia to nitrite requires 3.43 mg/l of oxygen which is subsequently converted to nitrate which requires 1.14 mg/l of oxygen. It has been found in recent experimentation [52] that due to this being a bacterial reaction, there is not a 100% efficiency in the transformations due to the synthesis of cell matter. Their findings yielded values of 3.22 mg/l of oxygen and 1.11 mg/l of oxygen for the oxidation of ammonia and nitrite, respectively.

The effect of variations in environmental conditions has been reviewed by Wild, et al. [55], Painter [59], DeMarco et al. [57], and Alexander [61]. The most comprehensive of these [59, 61] summarizes the environmental factors as follows:

1. The rate of ammonia oxidation is primarily affected by the existence of an adequate population of nitrifying bacteria. If the population is low or non-existent, a lag period will result before nitrification proceeds. Since this lag period corresponds to the time required for nitrifiers to replicate and is indirectly temperature dependent, the effect of temperature has been analyzed. Zanoni [62] found that with temperatures below 15°C, lag periods of up to 15 days occurred. Camp [28] indicated that nitrification is suppressed to negligible levels below 10°C.

2. The nitrification rate is directly related to the level of turbulence within the stream. Lower nitrification rates are associated with areas of low turbulence.

3. The presence of organics in the samples have shown several effects on the ammonium oxidation rate:

   a. If the initial ammonia nitrogen was not completely assimilated by the heterotrophic bacteria (decomposing carbonaceous BOD) during organic oxidation, simultaneous oxidation of carbonaceous and nitrogenous matter can take place without influence on the initial rate of nitrification provided that enough of the nitrifying population was present in the sample. Standard forms of secondary treatment, e.g. trickling filter and activated sludges, provide a system by which nitrification can start. Therefore, the effluent from these levels of treatment have already begun the oxidation of the nitrogen compounds and a nitrifying population is introduced into the river system by means of it.

b. If the ammonia nitrogen was completely assimilated during organic oxidation, nitrification could not begin until some ammonia nitrogen was released back into the solution by the death and lyse of heterotrophic bacteria.

c. In either a or b, when the ammonia was eliminated from the solution and the only source of ammonia for nitrification was from cellular organic nitrogen, the nitrification rate was controlled by the cell death rate, which is usually very slow.

4. The optimum pH for nitrification is 8.3. A 50 percent reduction in this rate occurs at pH less than 7.0 and greater than 9.8.

5. Nitrifiers are strict aerobes, thus requiring sufficient concentrations of dissolved oxygen to be present. The reaction rate decreases below DO levels of 2.0 mg/l. For all practical purposes, the process is assumed to be completely suppressed at levels below 1.5 mg/l. If anaerobic conditions occur, denitrification occurs

resulting in the reduction of nitrates primarily to free nitrogen (N_2) with lower levels of ammonia and nitrous oxide produced.

6. The carbon source for nitrifying bacteria is usually carbon dioxide or bicarbonate [8] which is seldom of short supply in limiting the nitrification process.

The reaction kinetics for the nitrification process are frequently represented by a decreasing first-order reaction, similar to the carbonaceous oxidation demand

$$\frac{dL^N}{dt} = -K_N L^N \tag{24}$$

where the terms have been defined previously. This mathematical description is only valid when the population of nitrifying bacteria is not a limiting factor in the process. When the populations of <u>Nitrosomonas</u> and <u>Nitrobacter</u> are below the optimum level for nitrification, the kinetics equation should be developed around quantification of their biomass, their growth rate, and the concentration of their respective substrates. Thomann et al. [63] has reviewed some of the considerations which should be made. Two studies which have used this approach are Stratton and McCarty [56] and Wezernak and Gannon [53]. Other methods of modeling this process have been studied by Thomann et al. [63] including the use of sequential reaction models, incorporation of a lag period within the system's equation, and feedback models.

Various methods have been proposed for the determination of the reaction rate of nitrification, K_n. This rate can be evaluated through the use of the standard BOD bottle test with application of a nitrification inhibitor that suppresses the activity of the autotrophic nitrifiers. Heterotrophic nitrifiers are normally not affected by this process, but their significance in the overall nitrification process is considered minimal [60]. Studies [64, 65, 61] using different inhibitors have yielded varying degrees of success. Examples of chemicals which have proven to be the most reliable through these studies are 2-chloro-6- (trichloromethyl) pyridine, allythiourea, and a marketed product labeled "N-Hib." Other chemicals have been analyzed but have shown to degrade and thereby become ineffective with sample incubation periods of over 10 days. A duplicate sample is processed identically without the inhibitor. By comparing the oxidation curve of the two samples, it is possible to differentiate between ultimate oxygen demand and carbonaceous oxygen demand with the difference between them being due to nitrogenous oxygen demand. One benefit of the bottle test is that it is possible to determine the lag period and when it occurs.

Another approach has been to perform a mass-balance of the various nitrogen compounds within the study area, and monitor their transformations. Personal experience of the author has shown that this method is extremely difficult when studying any large system, in that all sources and sinks must be adequately monitored, e.g. diffuse source loadings, side tributaries, discharges from industries or municipalities, and biological influences.

Since the nitrification process is biologically dependent, variations in temperature can affect its rate significantly. Temperature coefficients which have been found to be representative are [62]

$$K_T^N = K_{20}^N \times 1.097^{T-20} \text{ Range } 10°\text{-}22°C \qquad (25)$$

$$K_T^N = K_{20}^N \times 1.203 \times 0.877^{T-22} \text{ Range } 22°\text{-}30°C \qquad (26)$$

Values for K_{20}^N for ammonia oxidation have been found to be 1.47, 1.68, and 1.84 [56]; 0.24 [27]; 0.1 and 0.512 [63]; and 1.6 [17], all of which have been converted to 20°C and are in units/day. The higher reaction rates are indicative of high nitrogenous BOD relative to the carbonaceous fraction, optimum river temperatures, and the existence of an established population of nitrifiers. The reaction rate for nitrite oxidation has normally been higher, 4.90 [56] and would reflect the behavior of the bacteria involved.

Benthal Influence

As O'Connor [7] acknowledges, "when considering the stabilization of organic matter in natural streams, distinction should be made between those factors which affect its removal without necessarily utilizing oxygen and those which simultaneously remove the material and oxygen in a consistent fashion. In the first category are such physical phenomena as sedimentation, scour, and gas transfer from volatilization, while the second includes the various forms of chemical and biological oxidation." It is extremely difficult to differentiate between these various forms of reduction in carbonaceous BOD, therefore a term, K_r, has been designated to represent all means of removal. This term equals the overall BOD deoxygenation coefficient (K_d) plus that rate of removal of BOD by physical means while not exerting an oxygen demand (K_3). The former coefficient is comprised of the deoxygenation rate of free flowing water (K_1) along with a value attributable to biological extraction (B) first considered by Velz and Gannon [58]. Biological extraction accounts for that BOD which is removed through absorption by benthal bacterial and fungal growths, e.g. Sphaerotilus. Differences which have occurred between laboratory values of K_1 and that found for K_r in the stream can be due to the occurrences related to K_3 and B. These discrepancies have been discussed by Thomas [29], Camp [35], Dobbins [51], Velz and Gannon [58], and others.

The overall affect which biological extraction (B) has on the dissolved oxygen is believed to be related to the depth of the stream, the level of turbulence, and the type stream bed. The degrees of depth and turbulence are associated with the diffusion rate which would control the rate of transfer of the organic matter to the biological growths. The type of stream bed determines the potential for biological growths to occur. Rocky stream beds are more stable than sand and gravel, thus enabling larger growth of biological organisms, thus a greater transfer of BOD would occur. The influence of biological extraction is frequently combined with the term K_3, due to the difficulty in obtaining accurate measurements of it by itself.

Bottom deposits are formed in several ways depending on the types of wastes being discharged into the water. These are: a) the deposition of settlable solids from the wastes (allochthonous), b) deposition of solids which have formed through flocculation and coagulation of suspended and colloidal solids within the stream (autochthonous), and

c) development of biological growths [66]. With the incorporation of levels of secondary treatment for municipal waste treatment plants, the importance of the first source of deposits has been minimized. Settlable solids normally are considered to settle out when the stream velocity falls in the range of 0.60 to 1.0 fps. Resuspension of the deposits occur when the velocity increases to between 1.0 to 1.5 fps. [17].

Although the immediate BOD of the free flowing water is reduced by the settling of solids, the uptake of dissolved oxygen by these deposits still occurs through "1.) diffusion of the anaerobic decomposition products of the deposit into the overlying water; 2.) diffusion of DO from the overlying water into the aerobic zone of the deposit; and 3.) resuspension of the solids through scouring or volatilization from anaerobic decomposition" [3]. Normally, those periods of resuspension of the solids through scouring is during periods of high flow when the water quality is not at its most critical condition. Though consideration must be made for the fraction of these solids which will eventually settle upon attaining the proper hydraulic conditions. The importance of the influence of resuspension of solids on the BOD was shown by Berg [67] and Edwards and Rolley [68], where the BOD greatly increased upon resuspension. The first process was considered to be the most important through a study by Fair, Moore, and Thomas [69]. Since the aerobic zone in benthal deposits is usually quite small, 1 cm, its overall influence is minimal [7].

The rate of addition of BOD to the free flowing water was evaluated by Camp [35] and was termed, m. "In situ measurements of this rate involve the submersion of a bell jar device on the bottom and then measuring the oxygen uptake over time. Laboratory measurements are conducted by removing a sample of the river bottom (preferably undisturbed), placing the sample in a large vessel with oxygenated water. DO reduction overtime is a measure of the uptake of the bottom muds [70]. Numerous investigations have been involved in measuring this rate; Baity [71], Davison and Hanes [72], Hanes and Irvine [73], McDonnell and Hall [74, 75], Mills [76], Oldaker et al. [77], Rudolfs [78], and Fair et al. [69]. Thomann [70] summarized several of these studies to present typical values for various classifications of river bottoms and presented in Table 2. In order to obtain S_B in equation 23, the areal benthal oxygen deman, assuming complete vertical mixing of the overlying water, must be divided by the mean depth

$$S_B = \frac{O_2 \text{ uptake } (\text{gm/m}^2\text{-day})}{H} \qquad (27)$$

Correction for temperature variations can be made by

$$(S_B)_T = (S_B)_{20} \times 1.065^{T-20} \qquad (28)$$

for temperature ranges of 10-30°C. Below 10°C the effect of S_B decreases faster than represented by equation 28 and approaches zero at temperatures from 0 to 5°C [70].

The affect of depth of the sludge deposits has been debated, with many contradictory results. Bennett and Rathburn [2] reviewed several studies and reported McDonnell and Hall's [75] conclusion that the consumption rate was independent of the depth of the deposits. Baity [71]

Table 2. Average Values of Oxygen Uptake of River Bottoms

Bottom Type and Location	Uptake (gms O_2/m^2-day) @ 20°C Range	 Approx. Average
Sphaerotilus--(10 gm dry wt./m^2)	---	7
Municipal Sewage Sludge--Outfall Vicinity	2-10.0	4
Municipal Sewage Sludge--"Aged" Downstream of Outfall	1-2	1.5
Cellulosic Fiber Sludge	4-10	7
Estuarine mud	1-2	1.5
Sandy bottom	0.2-1.0	0.5
Mineral soils	0.05-0.1	0.07

and Fair et al. [69] found that the DO uptake rate, ω, was dependent on the depth, d_m, of the deposit

$$\omega = a_1 d_M^{0.485} \qquad (29)$$

where a_1 is a constant.

Algal and Vascular Plant Influences

The presence of benthic algae, phytoplankton, and aquatic vascular plants in a river system have several influences on the dissolved oxygen balance, either directly or indirectly: 1) they can increase the DO concentrations during the day through the process of photosynthesis, 2) they can decrease the DO concentration at night when the process of respiration predominates, 3) they can uptake nutrient, e.g. ammonia, which would possibly lower the oxygen level through the nitrification process, and 4) if they become too abundant, they can "choke" the river bed and affect the hydraulics of the river thus altering the natural stream reaeration mechanism. The degree to which these influences are imposed on the system is dependent on the quantity and types of algae or vascular plants present. In conjunction with each other, the former two processes develop a diurnal variation in the DO concentration with the highest levels at midday during periods of maximum sun intensity with minimum values of DO during predawn hours.

The process of photosynthesis occurs in those organisms which contain light absorbing pigments which are capable of utilizing sunlight in an electron transport series to form organic compounds in cell synthesis from inorganic substances, primarily carbon dioxide and water, with oxygen being liberated in the process. The most common pigments associated in photosynthesis are the chlorophylls; a, b, and c. Other light absorbing pigments are carotenoids, phycocyanin, and phycoerythrin. Each of these groups of pigments are capable of absorbing wavelengths of light over specific bands between the range of 400 to 700 nm [79]. The latter groups of pigments, along with chlorophylls a and b are called accessory pigments, in that upon absorbing the energy they transfer it to chlorophyll a, which is the primary location of photosynthesis in the cell. The predominant forms of chlorophyll a which carry on photosynthesis are P690 and P700 which are an extremely small fraction of the total chlorophyll normally present in the cell [80]. Each group of algae has its respective arrangement of these pigments. Diatoms (Chrysophyta) possess both chlorophyll a and c, green algae (Chlorophyta) contain chlorophyll a and b, while blue-green algae (Cyanophyta) possess only chlorophyll a. The arrangement of the accessory pigments varies with the specific type of algae. Some algae are capable of adapting their respective quantities of these pigments to optimize their absorption capabilities of light. This phenomenon has been called chromatic adaptation [81].

The rate at which photosynthesis proceeds within an aquatic system is dependent primarily on the sunlight intensity, but is also affected by cell age, nutrient levels, DO concentration, and water temperature. The concentration of chlorophyll within the cell is only limiting at low light intensities [82]. This author also states that "at light saturation, where the overall rate of photosynthesis is determined by the rates of enzymatic processes, it is by no means a simple matter to find any relation between the concentrations of the pigments active in photosynthesis and the rate of photosynthesis." This view has been supported by Parker [80] who indicates that the measurement of chlorophyll a in algae is at best a measure of algal biomass, but not productivity. Although this opinion is becoming more common, the reference of productivity to chlorophyll a content is still fairly common practice. In a review of autotrophic indices by Weber [83], the percentage of cell structure being represented by chlorphyll a ranged from 0.2% to 2.5% depending on environmental conditions and the types of algae. These values are substantiated by Collins [84] who indicates that the maximum percentage of cell structure under optimum environmental conditions would be between 2.5 and 3.0.

The maximum rate of photosynthesis, in terms of carbon fixation, based on chlorophyll content has been estimated to be approximately 13 mg carbon fixed per mg chlorophyll a under uptimum conditions [85]. Using Chlorella vulgaris under varying light conditions, Steeman Nielson [82] obtained the rates of 0.49 and 0.42 mg C fixed per mg chlorophyll per hour at the illumination of one calorie per m^2 per second. Myers and Krate [86] found that 1.2 mg C is assimilated per mg chlorophyll a using the blue-green alga Anacystis nidulans under similar light conditions.

The rate of photosynthetic respiration varies widely depending on environmental conditions from 0.5 gm/m^2/day to greater than 10 gm/m^2/day [70]. This author further noted a possible relationship between respiration and chlorophyll a.

$$R(mg/l/hr) = 0.001\ (\text{chlorophyll a})(\mu g/l) \qquad (30)$$

The reliability of the photosynthetic process as being beneficial to the dissolved oxygen balance has seriously been questioned. The debate centers around the availability of oxygen production during critical flow conditions. Imhoff and Fair [87] and Camp [28] feel that this process should not be relied on since its effects will not always be present at adequate levels during the warmer months when it is needed. The sensitivity of this process to environmental variables; e.g. turbidity, cloud cover, and temperature, have shown that it should not be depended upon [88]. These authors have further studied this phenomenon and have concluded that in streams where the primary source of photosynthesis is associated with benthic algae and rooted vascular plants, that the overall effect of photosynthesis is detrimental to the dissolved oxygen balance. They base these findings on the premise that the dissolved oxygen which is produced is in a different volume of river water than the DO which is utilized during periods when respiration predominates. Therefore, the DO level can be reduced to an extremely low level. They found that in rivers which are deep and slow, phytoplankton are the predominant form of photosynthesizers. The oxygen which is produced and utilized by them remains in the same mass of water, and the DO concentration does not decrease to abnormal levels, although the spatial location does vary through time. Merritt et al. [89] feel that whether or not this process can be depended upon, its importance dictates the includance in all oxygen balance studies of streams where diurnal variations in DO occur. This philosophy is supported by Hull [34] who states that the controversy lies with the significance of the process and not whether it should be included in the simulation of the DO balance. An example of the significance of the oxygen generation through photosynthesis versus surface reaeration was shown by Camp [35], where it was found that 67 percent of the DO was furnished by photosynthesis, and that this process must be considered. Most of the more recent models which have been developed include an expression for the photosynthetic process [9, 28, 51, etc.].

Many methods have been developed for measuring the influence of the photosynthetic process on the dissolved oxygen balance. Thomann [70] summarizes several of these to be: 1) light and dark bottle technique, 2) the use of photosynthetic chambers, 3) evaluation of diurnal DO measurements, and 4) the use of radioactive carbon techniques. The light and dark bottle technique consists of collection of water samples at several distances and depths at a point in a river to properly represent the cross section. Each of the samples is split into three portions; one is placed in a transparent glass bottle, another in a glass bottle which is opaque, and a third is used for DO analysis. The light and dark bottles are incubated at the point of collection in the river for a specified period. Upon the completion of the incubation period, these samples are analyzed for dissolved oxygen. The rate of the photosynthetic process is

$$P = C_{lf} - C_{df} \tag{31}$$

and the respiration rate is

$$R_d = C_{di} - C_{df} \tag{32}$$

where,

C = dissolved oxygen concentration, mg/l

P = photosynthetic rate

R = gross respiration rate

l = light bottle

d = dark bottle

i = initial DO concentration

f = final DO concentration

Several problems with this technique have been brought out by Symons [32] as being an unnaturally large surface-to-volume ratio in the bottles, the lack of mixing in the bottles, inhibition of vertical migration of plankton, the lengthy incubation period, and the actual removal of the water samples from the river which might alter the physiological capabilities of the plankton. Another limitation to this technique is that it measures only planktonic influences and not benthic.

Several of these restrictions have been overcome with the use of photosynthetic chambers. A study by Stay et al. [90] showed that the chambers can separate the effects of photosynthesis, diffusion, and respiration according to their relationship to benthic and planktonic organisms. Procedures for determining the actual rates is similar to those used in the light and dark bottle technique.

Analysis of the diurnal DO measurements has mainly centered around work performed by Odum [91] and has been called the "upstream-downstream" method. The basis for the procedure is evaluating the differences of the dissolved oxygen balance at the beginning and end of a stream reach. A plot is constructed of the changes in DO against time. The area under this curve for the period between sunrise and the time near sunset when that DO concentration is repeated, multiplied by the flow of the stream, and divided by the surface area between the two stations, gives the net rate of oxygen production per unit area. By dividing this value by the mean depth, the rate is translated into terms of concentration. The respiration rate can be determined in a similar fashion by plotting the DO concentration during the nighttime hours against time. It is assumed that respiration and atmospheric reaeration are the only processes occurring and that their rates remain constant during this period. The rate of oxygen production by photosynthesis is determined from the difference between the observed net rate of oxygen production and the rate of respiration. It is assumed that respiration occurs at the same rate in the day as at night [92].

Radioactive carbon techniques involve the use of a radioactive isotope of carbon, and monitoring its uptake through carbon fixation in the photosynthetic process.

METHODS AND MATERIALS

Description of Study Area

The South River is located in the Shenandoah Valley of northern Virginia. It originates in the southwest corner of Augusta County and flows in a northeasterly direction to where it joins the North and Middle Rivers near Port Republic in Rockingham County. The river is characterized by a coarse-trellis drainage pattern having few feeder streams and a low gradient resulting in frequent meandering of the stream. The stream channel is relatively wide and shallow with variations between riffles and "pooled" areas occurring. A sandy to rocky stream bed prevails through most of its length. Seasonal variations in stream flow occur through gradual transitions.

The drainage area of the South River along its 52.3 mile length is approximately 235.9 square miles. Much of the watershed is mountainous forests with the bottom lands converted to agricultural use. A U.S. Geological Survey gaging station near Waynesboro (No. 0162600) indicates an average daily flow of 134 cfs at that point with a projected 7-day-10-year low flow of 27 cfs. Based on the low flow conditions, areal contribution of surface water is approximately 0.18 cfs per square mile during these periods [94].

Although there are several small communities along the river, the city of Waynesboro is the only one which has developed into an industrial center. This city, with a population of 16,707, has several major industries located within its city limits; a synthetic fiber manufacturing plant owned by E. I. DuPont Co. and Crompton-Shenandoah Co., a fabric dye processing plant, as well as numerous smaller industrial firms. The city of Waynesboro's waste water treatment plant, along with the DuPont Co. and Crompton-Shenandoah Co. are the principal sources for direct waste water discharges to the South River. Throughout most of the remainder of the watershed there are moderate levels of diffuse source pollution such as agricultural runoff. Several recent studies have been made in attempts to delineate the differences in point and non-point sources of pollution with the South River basin [94 and 95].

The city of Waynesboro is serviced by a separate sewerage system, although there are many storm sewers which are connected to the sanitary sewers. This significantly increases the sewage flow during wet periods due to infiltration and the storm sewer connections. There are approximately 12,000 domestic connections and 10 industrial sources. The average daily flow has been around 2.6 mgd, increasing to 3.5-4.0 mgd during wet weather, which approaches the design capacity of 4.0 mgd. The treatment plant consists of a barscreen, two comminutors, degritter, raw sewage lift station, venturi meter with two high-rate stone media trickling filters and 100 percent recirculation capability, two secondary sedimentation tanks, chlorination, a primary and secondary heated sludge digester, vacuum filter, sludge drying beds, and a retention basin for overflows during peak flow periods [93]. Plant operation maintains an effluent quality within the design capabilities. Current BOD_5 loadings are around 287 pounds per day.

The E. I. DuPont Co. manufactures three synthetic fibers: cellulose acetate, orlon acrylic, and lycra spandex. Their waste treatment facilities are of the activated sludge type and contain the following unit operations: retention, neutralization, blending, and preaeration, cooling, mixing with recycled sludge, aeration in four aeration tanks, clarification in four clarifiers preceding discharge to the river [93]. The daily flow rate ranges from 6.6 to 9.1 with a design capacity of approximately 10.7 mgd. Their sanitary waste is discharged to the city sewerage system. There are four separate discharges from the plant, with three of these discharging cooling water, resulting in only one source of loading on the river. Approximately 770 pounds per day of BOD_5 is being discharged.

The Crompton-Shenandoah Co. is engaged in the dyeing and finishing of pile fabrics made of natural and synthetic fibers. Their waste treatment facilities are comprised of an equalization basin, an aerated lagoon, and a final clarifier. Their discharge rate is about 2.0 mgd and is discharged through a single outfall having an average BOD_5 loading of 50 pounds per day.

Under previous provisions [18] various loading rates have been designated for most of the constituents of these three discharge sources. These allowable loading rates were set on the basis of maintaining a dissolved oxygen level of 5.0 ppm and meeting other applicable water quality standards. The flow rates utilized in these determinations were based upon design capacities of the respective sources. Table 3 contains a listing of these provisions. The allowable loading rates for ammonia-N and organic nitrogen from E. I. DuPont Co. will be determined upon the completion of field studies on the South River being performed during the summer of 1975.

The South River has been divided into three stream segments in the Potomac-Shenandoah River Basin Water Quality Management Plan [93] under guidelines set by the U.S. Environmental Protection Agency. The upper South River from mile point 52.3 to 27.3 has been designated as effluent limitation in that existing water quality standards are being maintained throughout this section of the river. From river mile 27.3 to 7.3, the South River has been classified as a water quality segment due to violations in the water quality standards. It is in this area where the waste loadings of E. I. DuPont Co., Crompton-Shenandoah Co., and the Waynesboro STP occur. The primary problems associated with this area are high values of ammonia-nitrogen, total (Kjeldahl) nitrogen, phosphorus, fecal coliform, and low dissolved oxygen levels during low flow periods. The remainder of the South River, river mile 7.3 to 0.0, has been designated effluent limitation.

Model Description

The water quality model used for the sensitivity analysis of the South River was the QUAL-II, developed by Water Resources Engineers, Inc. for the U.S. Environmental Protection Agency [96]. The version of the QUAL-II which was utilized was the one applied to the Santee

Table 3. Summary of Allowable Waste Loadings for E. I. DuPont, Crompton-Shenandoah, and Waynesboro STP on the South River

Source	Flow (mgd)	BOD_5[a]	NH_3-N[a]	Org-N[a]	Total Phosphorus
E. I. Du Pont Co.	10.7	600	---[b]	---[b]	84
Crompton-Shenandoah	2.0	200	23	20	10
Waynesboro STP	4.0	250	66	66	120

[a] Units are in pounds/day.

[b] Loadings which have not yet been determined.

River Basin in South Carolina. This version of the model was further modified by Meta Systems, Inc. to include an option for the inclusion of organic nitrogen. Provisions have also been incorporated by the USEPA-Region 2 District Office to account for incremental runoff along the stream reaches.

The QUAL-II water quality model is designed to simulate the behavior of chlorophyll a, nitrogen (organic, ammonia, nitrite, and nitrate), phosphorus, carbonaceous BOD, benthic oxygen demand, dissolved oxygen, coliforms, and conservative substances under steady-state conditions. Any combination of these model components can be simulated depending on the type of analysis being performed. If algal concentrations are being simulated and either nitrate or phosphorus or both are not being simulated, the program assumes that the parameters not being simulated are not limiting. The following discussion of the model is based around information from the Computer Program Documentation for the Stream Quality Model QUAL-II [96].

The mathematical expressions utilized in the QUAL-II were derived from an integration of the advection-dispersion mass transport equation for all water quality constituents being modeled. The equation includes the effects of advection, dispersion; individual constituent changes, and sources and sinks; for any constituent, c, and can be expressed as

$$(A_x d_x)\ \frac{\partial c}{\partial t} = \frac{\partial(A_x D_L \frac{\partial c}{\partial x})}{\partial x}\, dx - \frac{\partial(A_x \bar{U}_c)}{\partial x}\, dx + (A_x d_x)\ \frac{dc}{dt} \pm S \qquad (33)$$

where,

c = concentration

x = distance

t = time

A_x = cross sectional area

D_L = dispersion coefficient

$\bar{U}$ = stream velocity

s = source or sink

The various mathematical expressions used to represent the models components are as follows:

Dissolved oxygen:

$$\frac{dO}{dt} = K_2(O^*-O) + (a_3\mu - a_4\rho)A-K_1L_1-K_4/A_x - a_5\ \beta_1\ N_1 - a_6\beta_2N_2 \qquad (34)$$

where,

O = dissolved oxygen concentration, mg/l

O^* = the saturation concentration of dissolved oxygen at the local temperature and pressure, mg/l

a_3 = the rate of oxygen production per unit of algae (photosynthesis), mgO/mgA.

a_4 = the rate of oxygen uptake per unit of algae respired, mgO/mgA

a_5 = the rate of oxygen uptake per unit of ammonia oxidation, mgO/mgN

a_6 = the rate of oxygen uptake per unit of nitrite nitrogen oxidation, mgO/mgN

K_2 = the reaeration coefficient, day^{-1} (base e)

μ = the local specific growth rate of algae, day^{-1}

ρ = the local algal respiration rate, day^{-1}

A = algal biomass, mg/l

K_1 = the decay rate for carbonaceous BOD, day^{-1} (base e)

L_1 = the concentration of carbonaceous BOD, mg/l

K_4 = constant benthic uptake, mg/day/ft (base e)

A_x = average stream cross sectional area, ft^2

β_1 = rate constant for the biological oxidation of ammonia nitrogen, day^{-1} (base e)

N_1 = concentration of ammonia nitrogen as nitrogen, mg/l

β_2 = rate constant for the biological oxidation of nitrite nitrogen as nitrogen, day^{-1} (base e)

N_2 = concentration of nitrite nitrogen as nitrogen, mg/l

Carbonaceous BOD:

$$\frac{dL_1}{dt} = -K_1L_1 - K_3L_1 \tag{35}$$

where,

K_3 = the rate of loss of carbonaceous BOD due to settling, day^{-1} (base e)

Benthic Oxygen Demand:

$$\frac{dL_2}{dt} = K_4/A_x \tag{36}$$

where,

L_2 = benthic oxygen demand, mg/l

Organic Nitrogen:

$$\frac{dN_o}{dt} = -\ \beta_oN_o \tag{37}$$

where,

N_o = concentration of organic nitrogen, mg/l

β_o = rate constant, day^{-1} (base e)

Ammonia Nitrogen:

$$\frac{dN_1}{dt} = a_1\rho A - \beta_1 N_1 + \sigma_3/A_x + \beta_o N_o \qquad (38)$$

where,

a_1 = fraction of respired algal biomass which is resolubilized as ammonia nitrogen by bacterial action, $\frac{mgN}{mgA}$

σ_1 = benthos source rate of ammonia nitrogen, $\frac{mgN}{day\text{-}ft}$

Nitrite Nitrogen:

$$\frac{dN_2}{dt} = \beta_1 N_1 - \beta_2 N_2 \qquad (39)$$

Nitrate Nitrogen:

$$\frac{dN_3}{dt} = \beta_2 N_2 - a_1\mu A \qquad (40)$$

Phosphorus:

$$\frac{dP}{dt} = a_2\rho A - a_2\mu A + \sigma_2/A_x \qquad (41)$$

where,

a_2 = fraction of algal biomass that is phosphate phosphorus, $\frac{m\ P}{mg\ A}$

σ_2 = benthos source rate for phosphorus, $\frac{mgP}{day\text{-}ft}$

P = phosphorus concentration, mg/l

Chlorophyll a:

Chlorophyll a is considered to be directly proportional to the concentration of phytoplanktonic algal biomass. Algal biomass is converted to chlorophyll a through

$$C = a_o A \tag{42}$$

where,

a_o = conversion factor

C = chlorophyll a concentration, μg/l thus the growth and production of algae (chlorophyll a) is

$$\frac{dA}{dt} = \mu A - \rho A - \frac{\sigma_1}{D} A \tag{43}$$

where

σ_1 = local settling rate for algae, ft/day

D = average stream depth, feet

The local specific growth rate of algae is coupled to the availability of required nutrients and light.

$$\mu = \hat{\mu} \frac{N_3}{N_3 + K_N} \cdot \frac{P}{P + K_p} \cdot \frac{1}{\lambda D} \ln \frac{K_L + L}{K_L + L_e^{-\lambda D}} \tag{44}$$

where,

$\hat{\mu}$ = maximum specific growth rate, day^{-1}

L = local intensity of light, Langleys/day

λ = light extinction coefficient in the fiver, ft^{-1}

K_N, K_p, K_1 = empirical half-saturation constants; mg/l, mg/l, Langleys/day

Coliforms:

$$\frac{dF}{dt} = -K_5 F \tag{45}$$

where,

K_5 = coliform die-off rate, day^{-1} (base e)

F = coliform concentration, 1000/100ml

All temperature dependent reactions are converted to ambient conditions by means of

$$X_T = X_{T_S} \, \theta^{(T-T_S)} \tag{46}$$

where,

X_T = value of the variable at local temperature, T

X_{T_S} = value of the variable at standard temperature, T_S

θ = empirical constant for each system variable

The QUAL-II model can be applied to any one-dimensional river system. The river is first subdivided into reaches, having "uniform" hydraulic properties. Each is further subdivided into elements of uniform distance, such that all reaches contain an integer number of elements. These elements are the computational increments which the model uses for the step wise integration of the mathematical equations. Hydraulic data, reaction rate coefficients, initial conditions, and incremental runoff are assumed constant for all computational elements within a reach.

The structure of the QUAL-II model consists of one main program, QUAL 2, and twenty subroutines. Details on the individual subroutines and the main program can be found in "Computer Program Documentation for the Stream Quality Model, QUAL-II"[96].

QUAL-II Application to the South River

In applying the QUAL-II water quality model to the South River, those subroutines which have either a direct or indirect relationship to the dissolved oxygen balance and the nitrification process were utilized. Two series of analyses were performed; the first followed the format that was used by the U.S. Environmental Protection Agency in their modeling of the South River, and the second incorporated the algae and phosphorus subroutines along with the initial series. The first set of sensitivity analyses were made to evaluate the existing application techniques, while the latter was performed to find if the model was sensitive to influences from the presence of algal biomass.

The information of the watershed which is required to operate the model is found in Table 4. The values of these parameters are primarily those which were set by the U.S. Environmental Protection Agency through their calibration and verification analysis between the data and the structure of the model. A brief description of how these values were devised, according to the respective types, is as follows:

Watershed Characteristics--Physical

The South River, from mile point 24.3 to the confluence with the Middle and North Rivers, was divided into twenty stream reaches each with relatively consistent hydraulic properties. The first reach begins immediately above the influences of the discharges from E. I. DuPont Co. and Crompton-Shenandoah Co. Since there are no major

Table 4. Data Requirements for Operation of the QUAL-II Model

Parameter Name	Units	Value(s)
Watershed Characteristics - Physical		
Number of reaches	-	20
Number of headwaters	-	1
Number of waste loads	-	3
Computational element size	mile	0.1
Critical flow areal contribution	cfs/sq.mi.	0.18
Hydraulic Characteristics		
Mannings roughness coefficient	-	0.030
Velocity calculations, $V = aQ^b$		
example, Reach 1, a	-	0.2916
b	-	0.3120
Depth calculations, $D = aQ^b$		
example, Reach 1, a	-	0.177
b	-	0.469
River System Characteristics		
Headwater:		
Flow	cfs	27.0
Temperature (2)	$^oF(^oC)$	77.0(25.0)
Dissolved Oxygen (2)	mg/l (%sat)	8.4(100.0)
BOD (ultimate)	mg/l	1.5
Organic Nitrogen	mg/l	0.25
Ammonia Nitrogen	mg/l	0.10
Nitrite Nitrogen	mg/l	0.01
Nitrate Nitrogen	mg/l	0.47
Phosphate-phosphorus	mg/l	0.03
Chlorophyll a	ug/l	5.00
Side Tributaries:		
Drainage area per reach	sq. mi.	
example, Reach 1		5.00
Temperature (2)	$^oF(^oC)$	77.0(25.0)
Dissolved Oxygen (2)	mg/l (%sat)	7.5(90.0)
BOD (ultimate)	mg/l	1.5

Table 4--Continued

Parameter	Units	Value(s)
Side Tributaries (cont)		
Organic Nitrogen	mg/l	0.25
Ammonia Nitrogen	mg/l	0.05
Nitrite Nitrogen	mg/l	0.01
Nitrate Nitrogen	mg/l	0.60
Phosphate-Phosphorus	mg/l	0.03
Chlorophyll a	ug/l	5.00
Reaction Rates		
Deoxygenation coefficient, K_1 (1)	day^{-1}	0.6,0.5,0.4,0.3
Carbonaceous BOD settling rate, K_3	day^{-1}	0.0
Reaeration coefficient, K_2	day^{-1}	
Predictive equation (O'Connor, 1958) $K_2 = \frac{(D_m v)^{0.5}}{D^{1.5}} \times 86{,}400$		
Predetermined, $K_2 = aQ^b$		
example, Reach 1, a		0.990
b		0.463
Organic nitrogen reaction rate, KORG	day^{-1}	0.08
Ammonia nitrogen reaction rate, KNH_3	day^{-1} (1)	1.2,1.0
Nitrite nitrogen reaction rate, KNO_2	day^{-1}	5.0
Benthos source rate of BOD	mg/day-ft	0.0
Point Source Characteristics		
DuPont		
Flow	cfs	16.5
Dissolved Oxygen	mg/l	2.0
BOD (ultimate)	mg/l	44.0
Organic nitrogen	mg/l	12.95
Ammonia nitrogen	mg/l	11.48
Nitrite nitrogen	mg/l	0.01
Nitrate nitrogen	mg/l	0.98
Phosphate-phosphorus	mg/l	0.94
Crompton-Shenandoah		
Flow	cfs	3.08
Dissolved Oxygen	mg/l	4.0
BOD (ultimate)	mg/l	10.3
Organic nitrogen	mg/l	1.2
Ammonia nitrogen	mg/l	1.4

Table 4--Continued

Parameter	Units	Value(s)
Crompton-Shenandoah (cont)		
Nitrite nitrogen	mg/l	0.10
Nitrate nitrogen	mg/l	1.90
Phosphate-phosphorus	mg/l	0.60
Waynesboro STP		
Flow	cfs	6.16
Dissolved Oxygen	mg/l	4.00
BOD (ultimate)	mg/l	61.1
Organic nitrogen	mg/l	2.00
Ammonia nitrogen	mg/l	10.00
Nitrite nitrogen	mg/l	0.20
Nitrate nitrogen	mg/l	4.00
Phosphate-phosphorus	mg/l	3.60
<u>Coefficients Related to Algal and Bacterial Activity</u>		
Oxygen Uptake by organic nitrogen	mg O/mg N	0.0
Oxygen Uptake by ammonia oxidation (2)	mg O/mg N	3.22
Oxygen Uptake by nitrite oxidation (2)	mg O/mg N	1.11
Oxygen Production by algae	mg O/mg A	0.021
Oxygen Utilization by algae	mg O/mg A	0.016
Nitrogen Content of algae	mg N/mg A	0.060
Phosphorus Content of algae	mg P/mg A	0.021
Algal maximum specific growth rate	day^{-1}	2.40
Algal respiration rate	day^{-1}	0.12
Nitrogen half saturation constant	mg/l	0.05
Phosphorus half saturation constant	mg/l	0.01
Light half saturation constant	Langleys/min.	0.156
Average light intensity	Langleys/min.	450
Ratio of chlorophyll a to algal biomass	ug Chl-a/mg A	15.0
Algal settling rate	ft/day	0.0
Light extinction coefficient	foot^{-1}	0.60

(1) Values decreased in a downstream direction.
(2) Values different than USEPA original application.

tributaries to the South River only one headwater was designated. The point sources attributable to E.I. DuPont Co., Crompton-Shenandoah, and the Waynesboro waste water treatment plant are the three primary sources of pollutant loadings and are being included for allocation analysis of waste loadings. A computational element distance of 0.1 mile was set in accordance with the requirement of an integer number of elements in each stream reach. The areal contribution of surface flow during critical flow conditions was found by dividing the area of the watershed (150 sq. mi.) by the 7-day-10 year low flow of 27 cfs.

Hydraulic Characteristics

The Mannings roughness coefficient of the stream bed was set at 0.030 being representative of streams of "regular" flow conditions with some stones and weeds present. Velocity and depth relationships to the corresponding flow conditions were determined by manual stream flow measurements by the Virginia State Water Control Board (SWCB). These measurements were used for determination of the length and locations of the stream reaches.

River System Characteristics

Headwater: The seven day-10 year low flow was calculated by the U.S. Geological Survey using the log Pearson type III frequency analysis based on data over a 23 year period collected at gaging station No. 0162600 near Waynesboro. The temperature of the headwater flow was set at 77°F being representative of stream conditions during critical flow months. The dissolved oxygen was set at 8.4 mg/l indicating 100 percent saturation conditions. The concentration levels of organic nitrogen (0.25), ammonia nitrogen (0.10), nitrite nitrogen (0.01), phosphate-phosphorus (0.03), and ultimate biochemical oxygen demand (1.5) were set based on sampling data collected by the SWCB during the summers of 1973 and 1974 at Route 664 upstream of the city of Waynesboro. Based on studies performed by DuPont, the ultimate BOD was found to be the BOD_5 multiplied by a conversion factor of from 2.0 to 5.0 and was set at 3.0 by the USEPA [14]. This conversion of the 5 day BOD to an ultimate BOD was utilized in all calculations of the BOD loadings. The chlorophyll a concentration of 5.0 mg/l was determined based on levels found to be representative of streams with "normal" background levels of nutrients.

Side Tributaries: The drainage area for each of the stream reaches was determined from an analysis of topographic maps by the SWCB and USEPA. The waters of the tributaries were set at 77°F to parallel that of the headwaters. Dissolved oxygen was set at approximately 90% saturation to properly represent conditions of streams receiving minor diffuse source pollution. This was the same reasoning in the determination for concentrations of BOD, ammonia-nitrogen, organic nitrogen, nitrite nitrogen, nitrate nitrogen, phosphate-phosphorus, and chlorophyll a.

Reaction Rates

The deoxygenation coefficients, K_1 at 20°C (0.6, 0.5, 0.5, 0.3) found by the USEPA to give the "best fit" of the data during their calibration of the model to the system. The decrease in rate in a downstream direction not only formed the "best fit" but follows the principal of decreasing "K" rates in a flowing system due to the decrease in readily oxidizable substrate [7]. Using data collected by DuPont during the summer months of 1973 and 1974, a linear regression analysis following the techniques developed by Theriault [20] resulted in an overall stream length deoxygenation rates varying from 0.289 to 0.609 with a mean value of 0.455 with a standard deviation of 0.111. These values correspond fairly well with the range developed by "best fit" by the USEPA. The reaction rates for organic nitrogen, ammonia nitrogen, and nitrite nitrogen were determined by the USEPA in a similar approach as was used for K_1 yielding 0.08, 1.2-1.0, and 5.0, respectively. Through linear regression of ammonia nitrogen and organic nitrogen data collected by the SWCB during the summer months of 1973 and 1974, a mean ammonia nitrogen oxidation rate of 0.362 was found with a standard deviation of 0.091 (range 0.217 to 0.495 at 20°C); a mean reaction rate for organic nitrogen was calculated to be 0.043 with a standard deviation of 0.023 (range 0.015 to 0.069). In determining the oxidation rate of ammonia nitrogen, consideration was not made for the production of ammonia through the decomposition of organic nitrogen, since its rate was so small and the fact that not all of the organic nitrogen was converted to ammonia nitrogen. The reaeration coefficient, K_2, for each stream segment was calculated in either of two ways. Sixteen of the stream reaches had their values of K_2 calculated by application of O'Connors and Dobbins' [39] predictive equation. The remaining four reaches (1, 3, 4 and 10) utilized the equation

$$K_2 = aQ^b \tag{47}$$

where,

a = coefficient of reaeration

b = exponent of reaeration

Q = stream flow, cfs

This equation was applied to these stream reaches since it yielded better correlation to natural data during the calibration analysis by the USEPA. The use of O'Connor and Dobbins formula for reaeration prediction by the USEPA was based on calibration analysis and past experience with its application. The settling rate of carbonaceous BOD, K_3, was set at 0.0 based on the existing levels of treatment which are incorporated at the various sources. This treatment theoretically removes nearly all of the settleable solids in the effluent which normally are the fraction of BOD which settle out and form benthal deposits. Corresponding to this theory, the benthal source rate of BOD, m, S_B, or K_4, has been initialized at 0.0 signifying that there are no existing benthal deposits.

Point Source Characteristics

The flow rates of the various point sources are based upon the design capacity of their respective treatment facilities according to their NPDES permits. The chemical characteristics are based upon samples collected by the USEPA, SWCB, and the entities themselves with the following exceptions: Crompton-Shenandoah Co. has their levels of organic nitrogen, ammonia nitrogen, and phosphate-phosphorus based on maximum levels which can be discharged under provisions of their NPDES permit. This same basis was used with the concentrations of organic nitrogen and phosphate-phosphorus for the Waynesboro waste water treatment plant.

Coefficients Related to Algal and Bacterial Activity

Since the breakdown of organic nitrogen is primarily a hydrolytic reaction, there was considered to be no oxygen utilization in the process. Ammonia oxidation by Nitrosomonas on a stoichimetric basis utilized 3.43 mg/l of oxygen per mg ammonia nitrogen. However, it was found that due to this being a biological reaction and not being 100 percent efficient, only 3.22 mg of oxygen were utilized [52]. Due to the same principle concerning the oxidation of nitrite by Nitrobacter, the oxygen utilization was reduced from 1.14 mg oxygen uptake to 1.11 mg oxygen.

Due to lack of actual data concerning the algal populations in the South River and their respective behavior, values for those parameters used in the algal subroutine were estimated upon data collected from literature review. This data does not represent the system under study but does enable generalized definition of the values which could possibly occur in the South River. The values discussed below are representative of possible occurrences and are being used to develop a "controlled" set of values to be used later in the sensitivity analysis of the algal subroutine.

A common value for the ratio of chlorophyll a to algal cell biomass was found to be .015 or 1.5 percent [83, 84, 85]. Based on this value and the fact that the 1.31 mg of oxygen are produced per mg chlorophyll a [82] in a common Green algae, it was determined that approximately

0.021 mg oxygen would be produced per mg of algal biomass. Since this value represents the production of oxygen by a single species of algae, it must be understood that it is only an estimate and not necessarily representative of a natural heterogeneous community. A photosynthetic to respiration ratio for a stream would be 1.3, therefore this value was used to obtain the rate of oxygen utilization through respiration by algae as 0.016 mg oxygen per mg algal biomass. Again this is only an estimate and is being treated accordingly in its application within the model. A review of the various levels of nitrogen and phosphorus content in various classes of algae was presented by DiToro et al. [97], listing common values of 0.06 and 0.021 mg of nitrogen and phosphorus, respectively, per mg algal biomass. The value for nitrogen content was substantiated by Fogg et al. [79]. Both of these, along with Larsen et al. [98], also indicated that the maximum specific growth rate could be about 2.4 per day. DiToro and his colleagues also presented ranges for algal respiration rate, nitrogen half-saturation constants, and phosphorus half saturation constants with possible values of 0.12 per day, 0.05 mg/l, and 0.01 mg/l, respectively. The value of the respiration rate was approximated by using 0.005 $\text{day}^{-1}\,{}^{\circ}\text{C}^{-1}$ at 25°C of the system. The average light intensity was set at 450 Langley/day based on a typical value by Velz [17] for this approximate latitude and time of year. Based on this sunlight intensity, the light half saturation constant was calculated by multiplying the average sunlight intensity by a factor of 0.52. This factor was determined by data presented by Larsen et al. [98] who found that the total daily ratiation which one-half the maximum value of the fractional reduction in specific growth rate is achieved was 150 ly/day at a sunlight intensity of 288 ly/day.

Sensitivity Analysis of Existing Model Format--Series I

Sensitivity analysis was performed on the various reaction coefficients and the critical rate of discharge. Each of these variables were tested through a range of possible values for the system being simulated. These ranges were determined by analysis of the existing data or by values which were found to be representative in other studies. During each analysis, only that variable which is being analyzed was varied. This enables a direct comparison of outputs from the different variable values to be made. The model variables which were analyzed and the ranges in which they were tested are presented in Tables 5 and 6. The reaction coefficients related to oxygen demanding substances and those involved in the oxidation of nitrogen compounds along with the critical rate of discharge are listed in Table 5. The reaction rates were made to decrease in a downstream direction for the deoxygenation coefficient and the oxidation of ammonia nitrogen to represent the decrease in the substrate concentrations. The basis for the development of these variables ranges will be presented during the discussion of the results. The variations in the reaeration coefficients through the use of different prediction equations is listed in Table 6. Stream reaches 1, 3, 4, and 10 utilized the equation, $K_2 = aQ^b$, due to its better simulating the system during the USEPA's calibration analysis. Due to difficulties in adequate representation of these equations, a limitation of these equations as they apply to small streams was found by the USEPA. Therefore, they introduced a conditional equation for

Table 5. Input Variables Utilized in Sensitivity Analysis--Series I, of the South River, Virginia

Variable Name	Units	Symbol	Variable Range minimum	 common	 maximum
Deoxygenation Coefficient	day^{-1}	K_1	0.30 0.25 0.20 0.15	0.60 0.50 0.40 0.30[a]	0.80 0.70 0.60 0.50
Organic Nitrogen Reaction Rate	day^{-1}	KORG	0.04	0.08[a]	0.12
Ammonia Nitrogen Reaction Rate	day^{-1}	KNH_3	0.20 0.20	0.50 0.45	1.20 1.00[a]
Nitrite Nitrogen Reaction Rate	day^{-1}	KNO_2	1.00	5.00[a]	8.00
Carbonaceous BOD Sink Rate	day^{-1}	K_3	0.00[a]	0.03	0.05
Benthal Oxygen Demand	mg/day-ft	m or S_B	0.00[a]	5.30	15.91
Critical Rate of Discharge	cfs/sq.mi.	---	0.004	0.100	0.180[a]

[a] Values used by the USEPA in their calibration and verification analysis.

Table 6. Variations in Reaeration Coefficients, K_2, through Application of Different Predictive Equations on the South River, Virginia

Model	Reach Number									
	1*	2	3*	4*	5	6	7	8	9	10*
O'Connor and Dobbin [39]	5.679	2.523	3.595	7.860	0.912	6.095	2.476	1.854	1.268	1.702
Churchill, et al. [48]	5.679	1.140	3.595	7.860	0.583+	4.081	1.162	0.840	0.530	1.702
Owens, et al. [30]	5.679	2.706	3.595	7.860	0.755	8.341	2.658	1.859	1.159	1.702
Thackston [44]	5.679	1.004+	3.595	7.860	0.583+	1.523	0.960	0.792	0.635	1.702
Langbein & Durum [49]	5.679	1.004+	3.595	7.860	0.583+	2.960	0.960	0.792	0.635	1.702
Maximum Value	8.341	2.706	3.222	10.186	0.912	8.341	2.658	1.859	1.268	1.859
Minimum Value	1.523	1.004	0.962	1.947	0.583	1.523	0.960	0.792	0.635	0.792

*Reaeration coefficients predefined through application of $K_2 = aQ^b$, minimum and maximum values set corresponding to similar values generated by O'Connor and Dobbin formula.

+If $K_2 < 2.0$/depth, then $K_2 = 2.0$/depth.

Table 6--Continued

Model	Reach Number									
	11	12	13	14	15	16	17	18	19	20
O'Connor and Dobbin [37]	3.222	0.529	7.116	13.436	6.324	1.526	0.532	1.840	0.371	15.326
Churchill et al. [48]	1.931	0.436	5.192	13.162	4.362	0.800	0.416	0.841	0.355	14.625
Owens et al. [30]	3.781	0.436	10.186	22.954	8.826	1.431	0.416	1.845	0.355	26.855
Thackston [44]	0.962	0.436	1.947	4.858	1.819	0.800	0.416	0.783	0.355	5.030
Langbein and Durum [49]	1.597	0.436	3.728	8.832	3.432	0.800	0.416	0.783	0.355	9.388
Maximum Value	3.222	0.529	10.186	22.954	8.826	1.526	0.532	1.845	0.371	26.855
Minimum Value	0.962	0.436	1.947	4.858	1.819	0.800	0.416	0.783	0.355	5.030

the reaeration coefficient which stipulates that if K_2 is less than 2.0 divided by the mean depth, then K_2 is set equal to this latter value. The value of 2.0 was determined by studies performed by O'Connor, and enables the reaeration coefficient to be a greater value than would be predicted by the original predictive equations. Sensitivity analysis was performed on maximum and minimum values for each stream as determined by the five equations.

The loading rates of the three point sources which were used during the analysis are based upon data collected by the SWCB. The flow rates are based upon design capabilities of the respective facilities.

Sensitivity Analysis of the Algal Subroutine--Series II

Due to the lack of quantitative data concerning the algal population and how they interact in the South River ecosystem, theoretical data was obtained through the literature to represent those values for variables which are included in the algal subroutine. A listing of the variables used and the ranges which were found to possibly occur are listed in Table 7. Although these values do not accurately represent the South River, they do develop values in a similar magnitude as would be expected to be found, thus enabling a test of sensitivity of each of the variables.

Variations in Waste Load Allocations

Upon evaluating the sensitivity of the input variables previously mentioned, various loading rates from E. I. DuPont Co. and the city of

Table 7. Variables Utilized in Connection with Algal Subroutine.

Variable Name	Units	Symbol	Variable Range		
			minimum	common	maximum
Ratio of chlorophyll a to algal biomass	$\frac{\text{ug Chl-a}}{\text{mg A}}$	ALPHA0	2.000	15.000	30.000
Fraction of algal biomass which is nitrogen	mg N/mg A	ALPHA1	0.027	0.060	0.091
Fraction of algal biomass which is phosphorus	mg P/mg A	ALPHA2	0.004	0.021	0.033
Oxygen production per unit of algal growth	mg O/mg A	ALPHA3	0.009	0.021	0.865
Oxygen uptake per unit of algal growth	mg O/mg A	ALPHA4	0.007	0.016	0.670
Maximum specific growth rate of algae	day^{-1}	GROMAX	1.000	2.400	4.000
Algae respiration rate	day^{-1}	RESPRT	0.100	0.120	0.170
Light extinction coefficient	$foot^{-1}$	--	0.200	0.600	1.222
Nitrogen half saturation constant	mg/l	CKN	0.014	0.050	0.130
Phosphorus half saturation constant	mg/l	CKP	0.006	0.010	0.025

Table 7--Continued

Variable Name	Units	Symbol	Variable Range		
			minimum	common	maximum
Light half saturation constant	Langleys/min.	CKL	0.069	0.156	0.208
Light intensity	Langleys/day	--	200.000	450.000	600.000

Waynesboro waste water treatment plant were tested with those variables which were found to be sensitive in their influence within the model. The object of this exercise was to see what levels of pollutants would be allowable with respective variations in the sensitive variables. The variables which were tested, the deoxygenation rate, the ammonia nitrogen oxidation rate, and the reaeration rate were grouped together into three categories as before which are representative of the ranges which were found possible for these parameters. The groupings and respective values were derived from Tables 6 and 7. These three variables were tested together within these common categories in order to analyze the extreme influences which they would have through additive interactions between each other. Those chemical loadings for these two sources which were analyzed were ultimate biochemical oxygen demand, ammonia nitrogen, and organic nitrogen. It is these parameters which affect the dissolved oxygen balance through oxidation of ammonia nitrogen, or carbonaceous organics. The level of reduction with each of the variables was found by determining that concentration of the constituent which maintained dissolved oxygen level throughout the length of the South River of 5.0 mg/l allowed by the applicable state water quality standards. The chemical loading rates of Crompton-Shenandoah Co. were not tested due to their present attainment of effluent quality guidelines and to the fact that their loading of oxygen demanding substances was minimal compared to the other two point sources.

One assumption which was changed during this analysis was that the ultimate BOD for the city's waste water treatment plant effluent was set at 2.0 times the 5-day BOD, rather than 3.0 which was used by the USEPA. This change follows consideration of the waste involved and follows closer consensus of the literature. Due to variations in the ratio of ammonia nitrogen to organic nitrogen in the DuPont effluent, a standard of twice the ammonia nitrogen concentration was set for organic nitrogen.

RESULTS

Sensitivity Analysis--Series I

Presentation of the sensitivity analysis results is made in the form of two sets of graphs. The first of these relates the response of the simulation of the river system to application of the various sets of parameters which were listed in Tables 5 and 6. The abscissa represents the mile points along the river's length flowing in a downstream manner, with mile point 24.3 being the beginning of the simulation of the first reach and 0.0 being the point of confluence with the North and Middle Rivers. E. I. DuPont Co. discharges their effluent at mile point 24.2 and Crompton-Shenandoah Co. discharges their effluent at mile point 24.1. The city of Waynesboro waste water treatment plant discharges at mile point 22.5. The graph's ordinate represents the various chemical concentrations in milligrams per liter. These graphs are presented in Figures 1 through 13. Only graphs which depicted a difference in the concentration of dissolved oxygen, biochemical oxygen demand, and ammonia nitrogen are presented. Based upon these figures a ranking of the influence of these parameters on the DO is made in Table 8. The input parameters are ranked in order of decreasing effect on the DO (i.e., the first variable listed had the greatest effect and the last parameter the least effect). Corresponding to the applicable ranges of these parameters, the reaeration rate,

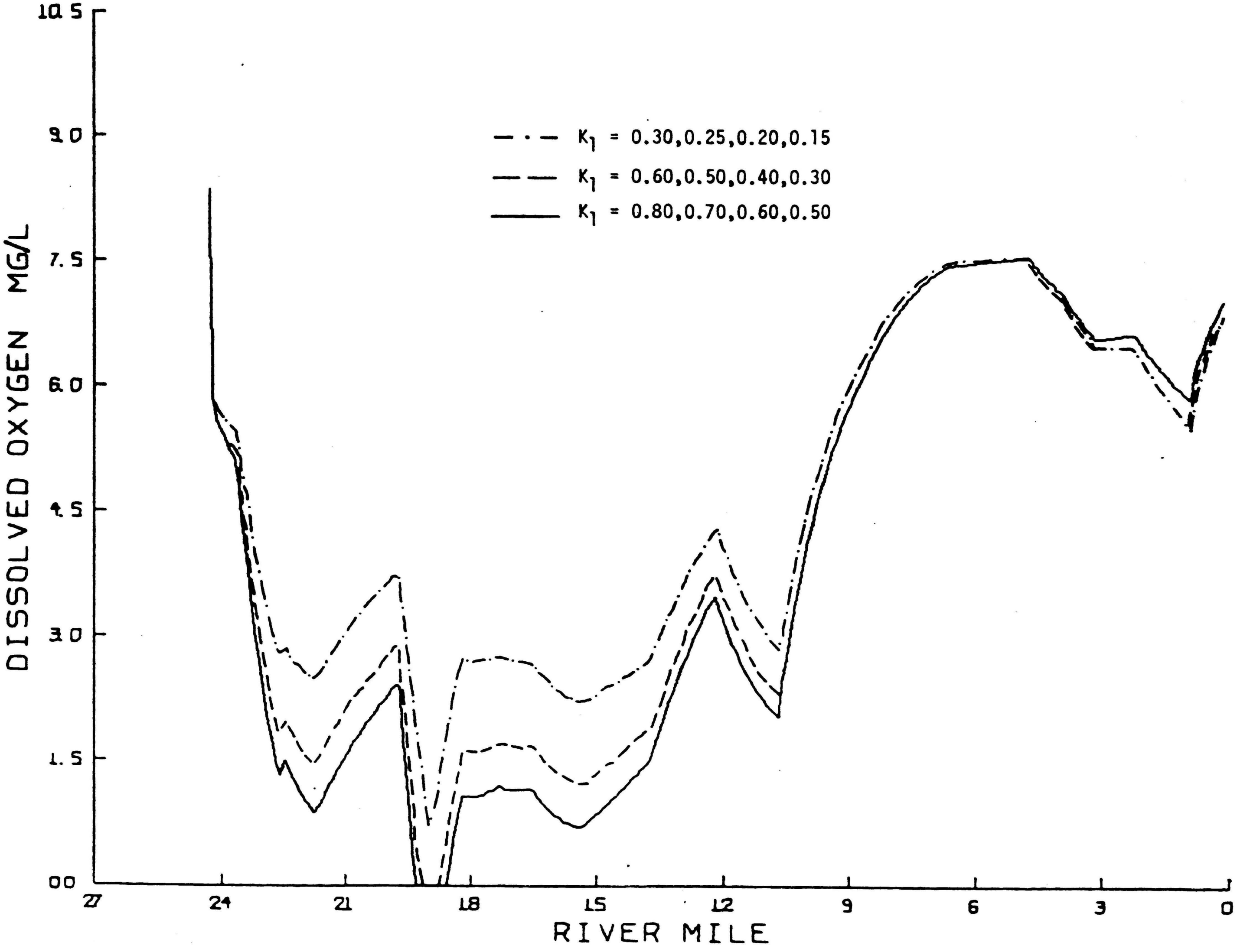

Figure 1. Sensitivity Analysis of the Deoxygenation Rate, K_1, Relating the DO Profile.

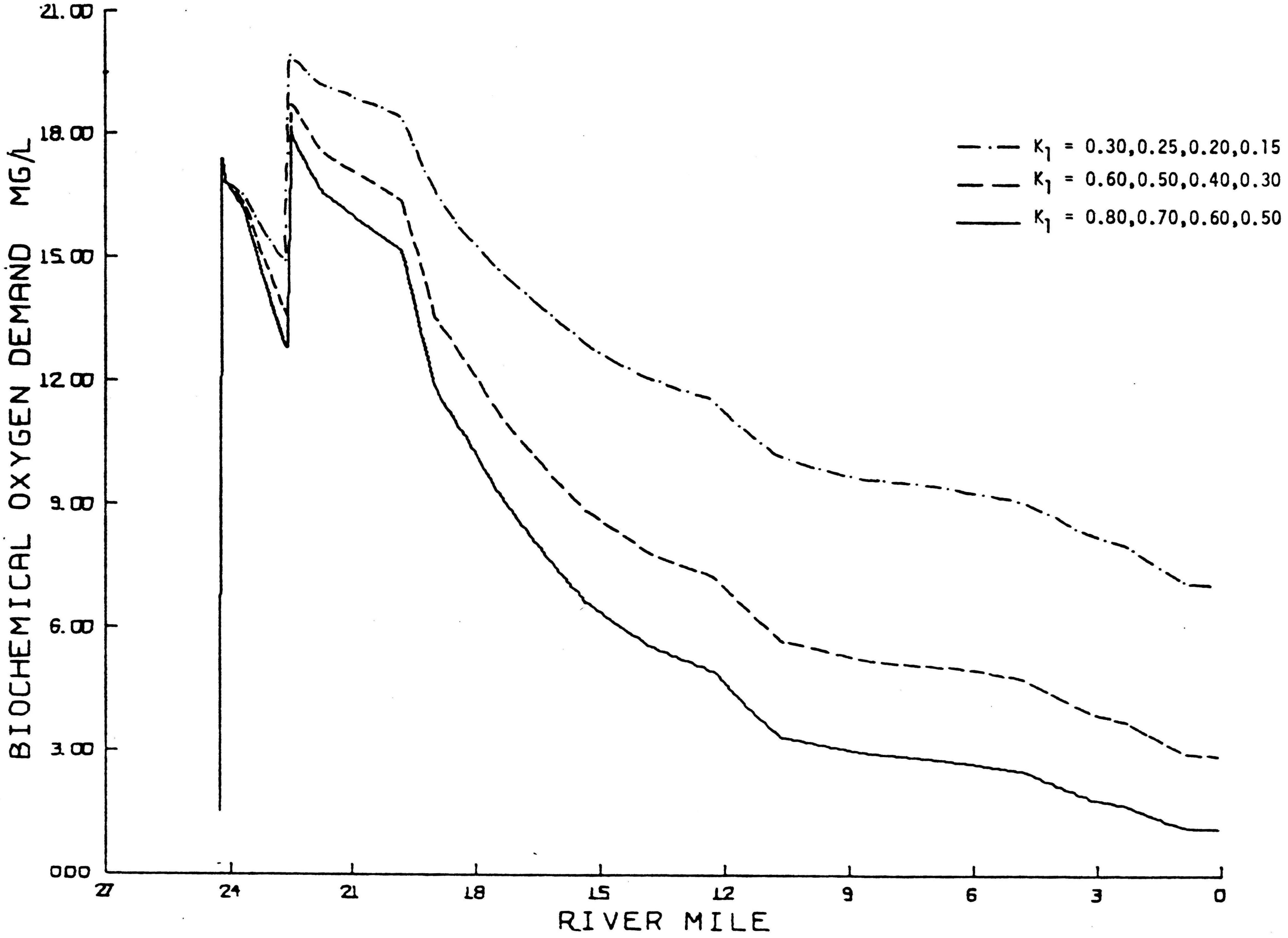

Figure 2. Sensitivity Analysis of the Deoxygenation Rate, K_1, Relating the BOD Profile.

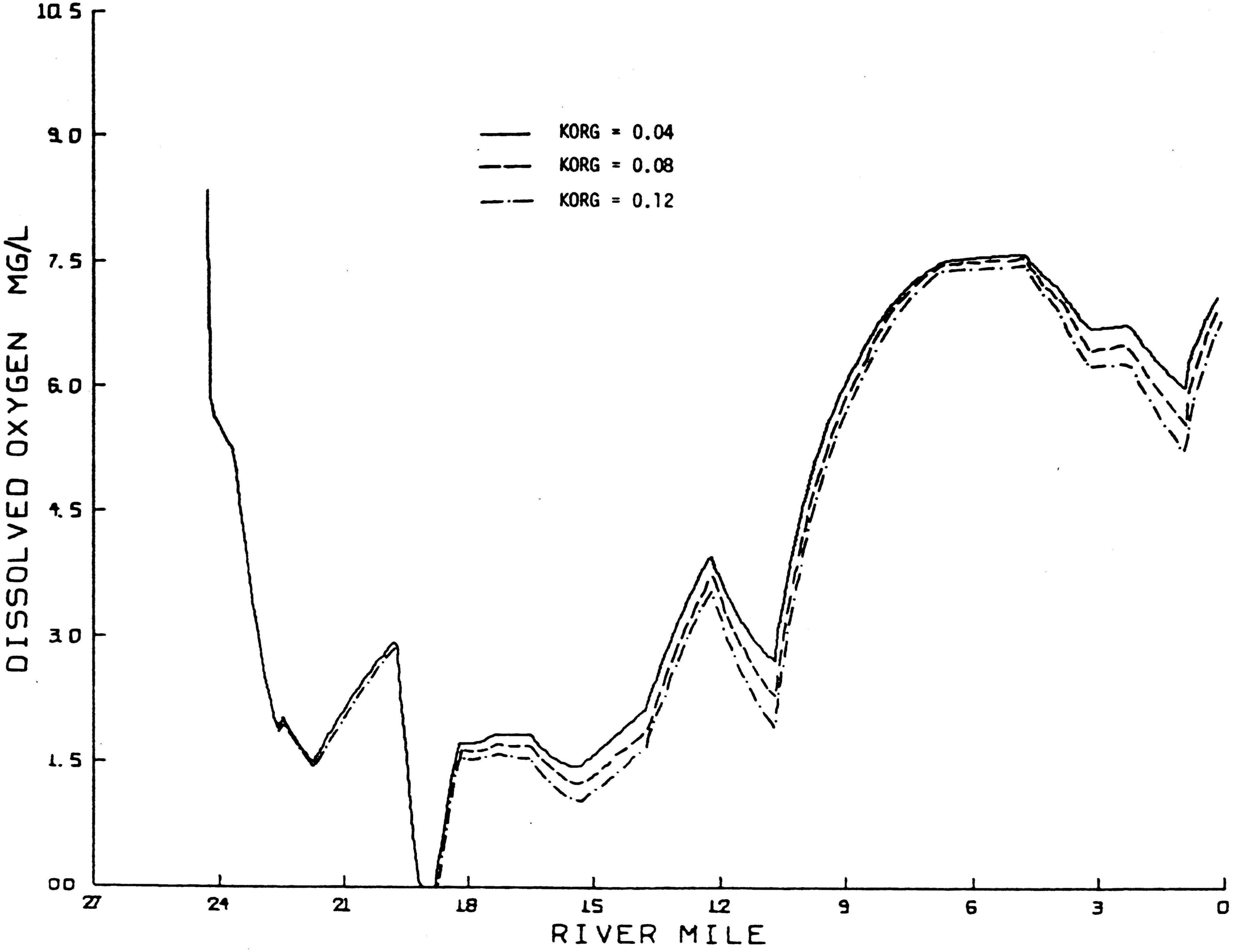

Figure 3. Sensitivity Analysis of the Organic Nitrogen Reaction Rate Relating the DO Profile.

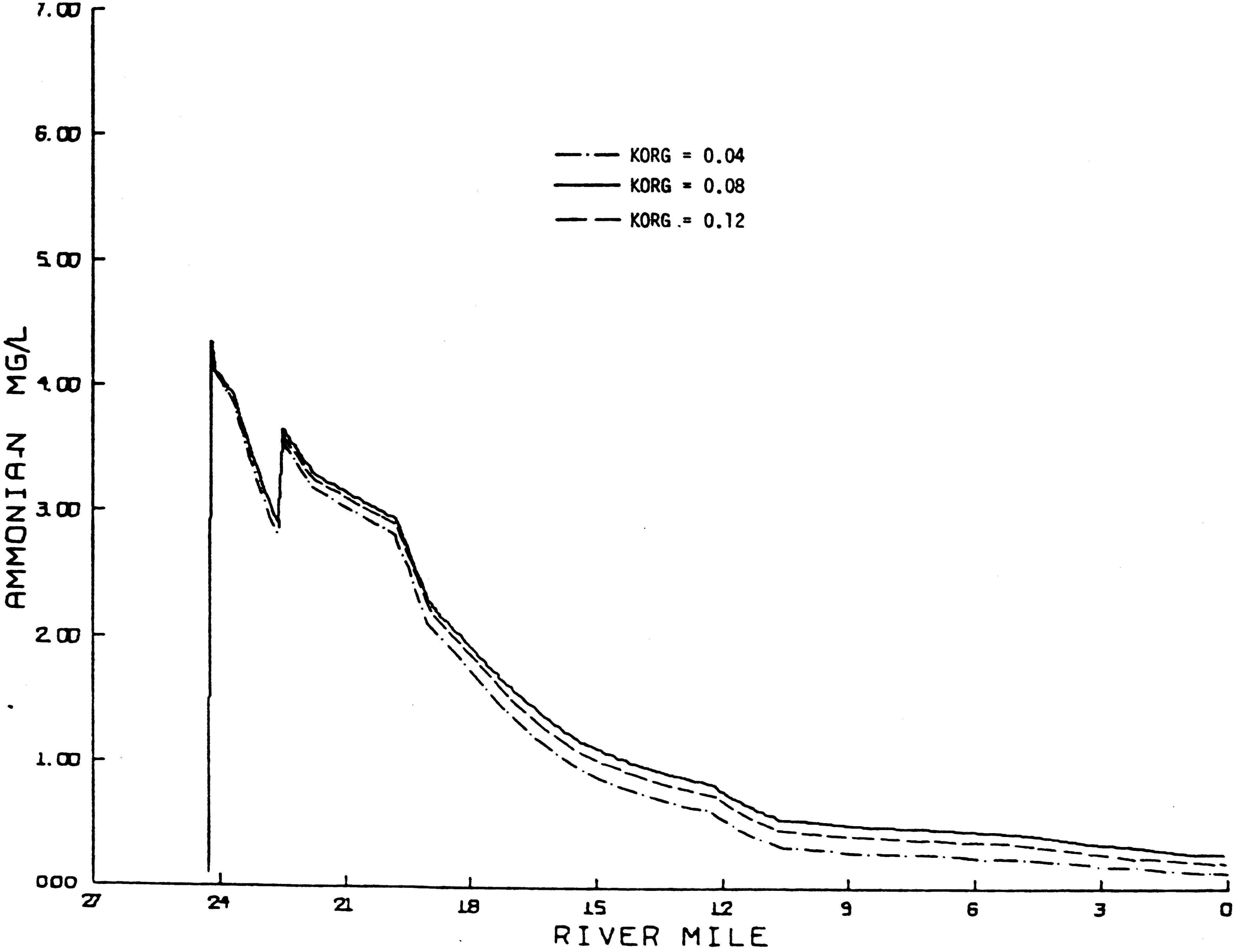

Figure 4. Sensitivity Analysis of the Organic Nitrogen Reaction Rate Relating the NH_3-N Profile.

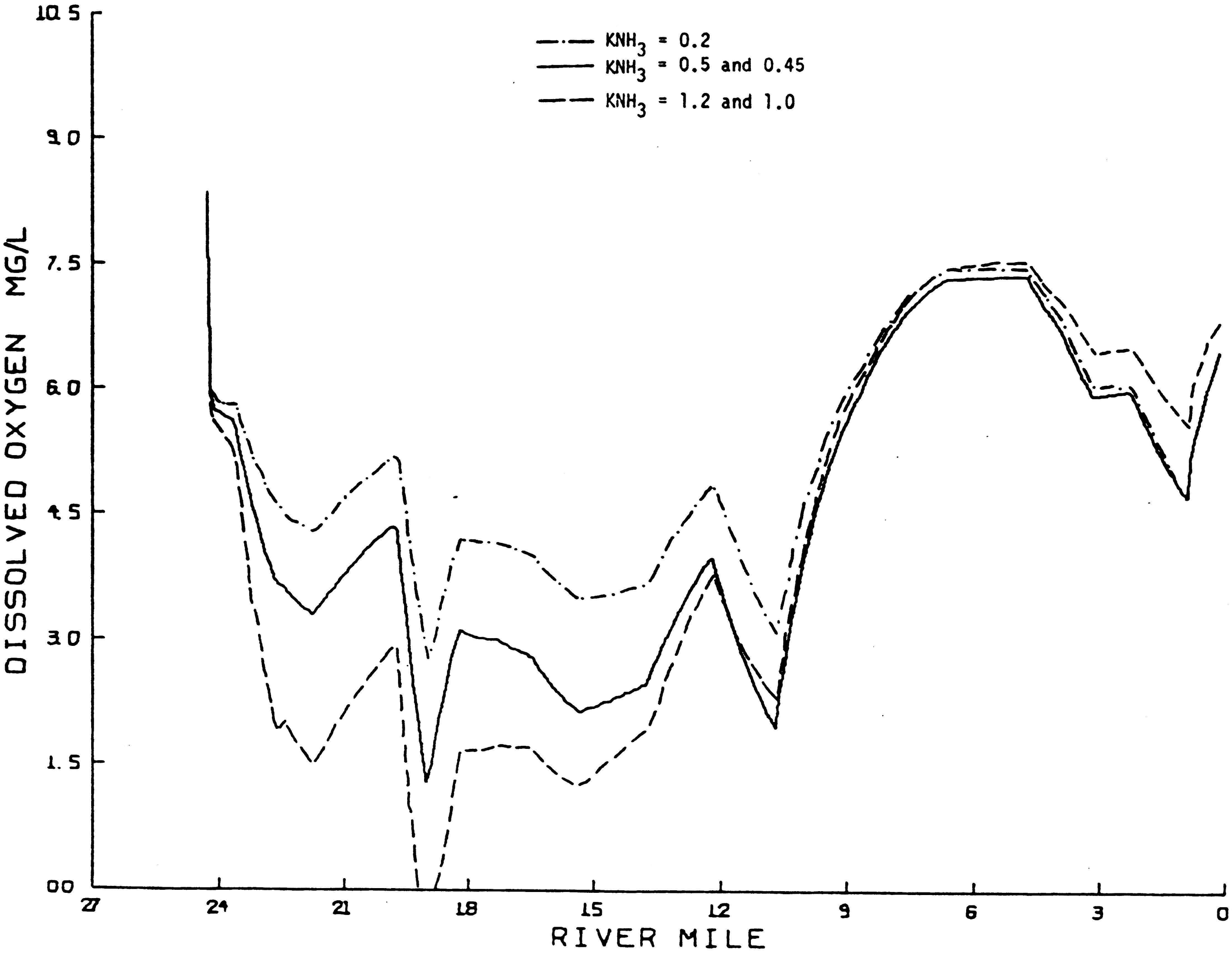

Figure 5. Sensitivity Analysis of the Ammonia Nitrogen Reaction Rate Relating the DO Profile.

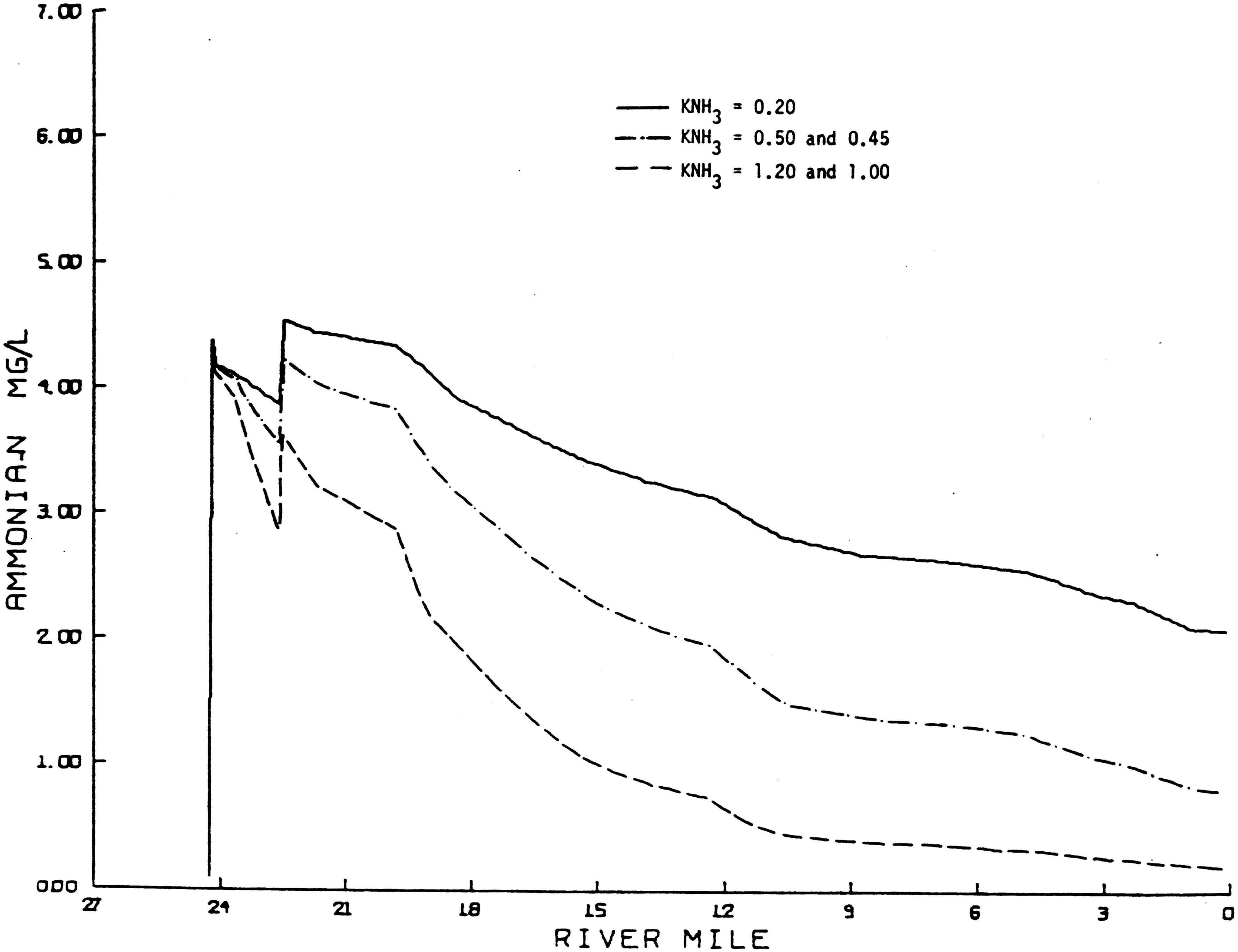

Figure 6. Sensitivity Analysis of the Ammonia Nitrogen Reaction Rate Relating the NH_3-N Profile.

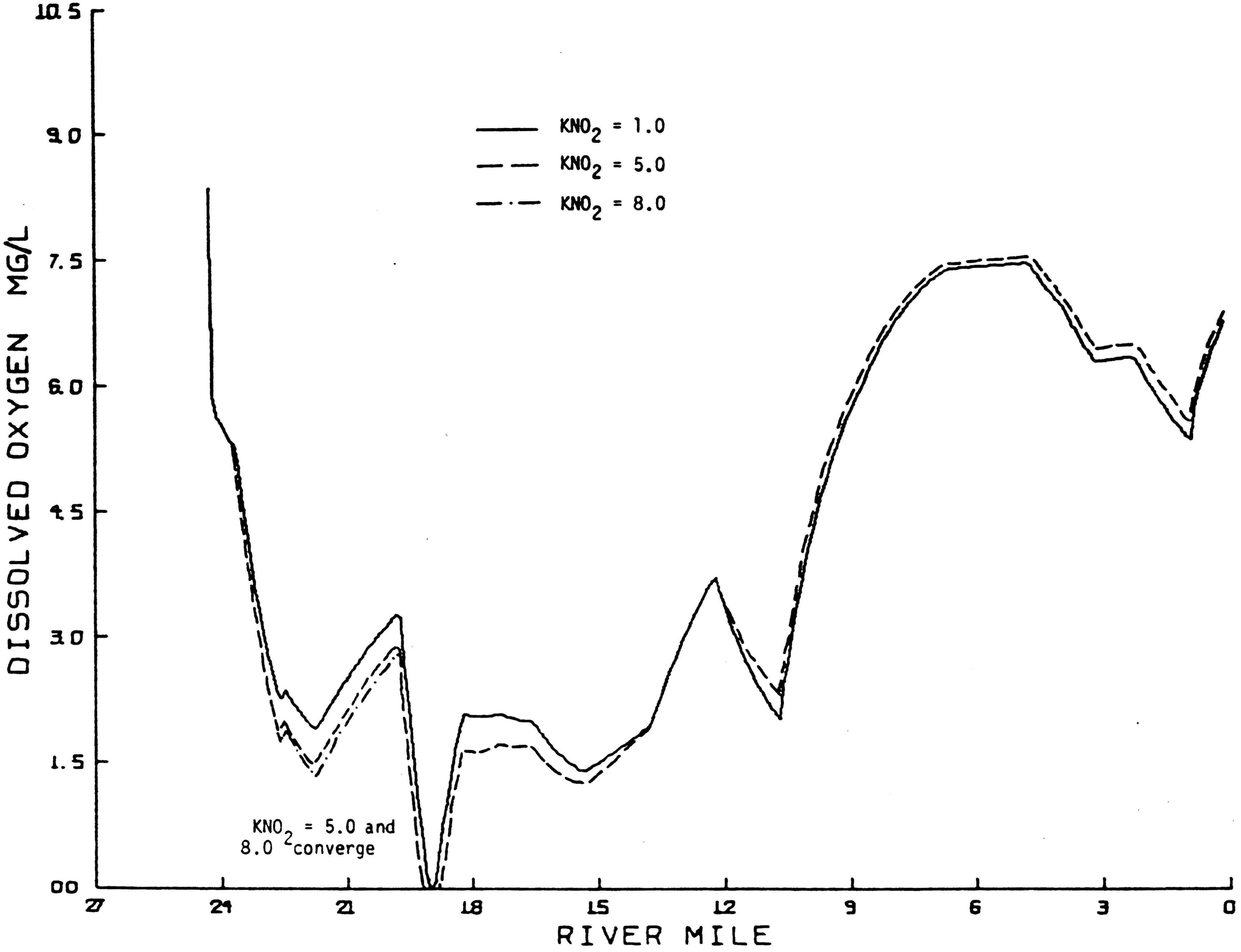

Figure 7. Sensitivity Analysis of the Nitrite Nitrogen Reaction Rate Relating the DO Profile.

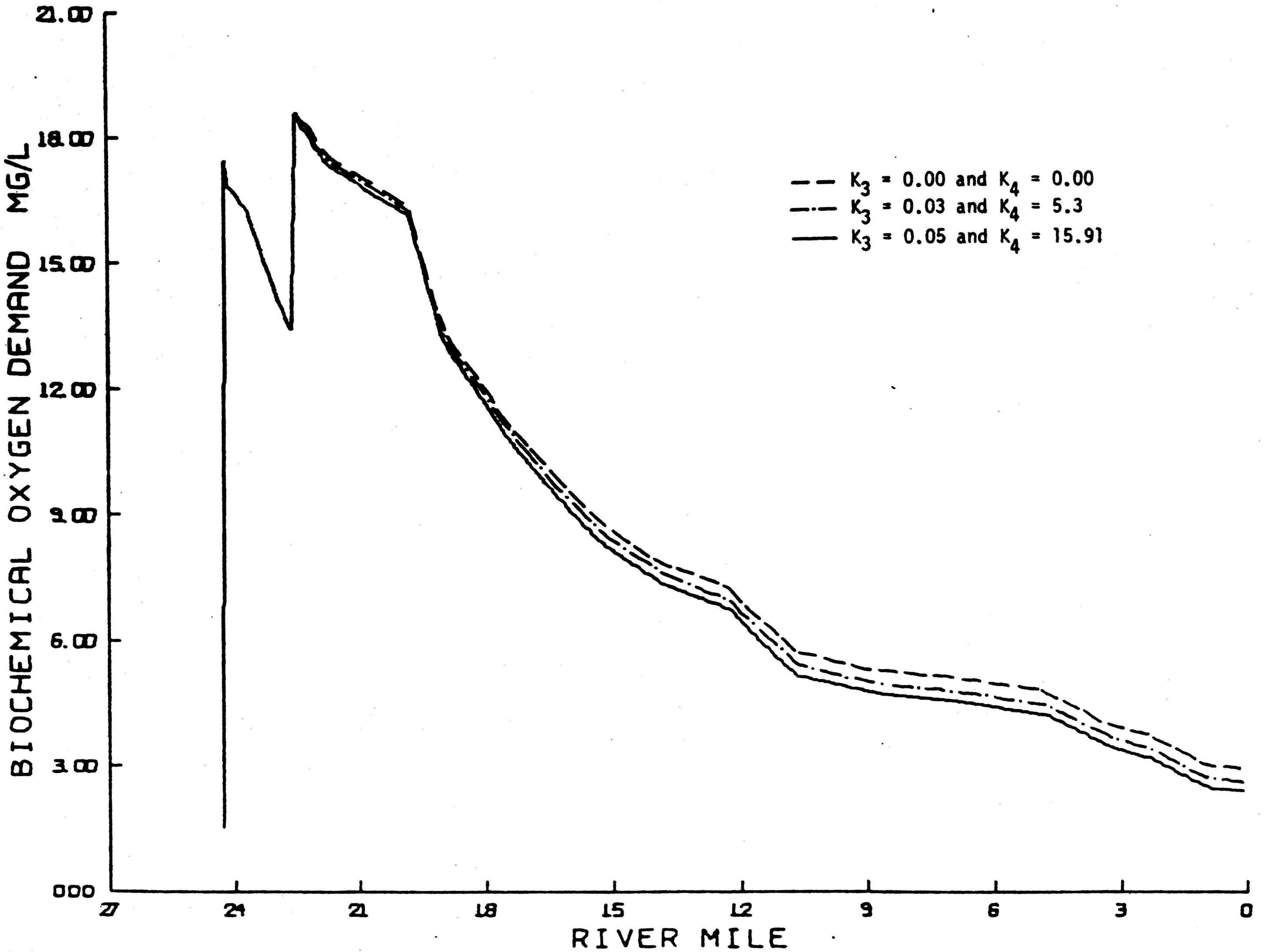

Figure 8. Sensitivity Analysis of the BOD Settling Rate, K_3, and the Benthos Source Rate of BOD, K_4, Relating the BOD Profile.

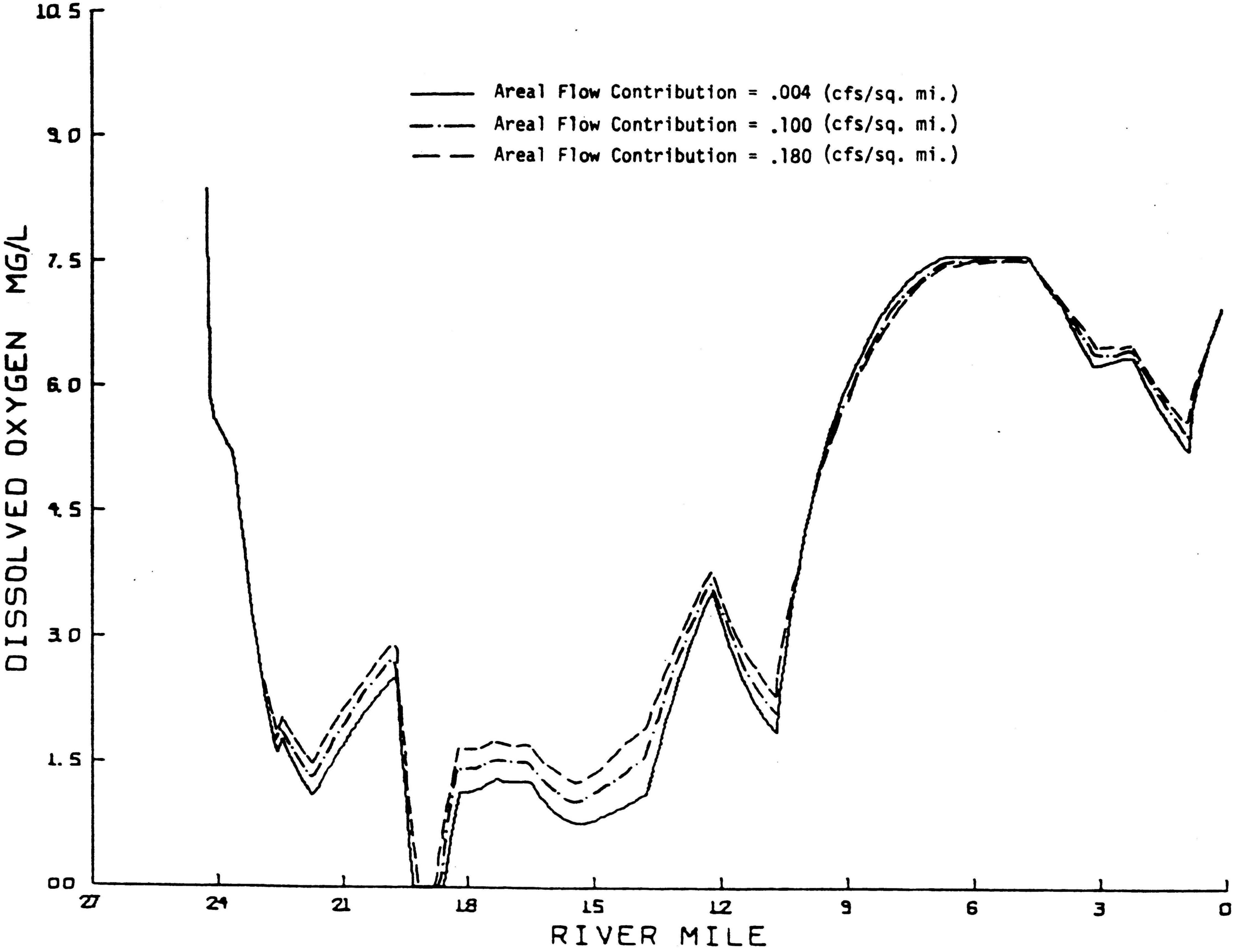

Figure 9. Sensitivity Analysis of the Areal Flow Contribution Relating the DO Profile.

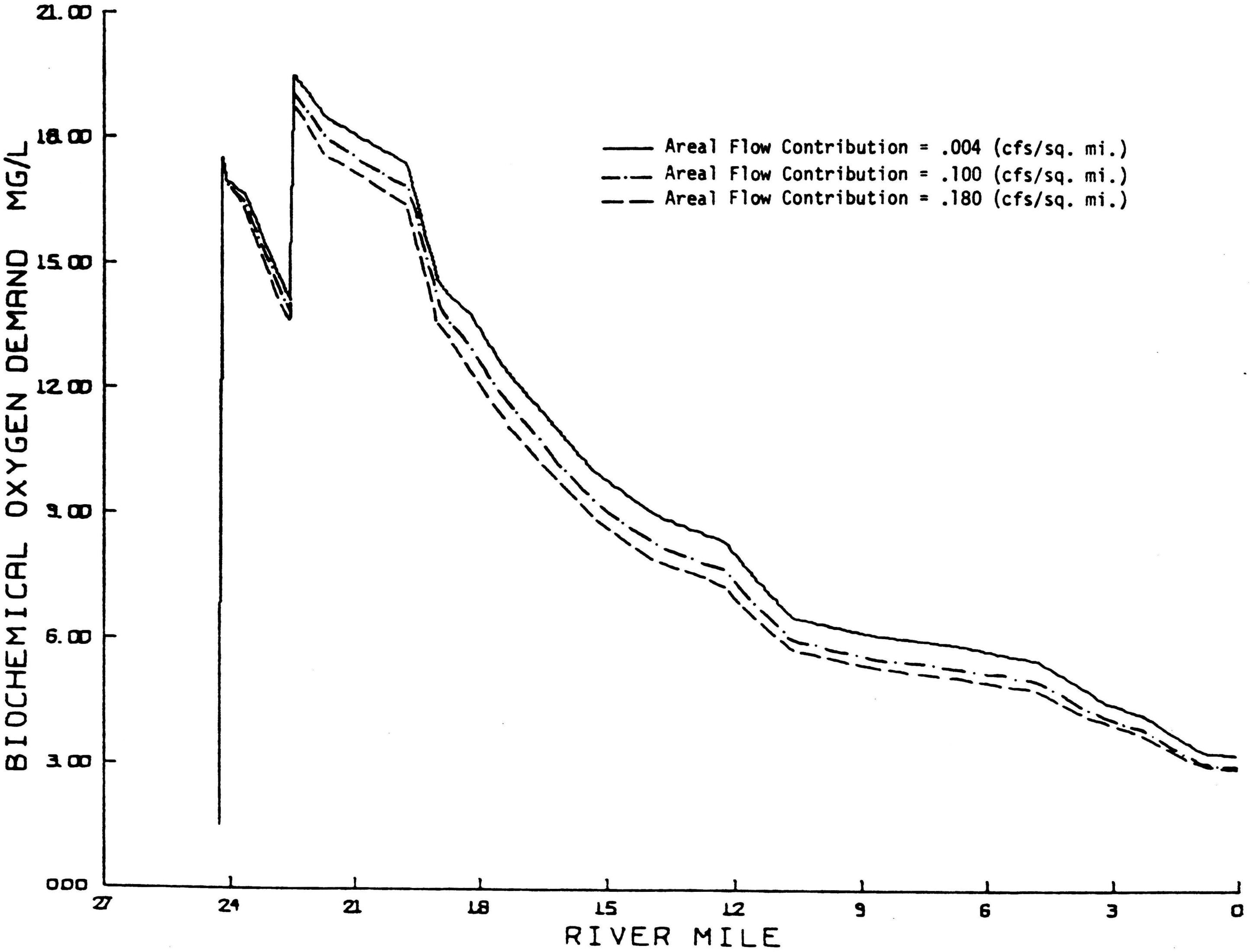

Figure 10. Sensitivity Analysis of the Areal Flow Contribution Relating the BOD Profile.

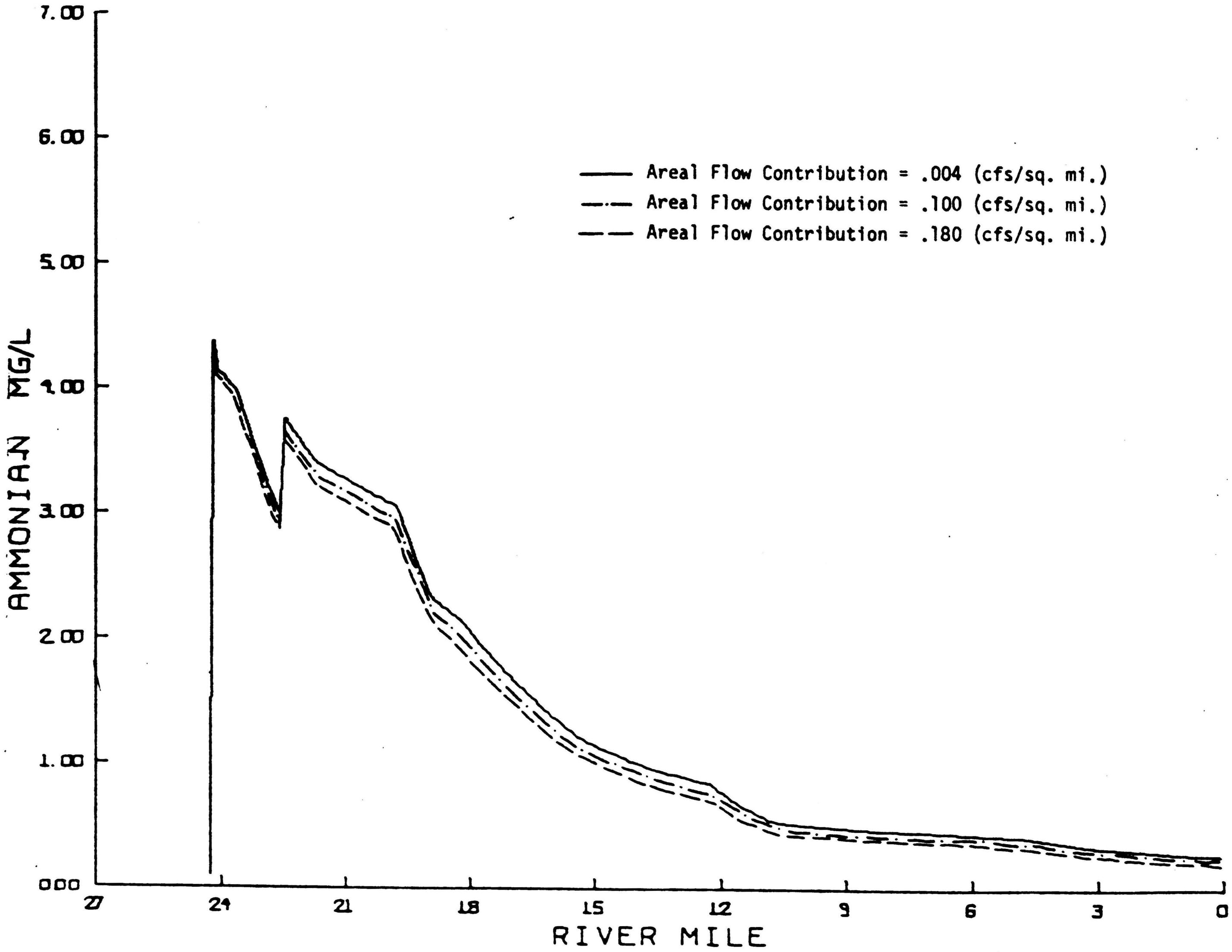

Figure 11. Sensitivity Analysis of the Areal Flow Contribution Relating the NH_3-N Profile.

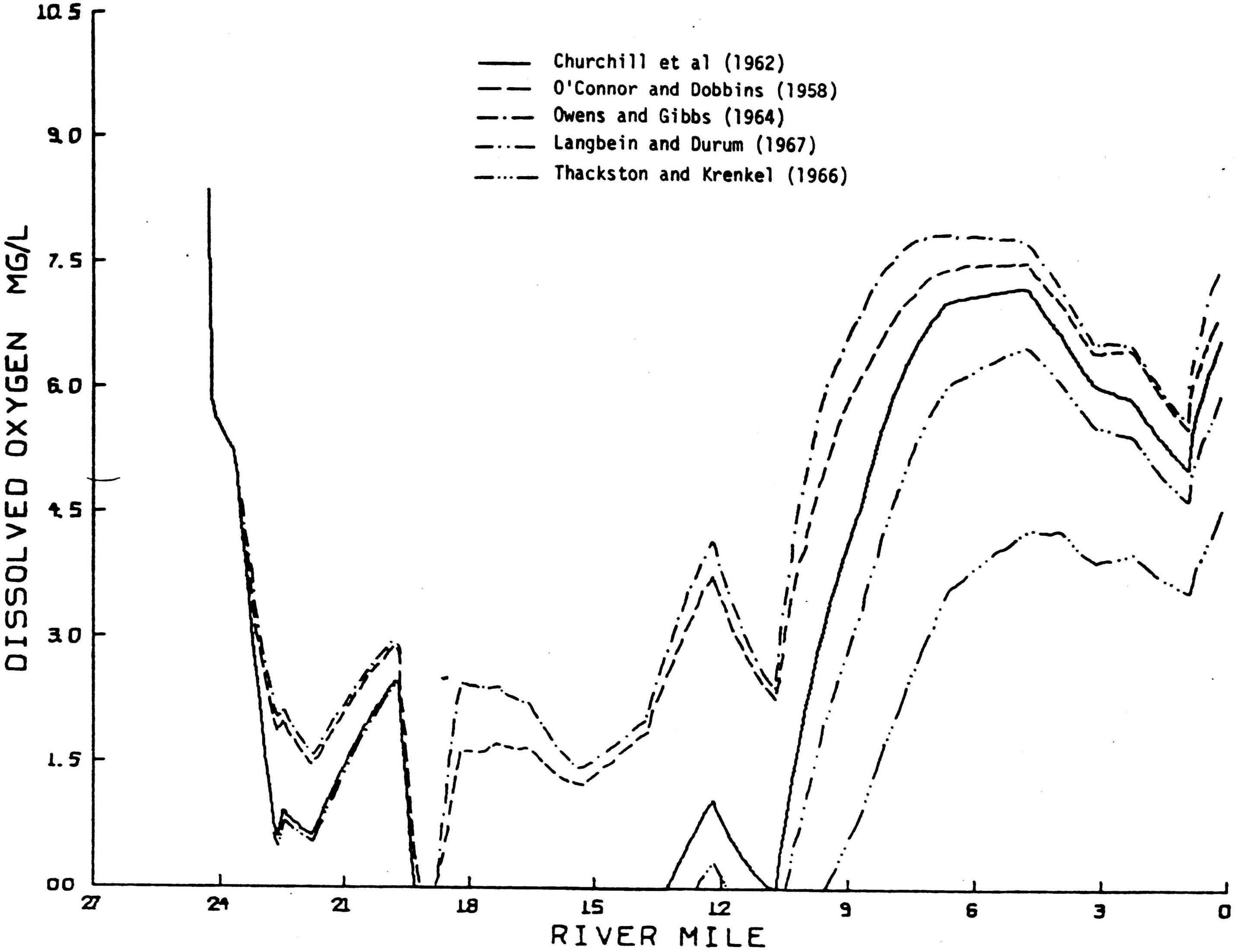

Figure 12. Comparison of Different Reaeration Prediction Equations.

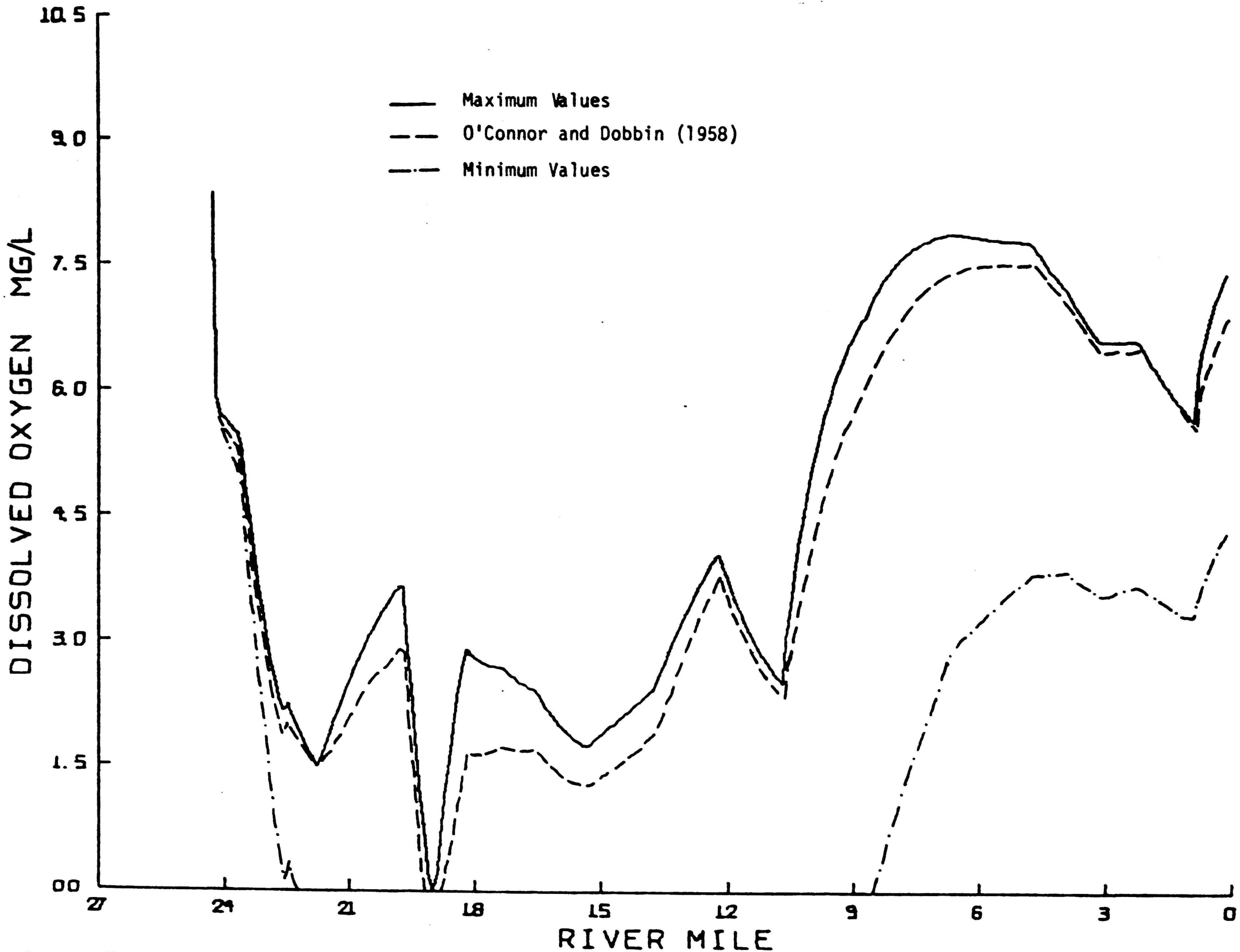

Figure 13. Sensitivity Analysis of the Calculated Maximum and Minimum Reaeration Rates in Reference to the O'Connor and Dobbin Equation Relating the DO Profile.

Table 8. Ranking of Effect of Input Variables on DO on the South River, Virginia over a Specified Range of Variables

Rank	Variables
1	Reaeration Rate, K_2
2	Oxidation Rate of Ammonia Nitrogen, KNH_3
3	Deoxygenation Rate, K_1
4	Areal Flow Contribution
5	Oxidation Rate of Nitrite Nitrogen, KNO_2
6	Organic Nitrogen Reaction Rate, KORG
7	Carbonaceous BOD Settling Rate, K_3, and Benthos Source Rate of BOD, K4

the oxidation rate of ammonia nitrogen, and the deoxygenation rate were quite sensitive to variations, in that order of severity. The areal flow contribution, the organic nitrogen reaction rate, and the oxidation rate of nitrite nitrogen were only mildly sensitive. The carbonaceous BOD settling rate and benthal oxygen demand, when applied together, were basically insensitive in their response within the model over the tested ranges.

As previously mentioned, the range of reaeration rates for the stream reaches was based upon the application of the five different predictive equations. The response in relation to the dissolved oxygen concentration is presented in Figure 12 showing variations which would occur through their use. Based on these results, a set of minimum and maximum values were found for each reach and analyzed against the predictive equation formulated by O'Connor and Dobbin [37], Figure 13. This was done not only to test the sensitivity of this parameter in the model, but to relate the variations which could occur through application of the different equations. The reaeration model devised by Owens and Gibbs [47] usually produced the maximum amount of reaeration. Whereas, that equation by Thackston [44] normally produced the lowest reaeration capacity, although exceptions were noted in both cases.

The second set of graphs, Figures 14 through 19, present the effects of variations of the different variables and how they affect the oxygen deficit in the middle of the sixth reach. This stream segment was chosen since it represents the approximate critical point of the dissolved oxygen concentration in the "sag curve." This method of

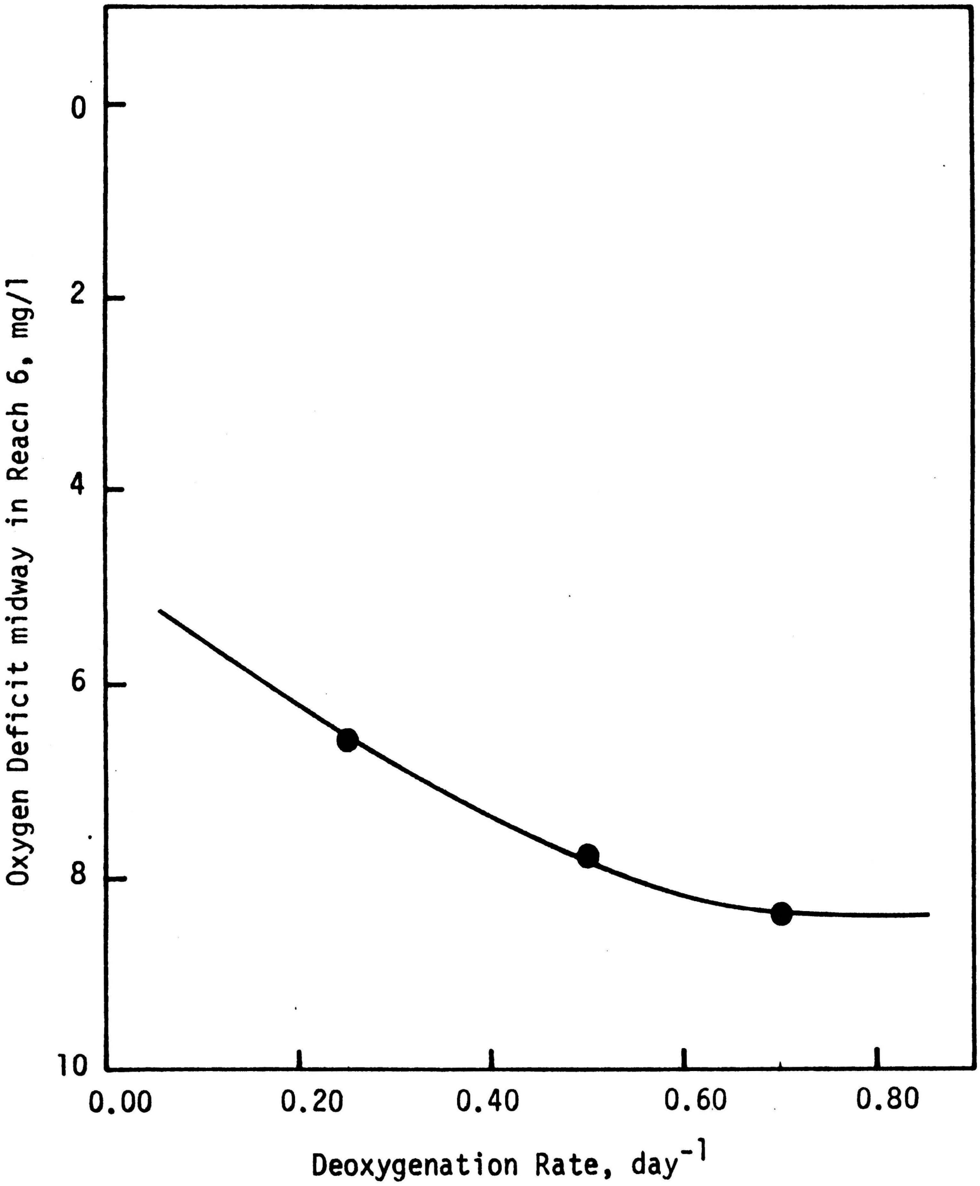

Figure 14. Effect of Variations of the Deoxygenation Rate, K_1, on the Oxygen Deficit Midway in Reach 6.

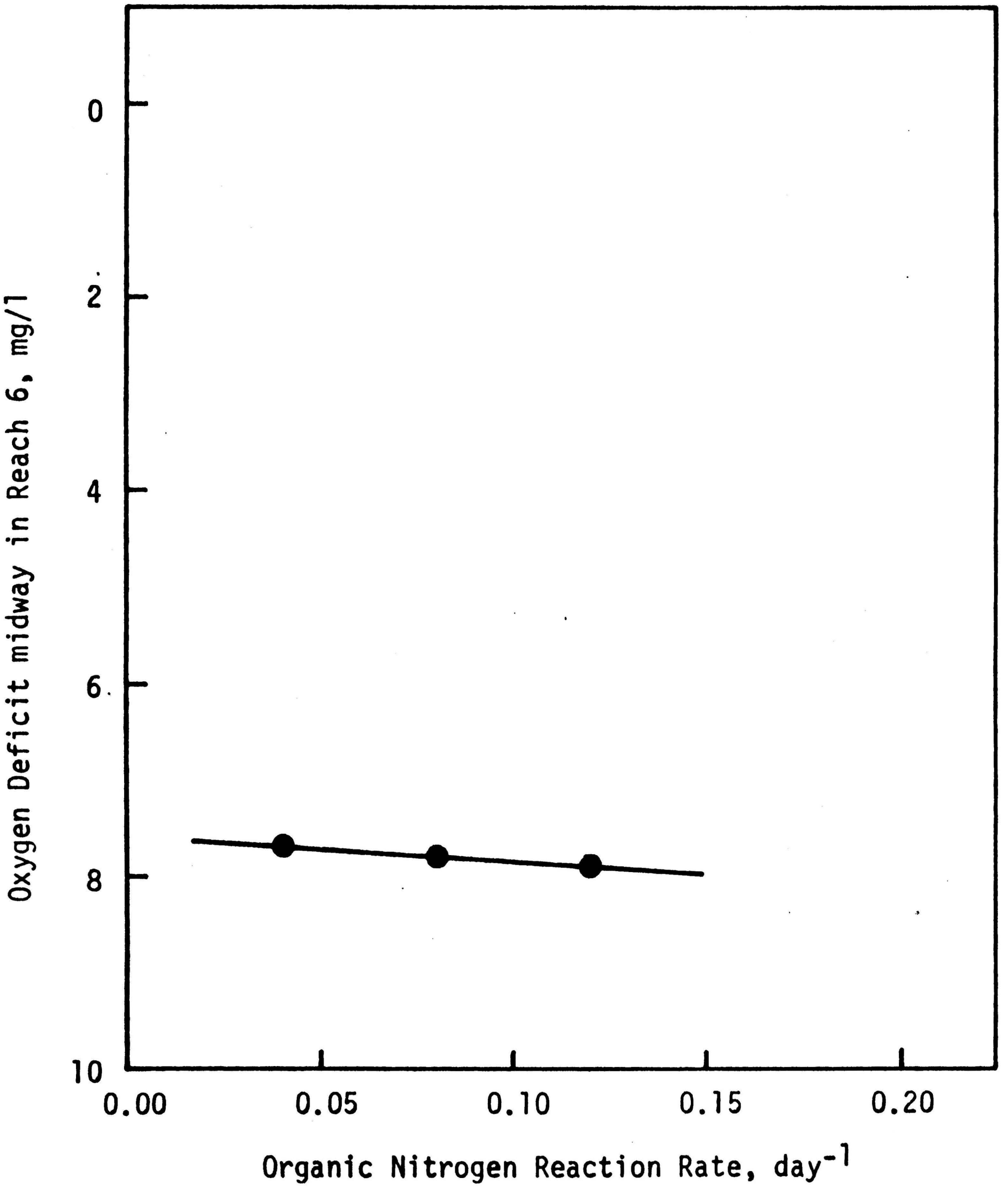

Figure 15. Effect of Variations of the Organic Nitrogen Reaction Rate, KORG, on the Oxygen Deficit Midway in Reach 6.

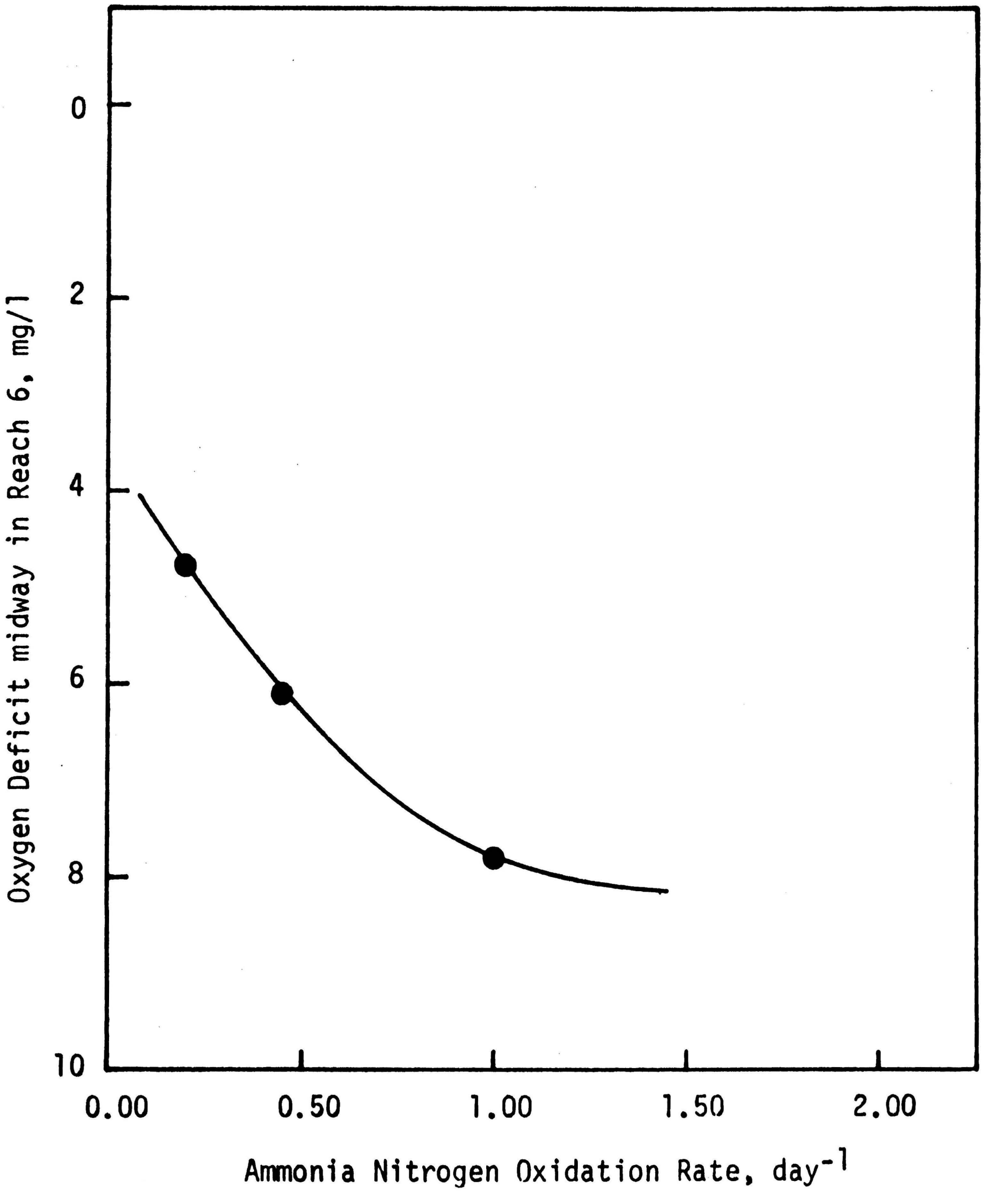

Figure 16. Effect of Variations of Ammonia Nitrogen Oxidation Rate, KNH_3, on the Oxygen Deficit Midway in Reach 6.

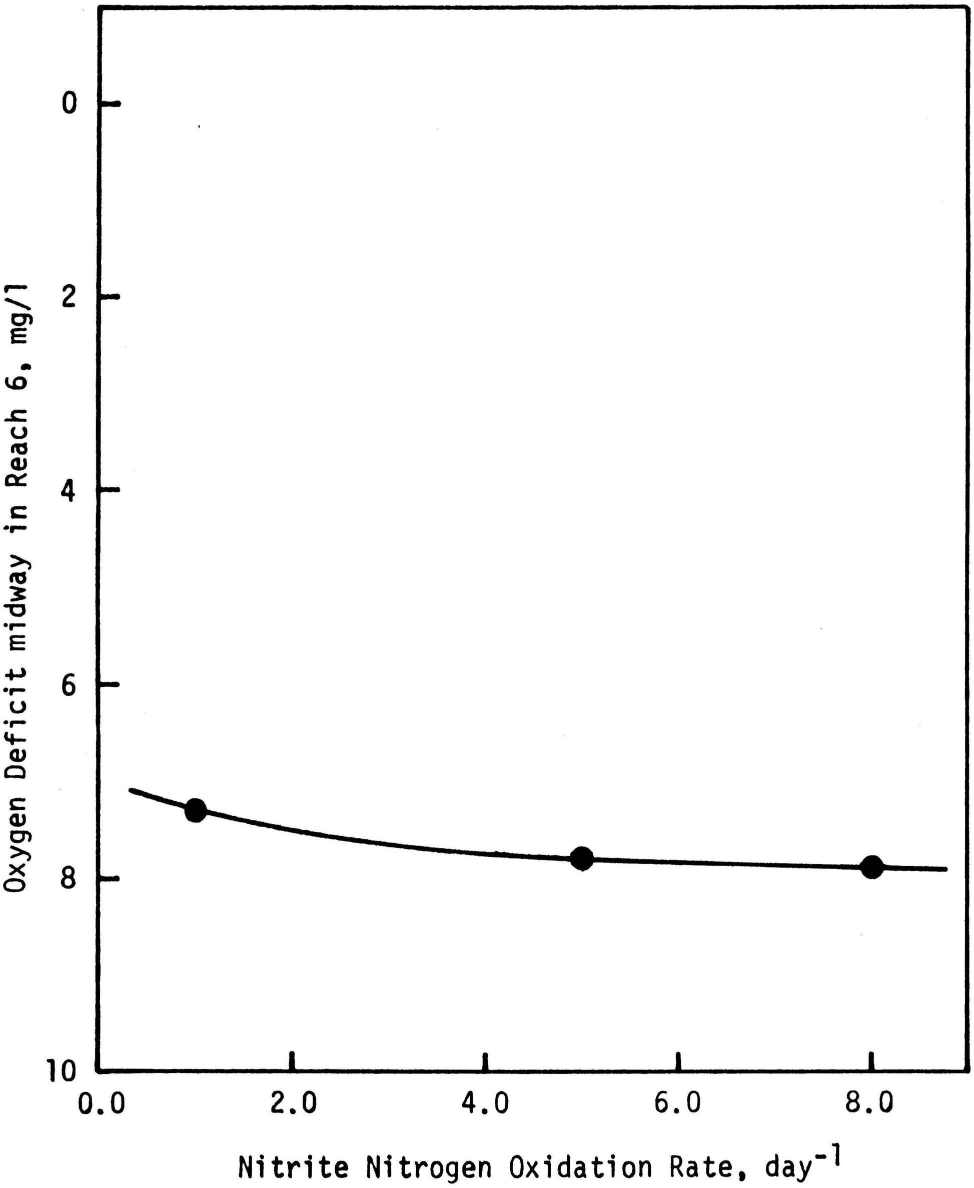

Figure 17. Effect of Variations of the Nitrite Nitrogen Oxidation Rate, KNO_2, on the Oxygen Deficit Midway in Reach 6.

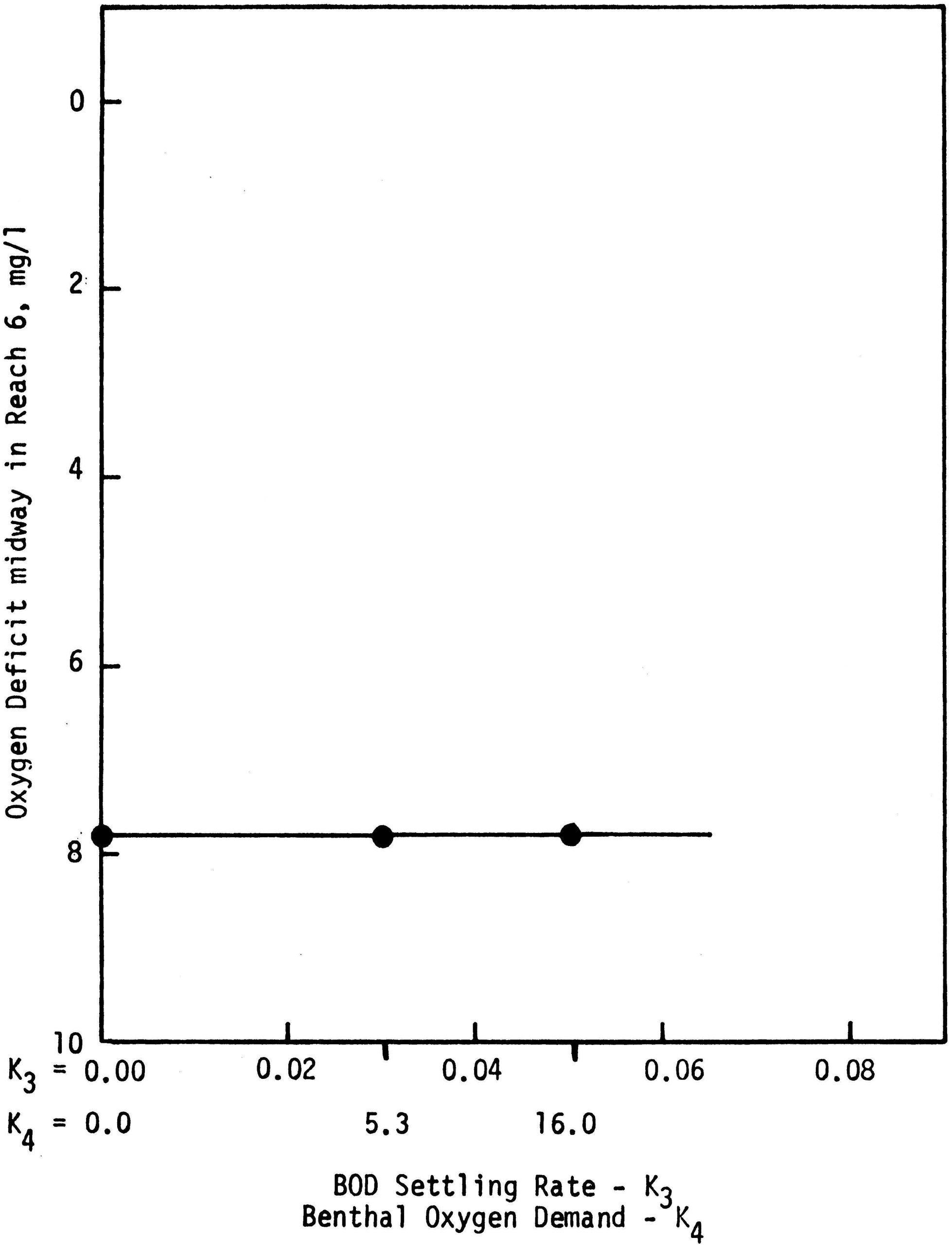

Figure 18. Effect of Variations of the BOD Settling Rate, K_3, and Benthal Oxygen Demand, K_4, on the Oxygen Deficit Midway in Reach 6.

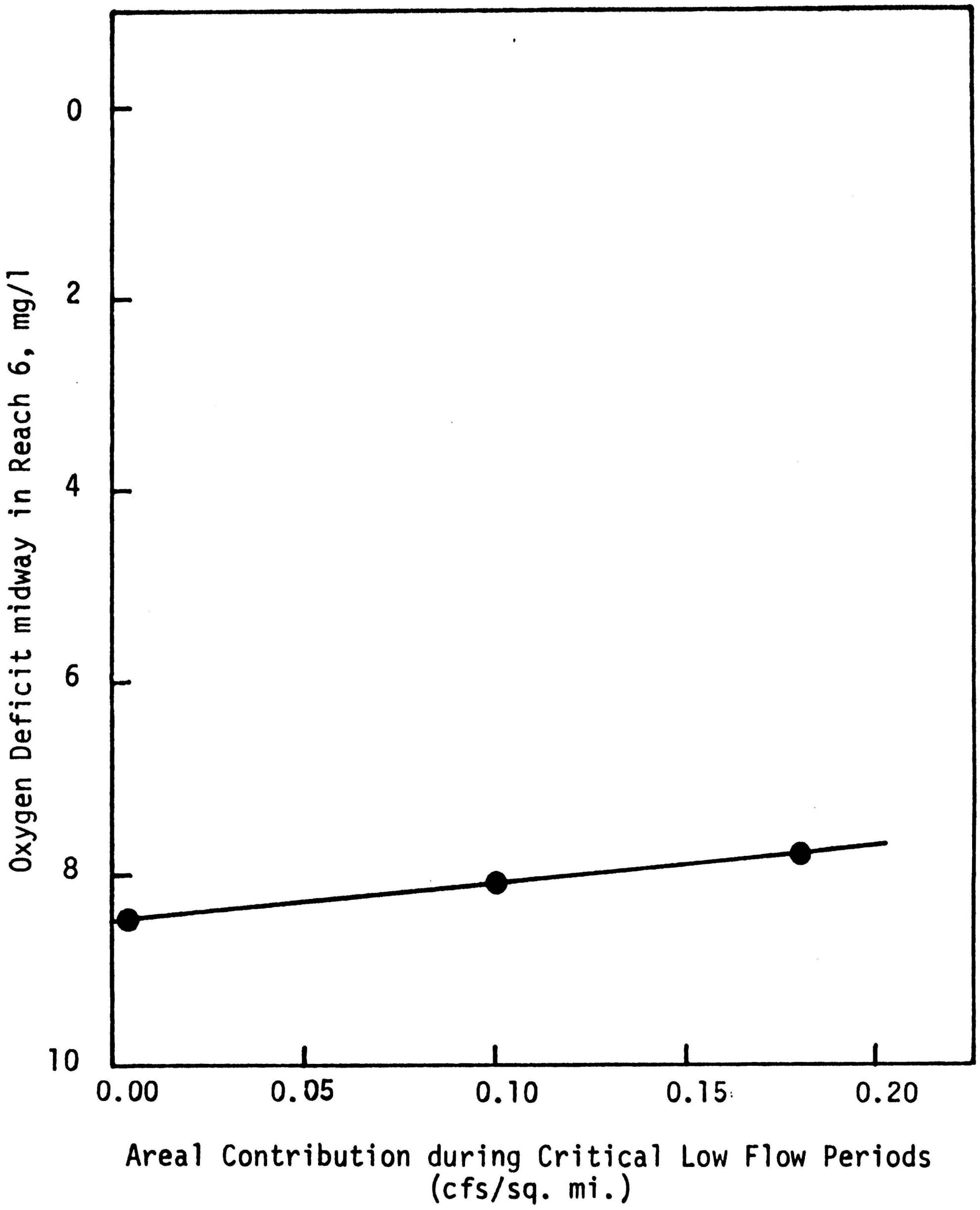

Figure 19. Effect of Variations of Areal Contribution During Low Flow on the Oxygen Deficit Midway in Reach 6.

analysis enables one to evaluate the significance of the parameter values through portions of the tested range and to see how sensitive a given value would be. As Figures 14 and 16 show, there was a very significant change in the oxygen deficit as the deoxygenation rate decreased below 0.6 per day and the ammonia nitrogen oxidation rate below 1.0 in the system being studied. Figures 15, 17, 18, and 19 indicate that through the ranges tested there was only a minor change in oxygen deficit at the critical sag point as the respective parameters were varied.

Sensitivity Analysis--Series II

During the sensitivity analysis of the different parameters within the algal subroutine in conjunction with the rest of the model, it was found that through the ranges tested, Table 7, there was very little response, if any, on the dissolved oxygen concentrations. This would indicate that this subroutine is very insensitive within the model under these conditions.

Variations in Waste Load Allocations

Upon applying the three sets of reaction rates to the model, it was found that distinct relationships existed in allowable loading rates of BOD, ammonia nitrogen, and organic nitrogen. During the evaluation of the loading rates for E. I. DuPont Co., the effluent concentrations of Waynesboro's STP were set at 40 mg/l ultimate BOD, 2.0 mg/l ammonia nitrogen, and 2.0 mg/l organic nitrogen. These concentrations were based upon levels which could be achieved by a properly operated secondary treatment plant with a nitrification-denitrification unit. A summary of possible loading rates for E. I. DuPont Co. based on the three reaction rate sets is shown in Table 9 and presented graphically in Figure 20. The "common" set of reaction rates yielded the least restrictive set of required loading rates to maintain the 5.0 mg/l of DO within the South River. The most restrictive loading rates were correlated with the application of the "maximum" set of reaction rates. In order to maintain an ammonia nitrogen concentration of 3.0 mg/l, it was found that the BOD_u could vary from 6.4 to 20.0 mg/l. Equally broad ranges were found with other levels of ammonia-nitrogen.

In evaluating the consequences of lowering the STP's BOD_u loading rate, its value was changed from 40.0 to 30.0 mg/l. This enabled an increase for the E. I. DuPont BOD_u loading from 9.8 mg/l to 13.5 mg/l while maintaining an ammonia nitrogen level of 2.5 mg/l. This analysis was performed using the "maximum" set of reaction rates.

Table 9. Possible Loading Rate, in mg/l, for E. I. DuPont Co. as Determined through Application of Three Reaction Rate Sets

Rate Set	BOD (ultimate)	Ammonia Nitrogen	Organic Nitrogen
Common Reaction Rates:	20.0	3.0	6.0
	17.5	3.5	7.0
	14.8	4.0	8.0
Minimum Reaction Rates:	15.3	3.0	6.0
	11.9	3.5	7.0
	8.5	4.0	8.0
Maximum Reaction Rates:	9.8	2.5	5.0
	6.4	3.0	6.0
	3.0	3.5	7.0

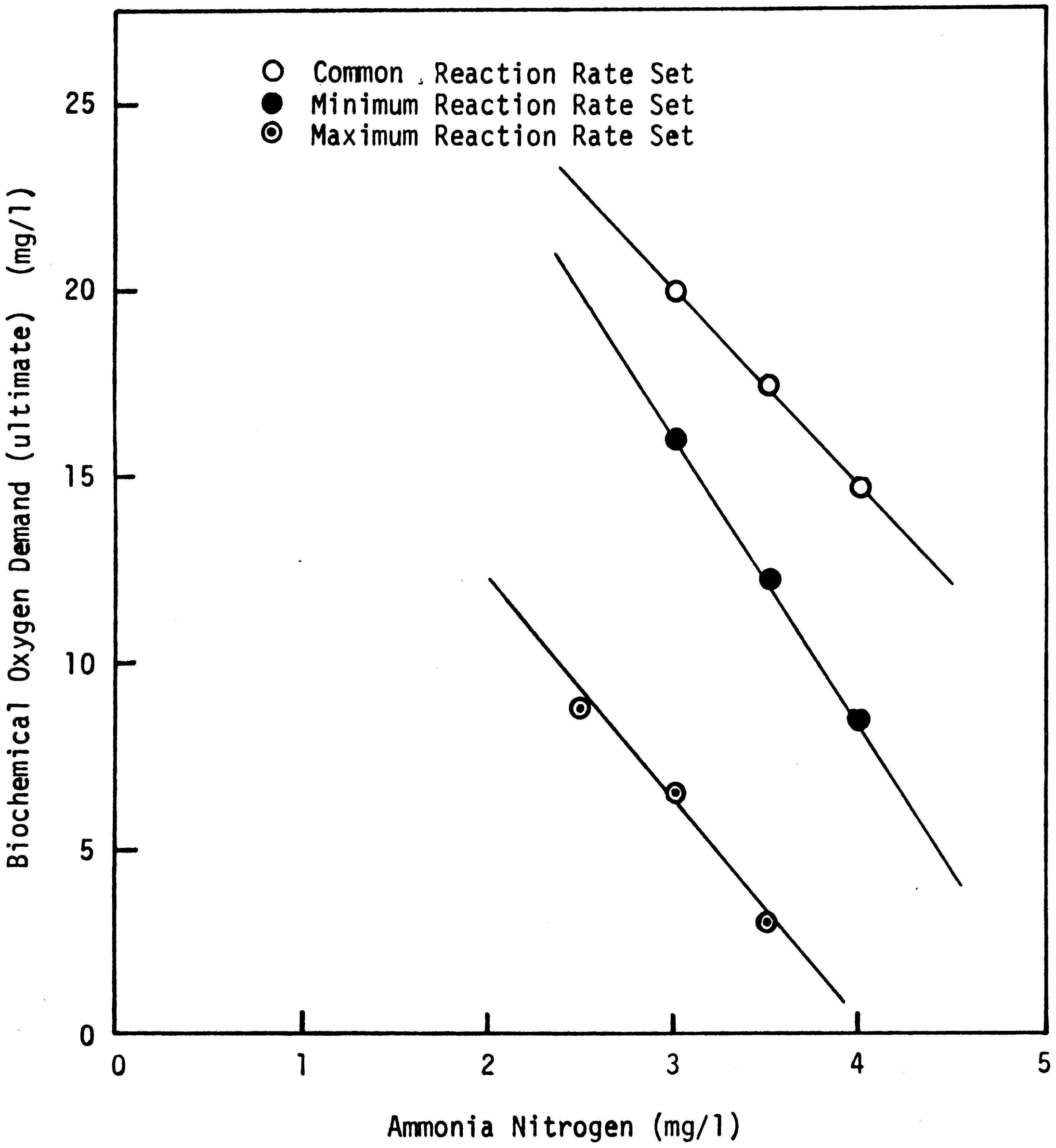

Figure 20. Corresponding Loading Rates Determined Through Application of Sensitivity Variable Sets.

DISCUSSION OF RESULTS

The primary objective of this study was twofold: first, to perform a sensitivity analysis of the QUAL-II water quality model based upon data from the South River and second, to evaluate the projected ranges of waste load allocations based upon the results of the sensitivity analysis. To properly review the results, each of the significant variables which was tested for sensitivity will be discussed separately.

Reaeration Rate

The method of evaluating the reaeration capacity of a river is extremely important in that it is normally the primary method of reintroduction of dissolved oxygen into the system. Most predictive models incorporate the use of empirical equations based on data from previous studies. As shown in this study, the use of these equations can produce wide variations in simulation, and that many of these equations are inadequate in even approaching the capability of simulating the reaeration capacity in a river different from the one in which they were derived, thus making this parameter the most sensitive variable within the model. The practice of incorporating any one of these equations in a river system with a complex dissolved oxygen balance, e.g. one with photosynthetic activity, benthal influences, etc., is extremely haphazard. Although adequate calibration can possibly be achieved, one is uncertain if the reaeration equation is simulating only the air to water interchange of oxygen or other variables which can affect the overall dissolved oxygen balance.

Through review of the literature, it is felt that in dealing with a complex river system as the South River, it is best to utilize the "tracer" technique developed by Tsivoglou [36, 41, 42, 43] and associates which is capable of separating the true surface reaeration process from photosynthetic activity and other influences. Another advantage of this method is that its measurements will take into account any adverse influences which might result from the presence of pollutants.

Oxidation Rate of Ammonia Nitrogen

The second most sensitive parameter was found to be the ammonia nitrogen oxidation rate. It was found that through a possible range of from 0.2 to 1.0 per day, a difference of 3.0 mg/l of dissolved oxygen resulted within the river near the critical sag point. This possible margin of error dictates accurate measurement of this process.

To properly monitor the uptake of ammonia nitrogen within a river system, several approaches should be considered depending on the nature of the system and its complexity. When the river is known to have nitrification occurring as well as algal and aquatic vascular plant activity, as in the South River, the following techniques should be considered. The overall changes in ammonia levels should be monitored on a "mass" basis (lbs/day). This requires not only the determination of the concentration (mg/l), but also the flow rate (cfs) at the point and time of sampling. Sampling times for all reaction determinations should be performed in conjunction with the "time of travel" of a single mass of water. The time of travel should preferably be determined through fluorescent dye studies, but in streams of homogeneous channel geometry this can be determined by manual measurements of the stream's velocity. By incorporating the "mass" of ammonia, it is possible to account for changes in concentration due to dilution or infiltration. By plotting the volume of ammonia against "time of travel" on semi-log paper, it is possible to calculate the overall reaction rate of ammonia nitrogen through regression analysis.

Since the disappearance of ammonia nitrogen can be due to nitrification, plant uptake, or volatilization, it is important to evaluate the importance of each of these influences. The rate of nitrification which occurs can be determined through the use of the BOD bottle test with the application of a nitrification inhibitor to one of two duplicate samples that are tested. By subtracting the uptake of the DO in the bottle with the inhibitor from the standard BOD bottle, one is able to monitor the uptake of dissolved oxygen due to nitrifying bacteria through time. Incubation procedures should follow those utilized in determination of the deoxygenate rate (carbonaceous). By comparing this time to the "time of travel" in the stream it is possible to evaluate its significance in the stream. This method also allows for the determination of the occurrence and extent of a lag period.

The importance of plant uptake of ammonia nitrogen can be evaluated by collection of representative samples of aquatic plant life from the stream and placing these in a solution containing ammonia and nitrification inhibitor. Any changes in the ammonia levels can thus be attributed to uptake by the plants through specified time.

Volatilization of ammonia nitrogen occurs only in river systems which are alkaline in nature which favor the ammonia to be in the gaseous form. It was theorized by Stratton [99], that in shallow turbulent streams, at pH's greater than 9.5 and temperatures greater than 25°C, ammonia can be lost to the atmosphere when it is present in significant amounts. Actual measurement of this effect is difficult, and would most likely be evaluated by mass balance determination of ammonia transformations in conjunction with the two previous techniques. By reviewing conditions occurring on the South River, it is felt that the former two influences are of major concern. The occurrence of benthic algae and aquatic vascular plants as being significant is related by a study on the South River by Cairns et al. [100].

Deoxygenation Coefficient (Carbonaceous)

The only other variable which was found to have significant sensitivity is the deoxygenation coefficient. It was determined that this rate could vary from 0.25 to 0.70 near the region of critical sag with corresponding higher values upstream. A change in dissolved oxygen concentration of 1.8 mg/l was found to occur between these extremes, thus enabling considerable error to possibly occur.

Proper measurement of this parameter can be done utilizing the standard BOD bottle test with several variations in procedure. The bottle should be darkened to make it opaque and the bottles should be incubated in the river at the point at which they were sampled. This enables proper temperature simulation and prevents oxygen production by phytoplankton. This latter consideration should be insignificant as applied to the South River, in that the predominance of algae is of benthic origin. For this same reason, several of the other problems with the bottle test are alleviated or minimized. A nitrification inhibitor should also be added to negate any influence by nitrifying bacteria. The incubation time length should be compared with the time of travel of a mass of water to flow through the river system in which the reactions take place. These methods are generally accounted for in the determination of the oxidation rate of ammonia nitrogen. The remainder of the procedure should follow standard techniques. The deoxygenation rate (carbonaceous) determined by the bottle test still may be lower than that found in the river, due to its lack of ability to account for the settling of BOD and biological extraction. These phenomena will be discussed shortly. The coefficient can be derived through regression analysis as described in the previous section.

Areal Flow Contribution

This parameter was found to have only moderate sensitivity through the range tested. For a variation from 0.004 to 0.180 cfs per square mile, only a 0.6 mg/l change in dissolved oxygen occurred near the sag point. This parameter is normally calculated by use of hydrologic data from a stream gaging station, as was the initial value used by the USEPA of 0.18 for the South River near Waynesboro. It has been postulated, however, by Smith [101] that this value can change depending on variations in the geologic formation within the watershed. Based on this study, a review of the variations in geologic material yielded values of from 0.004 to 0.18 for alluvial deposits and sedimentary rock of the Cambrian period, respectively. The latter formations predominate in the South River watershed and characteristically have significant spring water contribution (37 percent). It can be concluded that even if drought conditions reduced the spring yield resulting in a decrease of the areal flow contribution of 0.18 cfs/sq.mi., there would be only a minor influence on the dissolved oxygen balance.

Oxidation Rate of Nitrite Nitrogen

Only minor sensitivity of this variable was found within the model producing only a 0.6 mg/l change in dissolved oxygen through a range of 1.0 to 8.0 per day. The actual value of this rate is entirely dependent on the existence of an adequate population of Nitrobacter, which is in turn extremely dependent on proper environmental conditions including the presence of nitrite nitrogen. However, as seen by the sensitivity of this parameter, the exact measurement of it is not needed. It can be approximated by regression analysis of data from samples in a similar fashion as before.

Organic Nitrogen Reaction Rate

The rate of reaction of organic nitrogen through hydrolytic and bacterial means is normally extremely slow. Based on experimental and literature data, a range of from 0.04 to 0.12 was obtained for use in this sensitivity analysis. This yielded a low sensitivity of only 0.2 mg/l of DO near the initial sag point. It is believed that regression analysis of data collected as in the previous manner will yield adequate data for use in the model.

BOD Settling Rate and Benthos Source Rate of BOD

The least sensitive variables were the rate of BOD settling with the benthic addition of BOD. The values used for these rates were based upon previous studies and represented average rates of BOD settling and low rates for benthic BOD source rate which is representative of low organic stream bed sediment similar to that which is found on the South River. There was no change in dissolved oxygen through the application of these variables.

The reason for applying these variables together was based on the premise that if there was any settling of the BOD to the stream bed, it would produce a corresponding demand for oxygen. Although the BOD settling rate is normally considered to be low due to the low levels of settleable solids present in the effluents from the point sources, this variable could be significant if there is active bacterial and chemical floc formation within the river of suspended and colloidal matter. Determination of this parameter can be made by running parallel BOD samples, as described before, with the modification that one stream sample for each site should be analyzed for settleable solids with the supernatant being tested against the normal sample. Any difference in their BOD values would be reflective of the solids which had settled out.

Evaluation of the BOD exerted by the benthos is best performed with the use of submerged chambers or the extraction of benthic sediment and consequent testing in a laboratory.

If there exists filamentous fungus or bacteria, e.g. Sphaerotilus, biological extraction could be occurring. The best method of evaluation is through removal of a specified amount of the organisms, placing them in a flow-through water chamber and monitoring the changes in BOD over time. As can be determined by cursory review of the South River, none of these influences are believed to have any great significance.

Sensitivity Analysis of the Algal Subroutine

As analyzed, the variables within the algal subroutine were found to be very insensitive within the model, in that no significant changes occurred in relation to the dissolved oxygen concentrations or the nutrient levels. This type of response could be explained in either of two ways: either those values applied to the variables were not representative of a natural system and thus did not generatethe expected influences or the model, as presently structured in these analyses, does not perform properly. It is believed that the former explanation is more probable since the subroutine has worked with some success in earlier trials and that variations in these variables did generate changes in the algal concentrations, the algal growth rates, and the photosynthetic-respiration ratios.

The validity of applying this algal subroutine to the South River should be examined. This subroutine is structured around principles based on activities concerning phytoplankton. In the South River, however, the predominance of algal species are of a benthic nature and do not interact with the river system in the same manner. Some of the major differences are: 1) the algae are not evenly distributed throughout the water column, but located primarily in the benthos, 2) the interchange of dissolved oxygen and nutrients occur primarily at the lower depths, thus producing possible vertical stratification of these parameters where mixing is not complete, 3) the euphotic zone is less due to the greater depths, therefore less light reaches the majority of the algal cells. However, there may be a greater cell density due to the greater surface area available for attachment and growth. Thus the oxygen production and utilization could be greater or less than found in rivers where predominance of phytoplankton occurs, 4) where benthic algae are found in large "mats," only the cells at the surface are producing oxygen, while those beneath are utilizing it through respiration, which can partially negate gross productivity. Consideration should be made about restructuring this subroutine along principles utilized in measuring biological extraction rates. That is, determine the interactions of the DO and nutrients in an enclosed chamber over a specified area. Then determine the total area involved in similar biological activity and expand to determine the areal interactions. The type of stream bed should also be considered, since rockier bottoms are more apt to have greater surface area for attaching, greater stability for growth potential and greater turbulence for increased diffusion between cell and liquid interface.

Variations of Waste Load Allocations

When various waste load allocations are determined for discharges along a river, a specified set of reaction rates are usually determined and applied consistently as being the most accurate representation of the natural system. This assumption, however, negates the true variations in these rates due to the actual lack of steady state conditions and the improper determination based upon lack of adequate data. This error in defining the rate can also be attributed to its determination by "best fit" techniques, since this method often overlaps the influences of the coupled reactions and does not accurately define each variable. It is for this reason of variability of applied reaction rates that it is important to distinguish the most sensitive and significant parameters and evaluate the variation with which they can occur. The sensitivity analysis of the QUAL-II, as it was applied to the South River, indicated the most sensitive parameters to be the reaeration coefficient, the ammonia nitrogen oxidation rate, and the deoxygenation rate (carbonaceous), in decreasing order. It was therefore determined that these three coefficients should be tested through their variability to analyze what changes would result in the waste load allocations. As previously mentioned, the effluent concentrations for Crompton-Shenandoah Co. and the Waynesboro STP were kept constant due to either previous permit requirements or to standards which are obtainable through applicable forms of treatment. The loading rates of ultimate BOD, ammonia nitrogen, and organic nitrogen for E. I. DuPont Co. were left to be analyzed. By applying the three sets of reaction rates it was found that while maintaining an ammonia nitrogen level of 3.0 mg/l, the BOD_u could vary nearly 14 mg/l without decreasing the stream's DO below 5.0 mg/l depending on which set of reaction rates was used. Correspondingly it was found that while maintaining a consistent level of BOD_u at

9.0 mg/l, the ammonia nitrogen could vary from 2.5 mg/l to 5.2 mg/l while still maintaining water quality standards. These broad ranges in allowable effluent loadings relate the necessity of decreasing the reaction rate variations to a point where there is less question to the actual permissible discharge loading concentrations, especially to a point where any variations which do exist will remain within the same level of treatment requirements.

Although further "trade offs" are possible with the combinations of waste loadings between the city and DuPont, economic considerations on a community level must be made to justify them.

PROPOSED MODIFICATIONS FOR THE QUAL-II MODEL

During the operation of the QUAL-II water quality model several problems arose in which either discrepancies in expected output occurred or it was found that the present structure of the model does not properly represent the natural system. The two errors which were found concerned with the actual model operation were:

1. During computational exercises of applying "K" rates to analyze the effect of their variation, it was found that the oxygen sag location remained constant throughout the ranges analyzed and that only the oxygen deficit varied in magnitude. It would be expected that higher "K" rates would produce an oxygen sag closer to the origin of waste introduction than lower "K" rates due to the greater bacterial oxidation.
2. When applying the algal subroutine to the model, there was no significant interaction between algal growth and alterations in the dissolved oxygen and nutrient levels in the simulation as would be expected.

Several proposals for updating the model to better simulate occurrences in the natural system are presented below:

1. The algal subroutine should be restructured to be able to simulate benthic algae as well as phytoplankton. It is believed that there exists significant differences between

the interactions of these forms of algae and their environment, especially upon consideration of the diverse forms of river systems in which they respectively dominate.

2. A coefficient should be introduced into the equation which simulates organic nitrogen breakdown that would represent the fraction of the total organic nitrogen which is expected to be converted to ammonia nitrogen. Presently the equation assumes 100 percent conversion of organic nitrogen to ammonia, which seldom occurs in a natural environment.
3. A feedback mechanism should be introduced into the ammonia and nitrite subroutines which would prevent simulation of nitrification when the dissolved oxygen concentration falls below 1.5 mg/l. This would better represent the behavior of the nitrifying bacteria since their activity is inhibited under these environmental conditions.
4. Introduction of a time element to represent the lag time for the development of a nitrifying population should be made to that section of the oxygen deficit equation which simulates the nitrogenous oxygen demand. This would enable consideration of the existence of varying populations of nitrifiers.
5. The growth rate equation for algal populations should be expanded to account for uptake of ammonia nitrogen as well as nitrate nitrogen. It is well known that certain algal species will preferentially utilize ammonia as a nitrogen source rather than nitrate since it requires less expenditure

of energy to convert ammonia to the various organic forms within the cell. This is an important consideration when the effects of stream nitrification are prevalent, since any decrease in ammonia through algal uptake will reduce the amount which would be oxidized by *Nitrosomonas* thus reducing the level of oxygen utilization.

CONCLUSIONS

The following conclusions were made based on the results of this study:

1. The most sensitive parameters found within the QUAL-II water quality model are, in decreasing order: the reaeration rate, K_2, the ammonia oxidation rate, and the deoxygenation coefficient (carbonaceous), K_1.
2. The other model parameters tested: areal flow contribution, nitrite nitrogen oxidation rate, organic nitrogen reaction rate, BOD settling rate, and benthos source rate, had only moderate sensitivity with the latter two variables being insensitive through the ranges analyzed.
3. Based on the projected variations within the most sensitive parameters (reaeration rate, NH_3-N oxidation rate, and deoxygenation coefficient), the waste load allocations are too variable for proper application. Detailed analysis of these variables are needed to decrease their variability so that accurate simulation of the South River can be performed, and corresponding allocations determined.
4. The QUAL-II water quality model, as applied to the South River, should include a revised algal subroutine which can properly simulate the interactions of benthic algae with the river system. The process of photosynthesis is too significant in the South River for it not to be properly included.

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VARIATIONS IN WASTE LOAD ALLOCATIONS THROUGH SENSITIVITY ANALYSIS OF THE QUAL-II WATER QUALITY MODEL ON THE SOUTH RIVER, VIRGINIA

by

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(ABSTRACT)

Sensitivity analysis was performed on the QUAL-II water quality model. The reaeration rate, the ammonia nitrogen oxidation rate, and the carbonaceous deoxygenation coefficient were found to be highly sensitive in the model. Only moderate sensitivity was found with the areal flow contribution, the oxidation rate of nitrite nitrogen, and the organic nitrogen reaction rate. Through the ranges tested, the combined effect of the BOD settling rate and the benthos source rate were found to be insensitive. Based on the projected variations within the most sensitive variables, resultant waste load allocations were found to be too variable for adequate application towards treatment requirements. It is also postulated that due to the complexity of the dissolved oxygen balance within the South River, Virginia, that a revised algal subroutine must be incorporated in the model's application to that system.