

WATER QUALITY MODELING FOR UNCONVENTIONAL BOD

A Thesis

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ABSTRACT

Predictions of the dissolved oxygen (DO) concentration in a stream are sensitive to the choice of Biochemical Oxygen Demand (BOD) reaction model which frequently is assumed to be first order, although published BOD data sets from analyses of samples from rivers show that many are described best by second order or three-halves order BOD reaction. Two DO models for a stream are developed, one with a second order and the other with a three-halves order BOD reaction. The DO equations are solved using Laplace transform method which simplifies the mathematical solution of the model equations by avoiding difficult to evaluate integrals. The DO sag equation incorporates exponential integral functions, calculated by exact or approximate series. The time at which the minimum DO concentration occurs is calculated numerically. The models are useful in calculating Total Maximum Daily Loads (TMDL) of streams.

In addition, this study examines change in stream water quality due to logging debris and leaf burden from forests which adds to BOD in the stream water and increases the sedimentation rate at which solids containing BOD are removed from the stream water. The first and second order BOD models included sedimentation are incorporated into a DO balance equation. The BOD models are applied in remediation design examples using published BOD data collected from Douglas fir needles in stream water. Results obtained from data analysis shows that the logging debris data set is best described by second order BOD model. A treatment system designed based on second order BOD model to treat the logging debris wastewater before effluent is released.

BOD data, collected at daily intervals to five days from a respirometer for mixtures of glucose and glutamic acid, were tested using the root mean squared error

method to determine their goodness-of-fit to three BOD reaction models: a first order model, a half-order model, and an order n model. The mixtures ranged in increments of 10% from 10% strength (90% dilution) to 100% strength (no dilution). There were ten replications of each strength of sample, so that the BOD of 100 samples measured at daily intervals were available.

CHAPTER 1. INTRODUCTION

The dissolved oxygen (DO) concentration is a primary measure of a stream's health, but the dissolved oxygen concentration responds to the biochemical oxygen demand (BOD) load. Many streams and rivers in Louisiana and other parts of the U.S. have suffered from DO deficit, which is very critical to aquatic life. Investigators have continuously studied the dissolved oxygen uptake characteristics in stream water in relation to different sinks and sources in order to develop mathematical models describing the DO consumption. The minimum value of the DO concentration has been of particular significance in wastewater treatment design calculations and to regulatory agencies.

Water quality modeling in a river has developed from the pioneering work of Streeter and Phelps (1925) who developed a balance between the dissolved oxygen supply rate from reaeration and the dissolved oxygen consumption rate from stabilization of an organic waste in which the biochemical oxygen demand (BOD) deoxygenation rate was expressed as an empirical first order reaction, producing the classic dissolved oxygen sag (DO) model. When the dispersion process is considered, the governing equation becomes a partial differential equation. However, the effect of dispersion on BOD and DO in small rivers is negligible (Li, 1972; Thomann, 1974; McCutcheon, 1989). Several investigators (Thomas, 1957; Young and Clark, 1965; Clark and Viessman, 1965; Nemerow, 1974; Tebbutt and Berkun, 1976) presented data showing that second order rather than first order reactions frequently describe the stabilization of wastewaters, but none of these authors incorporated a second order BOD reaction into the DO sag equation. Butts and Kothandaraman (1970) analyzed stream samples from the Illinois

River and found that the majority of these samples' BOD decay was described better by a first order reaction model, while a minority of the samples' BOD decay was described by a second order reaction model. In spite of these results they did not develop a DO sag equation which included a second order BOD model. Adrian and Sanders (1998) developed an analytical solution for the DO sag equation which incorporated a second order BOD reaction, but their development involved integration of cumbersome equations.

Obviously, there is a long tradition and considerable justification to continue describing the DO sag in a stream using first order BOD reactions although there are applications for BOD reaction orders that are other than first order. Respirometry is a versatile method for measuring the degradation and the oxygen uptake characteristics of a wide variety of domestic and industrial wastewaters (Young and Cowan, 2004). Multiorder BOD data from Hewitt, *et al.* (1979) encouraged Adrian *et al.* (1999) to develop a DO sag equation for the three-halves order BOD reaction and a multiorder BOD reaction (Adrian *et al.* 2004). However, their development contained tedious mathematical expositions. The literature on BOD reaction orders which are less than first order has been reviewed by Adrian and Sanders (1992-93) while Adrian *et al.* (1999), Adrian and Sanders (1998), and Adrian, *et al.* (2004) reviewed three-halves order, second order, and multiorder BOD reactions, respectively.

First, this study is to demonstrate application of the Laplace transform method, which provides a user friendly approach to solution of differential equations, to develop a DO sag equation for a river in which a second order relationship describes the BOD decay of the loading to the river. Secondly, this study is to review the relationships

which describe a three-halves order BOD reaction and have been applied to estimate BOD parameters, then to incorporate these BOD relationships into the differential equation for dissolved oxygen for a stream. Because of its ease in application the Laplace transform method is selected to solve the dissolved oxygen sag equation. Also, a methodology for locating the minimum dissolved oxygen concentration in a stream is developed. Then, examples are presented to illustrate application of the models and to compare results for DO concentrations with those predicted with a first order model. Thirdly, this paper is to develop a DO model for a stream which would take into account the BOD exerted on the stream water by the decomposition characteristics of logging debris in water, then apply the model in the design of a treatment system to control the logging debris wastewater in order to meet the water quality standards before effluent is released. The BOD was to be expressed through two models: a classical model expressing the BOD as a first order reaction, and an alternative approach expressing the BOD as a second order reaction. Published data, a Douglas fir data set (Ponce, 1974), is analyzed to compare its fit to the first and second order BOD models. Finally, The BOD of a mixture of glucose and glutamic acid is accepted as a standard test solution which will provide a reasonably repeatable value of the five day BOD. The BOD reaction of the mixture normally is portrayed as a first order reaction. This study used BOD data which were collected at daily intervals to five days from a respirometer for mixtures of glucose and glutamic acid. The mixtures ranged in increments of 10% from 10% strength (90% dilution) to 100% strength (no dilution). There were ten replications of each strength of sample, so that the BOD of 100 samples measured at daily intervals were available. The BOD data were tested to determine their goodness-of-fit to three BOD

reaction models: a first order model, a half-order model, and an order n model in which the reaction order was determined from the BOD data. The root mean squared error was the criterion used to measure the goodness-of-fit.

CHAPTER 2. OBJECTIVES AND SCOPE

2.1 Objectives

The main objectives of this study are as follows:

1. To develop the DO sag equation for a second order BOD model using the Laplace transform and the convolution integral to simplify the mathematical solution of the model equation.
2. To review the relationships which describe a three-halves order BOD reaction, then to incorporate these BOD relationships into the differential equation for DO for a stream, with application of Laplace transform in solving the DO sag equation.
3. To develop a DO model for a stream which would take into account the BOD exerted on the stream water by the decomposition characteristics of logging debris in water, and to design a treatment system, applying these BOD and DO models to treat the logging debris wastewater in order to meet the water quality standards before releasing the effluent.
3. To examine all of Reining's disaggregated data sets in which the BOD data would be modeled as a first order model, a half order model, or an order n model. The root mean squared error was to be the criterion by which model fit to the data were evaluated.

2.2 Scope

The scope of this study includes the development of the second and the three-halves order BOD models using the new approach, the Laplace transform method, which was

selected to solve DO sag differential equations because of its ease in application. Effects of logging debris in stream water quality are examined. Previously published data sets were analyzed to compare the goodness of fit between BOD models. An unfortunate shortcoming of BOD measurements is that the amount of oxygen consumed in a sample in the first five days of a test, called the 5 day BOD, or BOD₅, is meaningful in domestic wastewater treatment, but provides little information about the BOD decay characteristics of leaves and logging debris which may decay slowly for a year, or more. It is essential that future investigators recognize the importance of collecting additional experimental laboratory and field data in order to generate better and more accurate results when examining the water quality models discussed in this thesis.

CHAPTER 3. SIMPLIFIED DEVELOPMENT OF OXYGEN SAG MODEL

3.1 Introduction

Water quality modeling in a river has developed from the pioneering work of Streeter and Phelps (1925) who developed a balance between the dissolved oxygen supply rate from reaeration and the dissolved oxygen consumption rate from stabilization of an organic waste in which the biochemical oxygen demand (BOD) deoxygenation rate was expressed as an empirical first order reaction, producing the classic dissolved oxygen sag (DO) model. When the dispersion process is considered, the governing equation becomes a partial differential equation. However, the effect of dispersion on BOD and DO in small rivers is negligible (Li 1972; Thomann, 1974; McCutcheon, 1989). The minimum value of the DO concentration has been of particular significance in wastewater treatment design calculations and to regulatory agencies. By contrast the BOD decay characteristics of leaves and logging debris are relatively unknown (Ponce, 1974), although these items represent sources of loads on streams and are important in Total Maximum Daily Load (TMDL) studies.

Several investigators (Thomas, 1957; Young and Clark, 1965; Clark and Viessman, 1965; Nemerow, 1974; Tebbutt and Berkun, 1976) presented data showing that second order rather than first order reactions frequently describe the stabilization of wastewaters, but none of these authors incorporated a second order BOD reaction into the DO sag equation. Butts and Kothandaraman (1970) analyzed stream samples from the Illinois River and found that the majority of these samples' BOD decay was described better by a first order reaction model, while a minority of the samples' BOD decay was

described by a second order reaction model. In spite of these results they did not develop a DO sag equation which included a second order BOD model. Adrian and Sanders (1998) developed an analytical solution for the DO sag equation which incorporated a second order BOD reaction but their development involved integration of cumbersome equations. The Laplace transform method provides a user friendly approach to solution of differential equations. The purpose of this study is to demonstrate application of the Laplace transform method to develop a DO sag equation for a river in which a second order relationship describes the BOD decay of the loading to the river.

3.2 DO Sag Model Formulation

The differential equation describing the DO concentration in a river subject to a BOD reaction is

$$\frac{dC}{dt} = k_s(C_s - C) - k_2 f(t) \quad (3.1)$$

where C is the DO concentration, g/m^3 , C_s is the saturation value for DO, g/m^3 , k_s is the reaeration rate, day^{-1} , t is flow time, days, k_2 is the rate constant in the BOD expression, and $f(t)$ is a function that expresses the BOD concentration as a function of time. The form of the BOD function is related to the expression selected to describe the BOD reaction. The units of the rate constant k_2 depend on the BOD function. Several investigators (Young and Clark, 1965; Clark and Viessman, 1965; Woodward, 1953) express the second order BOD equation as

$$L = \frac{L_0}{1 + k_2 L_0 t} \quad (3.2)$$

where L is the BOD yet to be satisfied, g/m^3 , t is time, days, k_2 is the second order rate

constant having units of volume/mass-time, such as m³/g-day, while L₀ is the initial ultimate first stage BOD. The term f(t) in equation (3.1) for a second order BOD reaction is given by the square of equation (3.2) which enables the differential equation for the DO concentration to be formed.

Conventional BOD tests give values of y, the amount of DO consumed by a sample, g/m³, as a function to time. The relationship L = L₀ - y can be substituted into equation (3.2) which is then rearranged to obtain

$$y = \frac{k_2 L_0^2 t}{1 + k_2 L_0 t} \quad (3.3)$$

which Woodward (1953) attributes by personal communication to H. A. Thomas. Examples are available of calculating the parameters k₂ and L₀ from linearized forms of equation (3.3) (Young and Clark, 1965; Butts and Kothandaraman, 1970; Weber and Carlson, 1965). A preferable procedure for determining k₂ and L₀ is to find their values such that the best fit in the least squares sense is obtained using equation (3.3) and the measured values of y versus t (Marske and Polkowski, 1972; Bates and Watts, 1988; Borsuk and Stow, 2000; Berthouex and Brown, 2002).

Adrian and Sanders (1998) applied an integrating factor to equation (3.1), after it had been modified to include f(t) equal to the square of equation (3.2), then integrated several rather unwieldy expressions to obtain the DO concentration. The Laplace transform method which is presented below is easier to follow than the previous solution.

Equation (3.1) is modified by noting f(t) = L², given by equation (3.2), then the Laplace transform of modified equation (3.1) is

$$p\bar{C} - C_0 + k_s\bar{C} = \frac{k_s C_s}{p} - \frac{1}{k_2} \mathcal{L}\left\{1/(a+t)^2\right\} \quad (3.4)$$

where $a = 1/(k_2 L_0)$, p is the parameter in the Laplace transform, the Laplace transform of $C(t)$ is designated by the overbar, C_0 is the initial DO concentration, and $\mathcal{L}\{1/(a+t)^2\}$ is the Laplace transform of $1/(a+t)^2$, which for $a > 0$ is (Nemerow, 1974)

$$\mathcal{L}\left\{\frac{1}{(a+t)^2}\right\} = \frac{1}{a} + p e^{ap} Ei(-ap) \quad (3.5)$$

in which the term $Ei(-ap)$ signifies the exponential integral with argument $(-ap)$.

Equation (3.4) is rearranged to show the Laplace transform of the DO concentration

$$\bar{C} = \frac{C_0}{p+k_s} + \frac{k_s C_s}{p(p+k_s)} - \frac{1}{k_2(p+k_s)} \left[\frac{1}{a} + p e^{ap} Ei(-ap) \right] \quad (3.6)$$

The inverse transform of equation (3.6) is expressed as

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) - \frac{1}{k_2} e^{-k_s t} * \frac{1}{(a+t)^2} \quad (3.7)$$

where the $*$ notation means $\exp(-k_s t)$ is convoluted with $1/(a+t)^2$ (Churchill, 1958). In other words

$$e^{-k_s t} * \frac{1}{(a+t)^2} = \int_0^t \frac{e^{-k_s(t-\tau)}}{(a+\tau)^2} d\tau = e^{-k_s(a+t)} \int_a^{a+t} \frac{e^{k_s x}}{x^2} dx \quad (3.8)$$

where τ and x are dummy variables of integration and the change in variable $x = a + \tau$ has been introduced. Gradshteyn and Ryzhik (1980) show

$$\int \frac{e^{k_s x}}{x^2} dx = -\frac{e^{k_s x}}{x} + k_s Ei(k_s x) \quad (3.9)$$

Thus, equation (3.7) is expressed as

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) + \frac{1}{k_2(a+t)} - \frac{e^{-k_s t}}{k_s a} - \frac{k_s}{k_2} e^{-k_s(a+t)} \left\{ Ei[k_s(a+t)] - Ei[k_s a] \right\} \quad (3.10)$$

Equation (3.10) is identical to the DO sag equation derived by Adrian and Sanders (1998). However, the Laplace transform method is easier to apply and involves fewer steps than the earlier method which used an integrating factor and several transformations of variables to integrate equation (3.1).

The DO deficit, $D = C_s - C$, g/m^3 , is commonly used instead of C . Equation (3.10) is rearranged to

$$D = D_0 \exp(-k_s t) + L_0 \exp(-k_s t) - \frac{L_0}{1 + k_2 L_0 t} + \frac{k_s}{k_2} \exp\left[-\left(\frac{k_2}{k_2 L_0} + k_s t\right)\right] \left[Ei\left(\frac{k_s}{k_2 L_0} + k_s t\right) - Ei\left(\frac{k_2}{k_2 L_0}\right) \right] \quad (3.11)$$

where D_0 is the DO deficit, g/m^3 , when $t = 0$.

3.2.1 The Exponential Integral

The exponential integral $Ei(x)$ is tabulated in mathematical tables (Abramowicz and Stegun, 1965). However, in equations (3.10) and (3.11) it is convenient to calculate the exponential integral directly from its series expansion. There are two series expansions for the exponential integral, one convenient to use for small values of the argument, x , and the other convenient to use for larger values of x . The first series expansion is (Abramowicz and Stegun, 1965)

$$Ei(x) = \gamma + \ln(x) + \sum_{n=1}^{\infty} \frac{x^n}{n \cdot n!} \quad (3.12)$$

where $\gamma = \text{Euler's constant} = 0.577215\dots$. This series converges for all values of x , however, it converges slowly for large values of x . An alternative method for calculating $Ei(x)$ for large values of x is to use an asymptotic expansion series (Abramowicz and Stegun, 1965)

$$Ei(x) = \frac{e^x}{x} \left(\frac{0!}{x^0} + \frac{1!}{x^1} + \frac{2!}{x^2} + \dots + \frac{n!}{x^n} \right) = \frac{e^x}{x} \sum_{m=0}^{m=n} \frac{m!}{x^m} \quad (3.13)$$

The asymptotic expansion is a divergent series if $n \rightarrow \infty$, yet the difference between the true value of $Ei(x)$ and the sum of a finite number of terms in the truncated series may be very small especially when x is large. Kaplan (1952) presents a simple, practical rule for selecting n : the best approximation of the asymptotic expansion series to $Ei(x)$ occurs when n is the closest integer to x . It is not permissible to differentiate an asymptotic expansion (Gradshteyn and Ryzhik, 1980). In DO sag modeling both small and large values of x are encountered. Equation (3.12) has been recommended for use instead of equation (3.13) when $x < 5$ due to error in the asymptotic expansion, but when $x \geq 5$ either equation (3.12) or (3.13) could be used if one was aware that equation (3.12) may require n to be large to converge (Adrian and Sanders, 1998). Examples presented later will show how large n may be for equation (3.12) to converge.

3.2.2 Two Forms of the Oxygen Sag Equation

Combining equation (3.10) with the asymptotic expansion, equation (3.13), yields

$$C(t) = C_s + (C_0 - C_s) \exp(-k_s t) + \frac{L_0}{1 + k_2 L_0 t} - L_0 e^{-k_s t} - \frac{k_s}{k_2} \left[\frac{k_2 L_0}{k_s (1 + k_2 L_0 t)} \sum_{n=0}^N n! \left(\frac{k_2 L_0}{k_s (1 + k_2 L_0 t)} \right)^n - \frac{k_2 L_0}{k_s} \exp(-k_s t) \sum_{n=0}^M n! \left(\frac{k_2 L_0}{k_s} \right)^n \right] \quad (3.14)$$

This expression is a computationally tractable approximate form of equation (3.10) which is suitable when the term $k_s / (k_2 L_0)$ is greater than 5. N and M are selected as the nearest integers to the arguments of the exponential integrals by using the roundoff function, where

$$M = \text{round} [k_s / (k_2 L_0)] \quad (3.15)$$

$$N = \text{round} [k_s / (k_2 L_0) + k_s t] \quad (3.16)$$

A form of the DO sag equation that is always applicable is obtained by combining equation (3.10) with the convergent series, equation (3.12). The result is

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) + \frac{L_0}{1 + k_2 L_0 t} - L_0 e^{-k_s t} - \frac{k_s}{k_2} e^{-\frac{k_s(1+k_2 L_0 t)}{k_2 L_0}} \left\{ \ln(1 + k_2 L_0 t) + \sum_{n=1}^{\infty} \frac{\left[\frac{k_s(1+k_2 L_0 t)}{k_2 L_0} \right]^n}{n \cdot n!} - \sum_{n=1}^{\infty} \frac{\left[\frac{k_s}{k_2 L_0} \right]^n}{n \cdot n!} \right\} \quad (3.17)$$

3.2.3 Minimum DO Concentration

The minimum DO concentration will occur either at $t = 0$ or at the time called the critical time, t_c , when $dC/dt = 0$ in equation (3.10). The derivative of equation (3.10) when $dC/dt = 0$ is

$$0 = k_s \left(C_s - C_0 + \frac{1}{k_2 a} \right) \exp(-k_s t) - \frac{1}{k_2 (a+t)^2} - \frac{k_s}{k_2 (a+t)} + \frac{k_s^2}{k_2} \exp[-k_s (a+t)] \{ Ei[k_s (a+t)] - Ei[k_s a] \} \quad (3.18)$$

This equation is solved for the root t_c by a numerical root finding method in a software package such as MATHCADTM with equation (3.12) or (3.13) used to evaluate the exponential integrals. If t_c is negative, then the minimum DO concentration occurs at $t = 0$ where $C(0) = C_0$. A positive t_c is substituted into equation (3.14) or (3.17) to calculate the minimum DO concentration. The value of N is not known a priori so a few trials may be needed to find the value of N that is consistent with t_c . An alternative procedure to find the minimum DO and t_c is to apply a series of times in equations (3.14) or (3.17) and record the value of the minimum DO concentration and the time to which it corresponds.

3.3 Application of the DO Sag Equation

The DO sag equation for a second order BOD demand is illustrated in an example developed from data presented by Ponce (1974) in which needles from Douglas Fir in samples prepared with stream water are tested for BOD. The second order reaction rate coefficient of $0.000440 \text{ m}^3/(\text{g}\cdot\text{day})$ is calculated from BOD test data. Assume that the streamflow and temperature are such that after mixing with the Douglas Fir needles the ultimate first stage BOD is 100 g/m^3 and the reaction rate coefficient remains unchanged (due to the small rate constant the 5 day BOD would be about 82 g/m^3). Ponce (1974) carried the BOD test out for 90 days yet found no evidence of nitrification. His data for Douglas Fir are presented in Table 3.1.

Table 3.1. BOD Data for Douglas Fir Needles (Ponce, 1974)^{1,2}.

Time [Day]	Oxygen Consumed [g/m ³]	Time [Day]	Oxygen Consumed [g/m ³]
0	0	45	432
5	252	60	440
10	312	90	460
20	408		

¹Each value of oxygen consumed is an average of four samples.

²Nonlinear least squares analysis yields rate coefficient $k_2 = 0.000440 \text{ m}^3/(\text{g day})$ and ultimate BOD $L_0 = 481.445 \text{ g/m}^3$ for second order BOD.

The DO saturation value in the application is 9.08 g/m^3 and the initial DO value is 7 g/m^3 . The reaeration rate is $0.6/\text{day}$. The DO concentrations are calculated at daily intervals for the first seven days using the exact and the approximate equations for the exponential integral, and the minimum DO concentration is found using equation (3.18). These data are input into equations (3.14) and (3.17) for comparison while the results are tabulated in Table 3.2. The value of $k_2/(k_2L_0)$ was calculated as 13.63, by equation (3.15), so M was set to 14, and N calculated from equation (3.16), varied with t as shown in Table 3. 2. The time $t_c = 3.3 \text{ day}$ was calculated using equation (3.18) with the exponential integral calculated by equation (3.13) instead of equation (3.12) due to the reduced number of calculations using equation (3.13) when M or N are larger than 5 or 6. The DO concentration was 3.516 g/m^3 at the critical time. The error was calculated by finding the difference between C(t) from equations (3.14) and (3.17). Negligible error was found in using equation (3.14) which contained the approximate series expression.

The complete DO sag curve is shown in Figure 3.1 using both equations (3.14) and (3.17). The DO sag curve is of interest in TMDL studies.

Table 3.2. Comparison of DO Concentrations for Second Order BOD Reaction.

t days	C Eq.(3.17) (Exact)	C Eq.(3.14) (Approximate)	N Eq.(3.16)	$C_{\text{exact}} - C_{\text{approx}}$ Error
0	7.000	7.000	14	0.000
1	4.781	7.782	14	- 0.001
2	3.819	3.819	15	0.000
3	3.516	3.516	15	0.000
3.3 = t_c	3.500	3.500	16	0.000
4	3.549	3.549	16	0.000
5	3.746	3.746	17	0.000
6	4.014	4.014	17	0.000
7	4.305	4.305	18	0.000

3.4 Conclusions

A DO sag equation for a stream has been developed in which the biochemical oxygen demand is evaluated as a second order reaction. The differential equation for the DO sag model was solved by applying the Laplace transform method. The DO sag model, equation (3.10), contains exponential integrals which are evaluated by either an exact series or an approximate asymptotic series. The location of the minimum DO concentration is found by calculating the time at which $dC/dt = 0$ in equation (3.18). Other simulations have shown the asymptotic series should not be used to calculate the

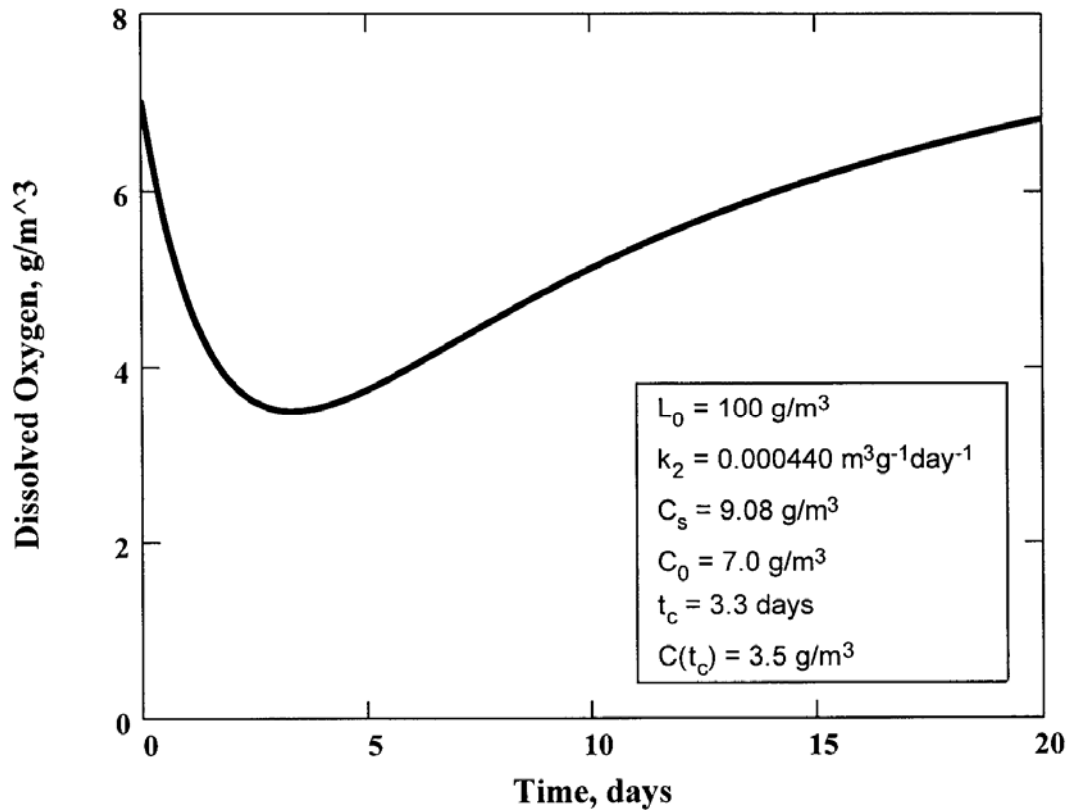


Figure 3.1. DO Sag Curve for a Stream Which Receives BOD Loading from Douglas Fir Needles. The BOD Reaction is Second Order. The Time at Which the Minimum DO Concentration Occurs Is 3.3 Days and the Minimum DO Concentration is 3.5 G/M³.

DO concentration in equation (3.10) or the critical time in equation (3.18) at which the minimum DO occurs if the values of M or N from equations (3.15) and (3.16) are less than five. Also, other simulations have shown that when N is less than 7 a plot of equation (3.14) may produce a rough appearing DO sag curve which may have a jump or a sudden change in slope each time N takes on a different integer value in equation

(3.16). It has been recommended that equation (3.14) not be used for M or N less than 5 (Adrian and Sanders, 1998). The example presented in this study in which Douglas Fir needles produced BOD, showed that the DO sag model which incorporated an asymptotic series was virtually identical in its predictions with $M = 14$ and N ranging from 14 to 18 to predictions using the exact series. It is necessary to experiment with equation (3.12), the exact series for the exponential integral, to find the number of terms to sum. 150 terms were used in the calculations in, although more terms may have been needed for calculations at larger times. Thus, the DO sag equation for second order BOD is not suitable for calculation without a computer. Figure 3.1 shows that the small value of the BOD reaction rate constant results in the stream being able to carry a large BOD concentration from Douglas Fir needles without having the DO concentration being exhausted. The result is of interest in TMDL studies involving waste load allocation to stream.

CHAPTER 4. LAPLACE TRANSFORM APPLICATION TO A NONTRADITIONAL DISSOLVED OXYGEN MODEL

4.1 Introduction

The empirical first order BOD decay equation has been widely applied since 1925 in modelling the dissolved oxygen (DO) in a stream (Streeter and Phelps, 1925). Literature reviews on BOD reaction orders which are three-halves order, second order, and multiorde are available (Adrian *et al.*, 1999; Adrian and Sanders, 1998; Adrian et al, 2004). The steady-state DO model developed Streeter and Phelps (1925), which predicts DO concentration in streams using first order BOD kinetics, is well understood and accepted (Mulligan and Brown, 1998). Modifications have included accounting for sedimentation (Thomas, 1948), benthic addition of BOD (Thomann, 1974), effects of algae (Beck and Young, 1975), and dispersion (Dresnack and Dobbins, 1968). The effect of dispersion on BOD and DO concentration in small rivers is negligible (McCutcheon, 1989). Few studies have examined the effect that BOD reaction orders which were other than first order have on the DO behavior in a stream.

Respirometry is a versatile method for measuring the BOD reaction characteristics of a wide variety of wastewaters and stream samples (Young and Cowan, 2004). Multiorde BOD data (Hewitt, et al, 1979) encouraged development of a DO sag equation for the three-halves order BOD reaction and a multiorde BOD reaction (Adrian, *et al.*, 1999; Adrian, *et al.*, 2004), although tedious mathematical expositions were plentiful. The purpose of this investigation is to review the relationships which describe a three-halves order BOD reaction, then to incorporate these BOD relationships into the differential equation for DO for a stream. Because of its ease in application the Laplace

transform method is selected to solve the DO sag equation. Also, a methodology for locating the minimum DO concentration in a stream is developed, and examples are presented to illustrate application of the models.

4.2 Three-halves Order BOD Equation

The three-halves order BOD equation is given by (Adrian *et al.*, 1999; Hewitt *et al.*, 1979)

$$\frac{dL}{dt} = -k_{3/2}L^{3/2} \quad (4.1)$$

where L is the BOD remaining, g/m^3 , at time t , and $k_{3/2}$ is the three-halves order rate constant having units of $(\text{m}^3/\text{g})^{1/2}/\text{day}$. Equation (4.1) is integrated, combined with $L_0 - y = L$ and rearranged to

$$y = L_0 - \frac{4}{k_{3/2}^2(T + t)^2} \quad (4.2)$$

where $T = 2 / (k_{3/2}\sqrt{L_0})$ is a time constant having units of days and L_0 is the carbonaceous BOD remaining at time zero. By comparison, the first order BOD equation is (Adrian *et al.*, 2004)

$$L = L_0 e^{-k_1 t} \quad (4.3)$$

where k_1 is the first order BOD rate constant with units of day^{-1} .

The conventional BOD test or respirometry gives values of y_i , the BOD exerted, or the amount of oxygen consumed by a sample at time, t_i (Young and Cowan, 2004). Parameters $k_{3/2}$ and L_0 are estimated from the measured y_i and t_i values with a nonlinear least squares procedure as those values which minimize the root mean squared error objective function

$$RMSE(k_{3/2}, L_0) = \sqrt{\frac{1}{N-2} \sum_{i=1}^{i=N} \left[y_i - L_0 + \frac{4}{k_{3/2}^2 \left(\frac{2}{k_{3/2}\sqrt{L_0}} + t_i \right)^2} \right]^2} \quad (4.4)$$

where $N - 2$ represents the number of degrees of freedom (Berthouex and Brown, 2002). The $RMSE(k_{3/2}, L_0)$ function is minimized by selecting the values of $k_{3/2}$ and L_0 for the data set consisting of the values of y_i on day t_i using an iterative technique, such as the Newton Raphson method or the Levenburg-Marquardt compromise (Bates and Watts, 1998). The RMSE methodology was applied to estimate the rate constant and ultimate BOD for samples taken from several New Jersey brooks and rivers (Hewitt *et al.*, 1979). A Bayesian estimation method is available for calculating rate constants and ultimate BOD while providing the probability distribution of the parameters (Borsuk and Stow, 2000). Table 4.1 shows the rate constant, designated as $k_{3/2}$, and the ultimate BOD, L_0 , reported in two investigations in which river samples were analyzed in respirometers to determine how well the BOD data fit first order and three-halves order reactions. In data sets 1-7 the RMSE was smaller for the three-halves order BOD model than for the first order reaction (Hewitt *et al.*, 1979; Rodriguez, 1999).

4.3 Laplace Transform of Oxygen Sag Equation for Three-halves Order BOD Reaction

The differential equation for DO concentration in a stream with a three-halves order BOD reaction is found from conservation of mass combined with equation (4.2) expressed as L to yield

$$\frac{dC}{dt} + k_s C = k_s C_s - \frac{8}{k_{3/2}^2} \frac{1}{(T+t)^3} \quad (4.6)$$

Table 4.1. BOD Reaction Orders, Rate Constants, Ultimate BODs and Root Mean Square Errors for First and Three-Halves Order BOD Reactions from Respirometer Data.

Data Set	Location	Rate Constant		Ultimate BOD		RMSE		Reference
		k ₁ First	k _{3/2} Three-halves	L ₀ First	L ₀ Three-halves	First	Three-halves	
		Day ⁻¹	(m ³ /g) ^{1/2} /day	g/m ³	g/m ³	g/m ³	g/m ³	
1	Passaic River, NJ	0.237	4.87 · 10 ⁻²	21.72	24.51	0.6870	0.6511	[12]
2	Passaic River, NJ	0.134	2.59 · 10 ⁻²	19.50	23.00	0.2386	0.1883	[12]
3	Passaic River, NJ	0.101	2.46 · 10 ⁻²	10.47	12.81	0.3491	0.1042	[12]
4	Whippany River, NJ	0.140	3.22 · 10 ⁻²	14.96	17.43	0.3349	0.1248	[12]
5	Mile Run, NJ	0.217	6.48 · 10 ⁻²	8.121	9.595	0.2106	0.1975	[12]
6	Rockaway River, NJ	0.123	4.11 · 10 ⁻²	5.648	6.870	0.0762	0.0681	[12]
7	Jarama River, Madrid, Spain ¹	NA	5.17 · 10 ⁻²	NA	101	NA	NA	[16]

¹NA = Not reported. Reaction order was reported as 1.5

where C is the DO concentration, g/m^3 , and k_s is the reaeration rate constant, day^{-1} (Adrian *et al.*, 1999). The DO concentration at time zero is C_0 and the saturation concentration is C_s . The Laplace transform of equation (4.6) yields (Oberhettinger and Badii, 1973)

$$p\bar{C} - C_0 + k_s\bar{C} = \frac{k_s C_s}{p} - \frac{8}{k_{3/2}^2} \mathcal{L} \left\{ \frac{1}{(T+t)^3} \right\} \quad (4.7)$$

where the Laplace transform of $C(t)$ is defined by

$$\mathcal{L} \{C(t)\} = \bar{C} = \int_0^{\infty} C(t) e^{-pt} dt \quad (4.8)$$

The inverse transform of equation (4.7) is found from Laplace transform tables and convolution (Oberhettinger and Badii, 1973)

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) - \frac{8}{k_{3/2}^2} e^{-k_s t} * \frac{1}{(T+t)^3} \quad (4.9)$$

where the symbol “*” means convolution

$$e^{-k_s t} * \frac{1}{(T+t)^3} = \int_0^t e^{-k_s(t-\tau)} \frac{1}{(T+\tau)^3} d\tau = k_s^2 e^{-k_s T} \int_{k_s T}^{k_s(T+t)} \frac{e^u}{u^3} du \quad (4.10)$$

with the change in variables $u = k_s(T + \tau)$. The integral in equation (4.10) is (Petit Bois, 1961; Abramowitz and Stegun, 1965)

$$\int_{k_s T}^{k_s(T+t)} \frac{e^u}{u^3} du = \left[-\frac{1}{2} e^u \left(\frac{1}{u^2} + \frac{1}{u} \right) + \frac{1}{2} \text{li}(e^u) \right] \Big|_{k_s T}^{k_s(T+t)} \quad (4.11)$$

where $\text{li}(e^u)$ is the logarithmic integral of e^u . The logarithmic integral is not commonly tabulated, but a related function, the exponential integral, is tabulated. The definition is $\text{li}(x) = \text{Ei}(\ln(x))$ for $x > 0$, where $\text{Ei}(\ln(x))$ is the exponential integral of $\ln(x)$ (Abramowitz and Stegun, 1965). After incorporating equations (4.10) and (4.11) into equation (4.9), the DO sag curve becomes

$$\begin{aligned}
C(t) = & C_s - (C_s - C_0) e^{-k_s t} \\
& + \frac{4k_s^2}{k_{3/2}^2} \left[\left(\frac{1}{k_s^2 (T+t)^2} + \frac{1}{k_s (T+t)} \right) - e^{-k_s t} \left(\frac{1}{k_s^2 T^2} + \frac{1}{k_s T} \right) \right] \\
& - \frac{4k_s^2}{k_{3/2}^2} \left\{ e^{-k_s (T+t)} \left[\text{Ei}(k_s (T+t)) - \text{Ei}(k_s T) \right] \right\}
\end{aligned} \tag{4.12}$$

This result, easily obtained by means of the Laplace transform and inversion using the convolution integral, agrees with a DO sag equation obtained by a more difficult procedure (Arian *et al.*, 2999). Equation (4.12) can be applied to rivers in a manner analogous to that used in applying the Streeter-Phelps DO sag equation (1925).

The exponential integral $\text{Ei}(x)$ which appears in equation (4.12) is calculated from its series expansion. There are two series expansions; one convenient for small values of argument x , and the other convenient for larger values of x . The first series expansion is (Abramowitz and Stegun, 1965)

$$\text{Ei}(x) = \gamma + \ln x + \sum_{n=1}^{\infty} \frac{x^n}{n n!} \tag{4.13}$$

where $\gamma = \text{Euler's constant} = 0.577215\dots$. This series converges for all values of x but may converge slowly for large values of x . For large values of x , an asymptotic expansion will converge more rapidly than equation (4.13) to an approximate value of $\text{Ei}(x)$

$$Ei(x) = \frac{e^x}{x} \left(\frac{0!}{x^0} + \frac{1!}{x^1} + \frac{2!}{x^2} + \frac{3!}{x^3} + \cdots + \frac{n!}{x^n} \right) = \frac{e^x}{x} \sum_{m=0}^{m=n} \frac{m!}{x^m} \quad (4.14)$$

where $n! = n(n - 1)(n - 2) \dots (3)(2)(1)$ and $0! = 1$. The asymptotic expansion is a divergent series, yet for a finite number of terms, the difference between the true value of $Ei(x)$ and the sum of a finite number of terms in the series may be small. For a fixed value of x , the closest approximation is obtained when n is the closest integer to x . The exact series expression should be used in DO modeling when $x < 5$ to reduce error (Adrian and Sanders, 1998).

4.4 Minimum DO Concentration

The time t_c at which the minimum DO concentration occurs is an important parameter which is found from equation (4.12) when $dC/dt = 0$. If $dC/dt \neq 0$, for $t > 0$, then the minimum DO concentration will occur when $t = 0$, for the case in which DO addition by reaeration is greater than the DO uptake rate by BOD. The derivative of equation (4.12), designated as $f(t_c)$, is

$$\begin{aligned} f(t_c) = & k_s(C_s - C_0) e^{-k_s t_c} \\ & + \frac{4k_s^2}{k_{3/2}^2} \left\{ k_s e^{-k_s t_c} \left[\frac{1}{k_s^2 T^2} + \frac{1}{k_s T} \right] - \left[\frac{2}{k_s^2 (T + t_c)^3} + \frac{1}{k_s (T + t_c)^2} \right] \right\} \\ & + \frac{4k_s^2}{k_{3/2}^2} \left\{ k_s e^{-k_s (T + t_c)} \left[Ei(k_s (T + t_c)) - Ei(k_s T) \right] - \frac{1}{T + t_c} \right\} \end{aligned} \quad (4.15)$$

The critical time occurs when $f(t_c) = 0$ which is found in root finding methods. An alternative to applying equation (4.15) is to find t_c directly from equation (4.12). In this case, one sets up equation (4.12) and uses a software package to calculate when $dC/dt = 0$. The derivative of equation (4.12) found by numerical methods and the corresponding time, t_c , are listed.

4.5 Application of the Oxygen Sag Equation

4.5.1 Example 1

DO sag equation (4.12) is illustrated in Figure 4.1 when initial BOD concentrations of 15, 25, and 35 g/m³ are applied with a reaction rate coefficient of 0.0517 (m³/g)^{1/2}/day. Time constants are calculated from $T = 2 / (k_{3/2} \sqrt{L_0})$ as 9.988, 7.737 and 6.539 day, respectively. The DO saturation is 9.2 g/m³, the initial DO is 6.0 g/m³, and the reaeration rate constant is 0.6 day⁻¹. Then $k_s T = 5.993, 4.642$ and 3.923 , respectively. These data are input to equation (4.12) to obtain the DO concentration. The value of t_c found from equation (4.15) was checked by setting the numerical derivative of equation (4.12) equal to zero, yielding $t_c = 1.069, 1.644$ and 1.733 days, respectively, while equation (4.12) showed $C(1.069) = 5.510, C(1.644) = 3.158$ and $C(1.733) = 0.386$ g/m³, respectively. Equation (4.14) was not used to calculate $Ei(x)$ in two cases as $k_s T < 5$.

4.5.2 Example 2

Data set 2 in Table 4.1 is for a river which has a three-halves order reaction rate coefficient of 0.0259 (m³/g)^{1/2}/day and an ultimate first stage BOD of 23.0 g/m³ (Hewitt et al., 1979). DO saturation is 9.2 g/m³, initial DO is 6.0 g/m³, and the reaeration rate constant is 0.6/day. Time constant $T = 2 / (k_{3/2} \sqrt{L_0}) = 16.101$ day and $k_s T = 9.661$. The corresponding rate constant and ultimate BOD for first order reaction are 0.134 day⁻¹ and 19.50 g/m³ (Hewitt et al., 1979). The appropriate rate constant and ultimate BOD are input to equation (4.12) to obtain the DO concentrations which are shown in Table 4.2. Both equation (4.13) with 50 terms and equation (4.14) can be used to calculate $Ei(x)$.

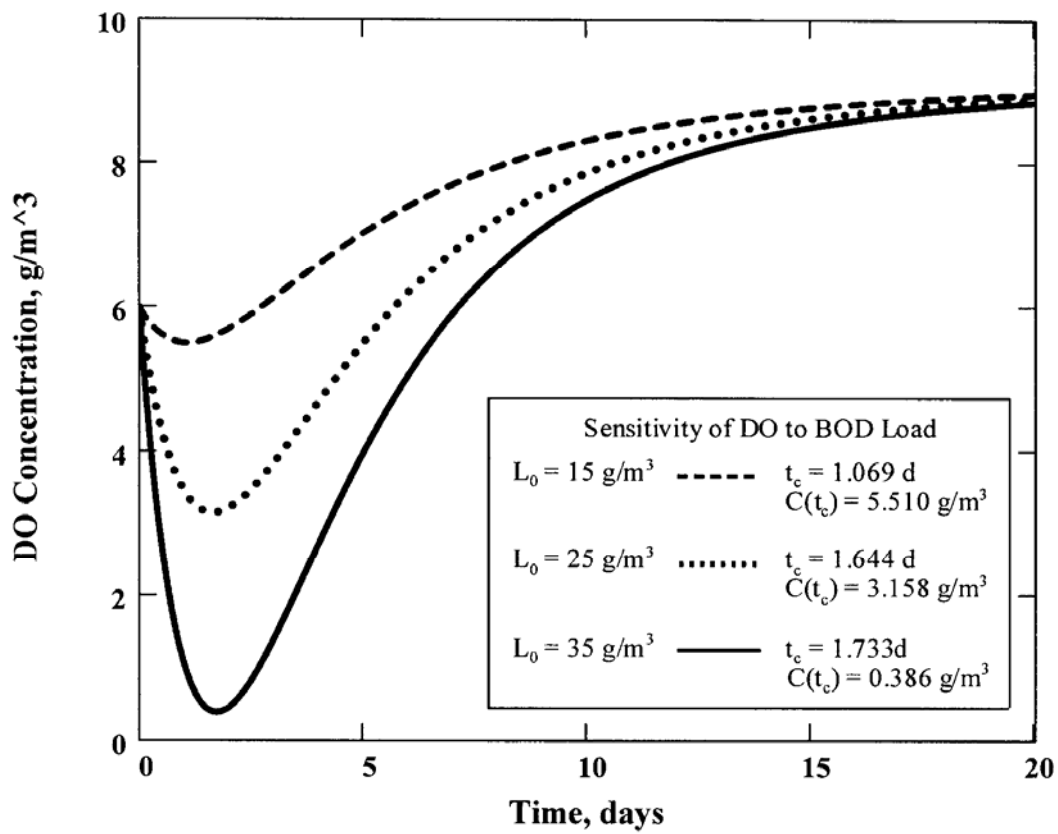


Figure 4.1. Effect of BOD Load on DO Sag Curves for Three-halves Order BOD Reaction.

M and N in Table 4.2 correspond to the nearest integer value of the argument of Ei(x) in equation (4.14) using

$$M = \text{round}\left[k_s(T + t)\right] \quad (4.16)$$

$$N = \text{round}\left[k_s T\right] \quad (4.17)$$

Thus, M and N are the optimum number of terms to include in equation (4.14) depending on the magnitude of the argument. The minimum DO concentration occurs at $t_c = 1.364$ days for the three-halves order BOD reaction using equation (4.15) and $t_c = 1.402$ days for the first order BOD reaction (Streeter and Phelps, 1925). Error is incurred when equation (4.14), the asymptotic expansion of Ei(x), is applied instead of (13), but as Table 4.2 illustrates the maximum error in the DO concentration is small, less than 0.79% on day 1.402, and is of little practical significance. Thus, either equation (4.13) or equation (4.14) can be applied to evaluate equation (4.12) to calculate the DO concentration. If equation (4.13) is selected, tests should be run to determine how many terms to include in the summation when the argument $k_s(T + t)$ takes its largest value. 50 terms were used to evaluate equation (4.13) for $t = 7$ days.

4.5.3 Example 3

The effect of the reaction rate coefficient, $k_{3/2}$, on the shape of the DO sag curve is illustrated in Figure 4.2 in which $k_{3/2} = 0.0487 \text{ (m}^3/\text{g)}^{1/2}/\text{day}$ has been changed by +/- 20% and $L_0 = 24.51 \text{ g/m}^3$. As expected, larger reaction rate constants affect both the magnitude of the minimum DO and its location. As the rate constant increases both the minimum DO and the critical time decrease. The time at which the minimum DO occurs is not very sensitive to the value of the BOD rate constant.

Table 4.2. BOD and DO Concentrations for First Order and Three-halves Order BOD Reactions.

t days	DO Calculated Using Three-halves Order BOD Reaction						DO Calculated Using First Order BOD Reaction	
	L g/m ³ (2)	C, g/m ³ (12) and (13) (Exact)	C, g/m ³ (12) and (14) (approximate)	M Round [k _s (T + t)]	N Round [k _s T]	Error, g/m ³ C _{ex.} - C _{app.}	L g/m ³ (3)	C g/m ³ (After [1])
0	23.00	6.000	6.000	10	10	0	19.50	6.000
1	20.39	5.498	5.534	10	10	- 0.036	17.05	5.617
1.364 = t _{c,3/2}	19.55	5.470	5.509	10	10	- 0.039	16.24	5.591
1.402 = t _{c,1}	19.46	5.470	5.513	11	10	-0.043	16.16	5.591
2	18.20	5.535	5.577	11	10	- 0.042	14.92	5.636
3	16.34	5.804	5.838	11	10	- 0.033	13.05	5.847
4	14.76	6.153	6.180	12	10	- 0.026	11.01	6.138
5	13.39	6.508	6.529	13	10	- 0.021	9.98	6.451
6	12.21	6.838	6.851	13	10	- 0.013	8.73	6.756
7	11.17	7.131	7.141	14	10	- 0.010	7.63	7.041

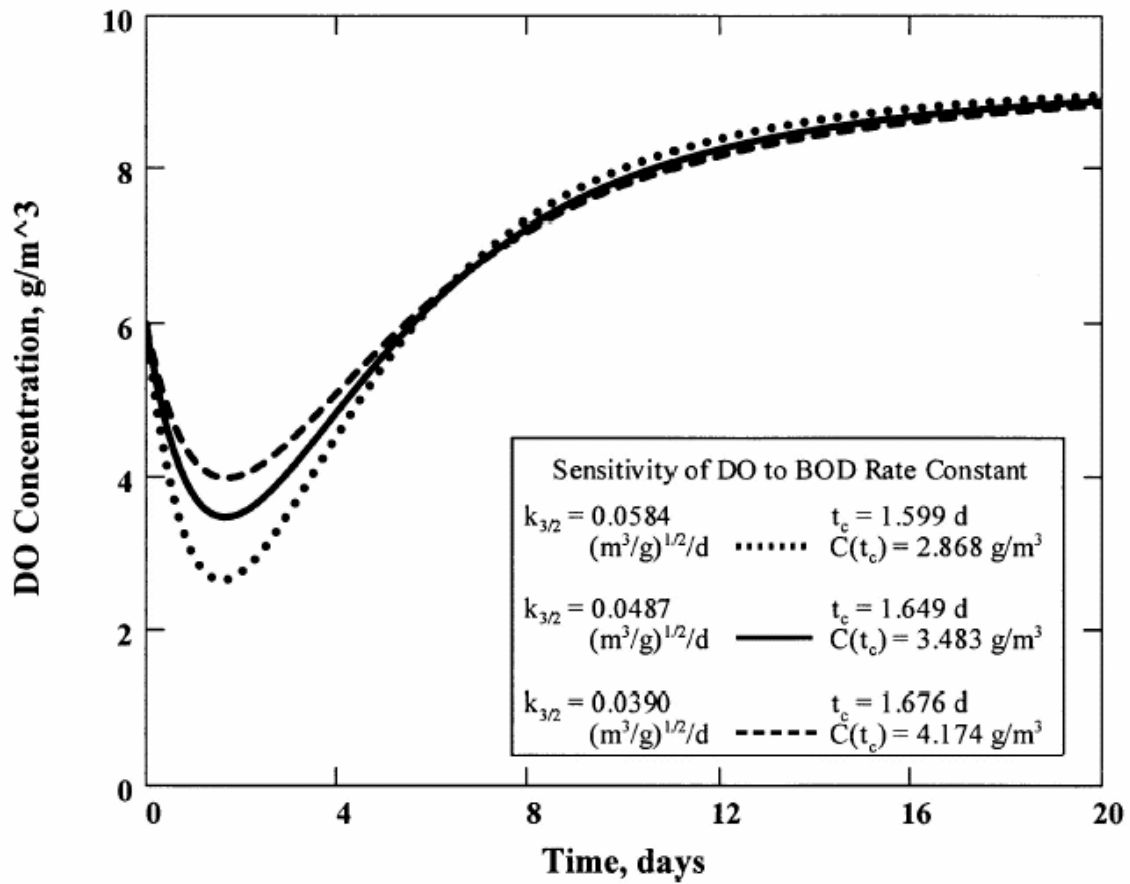


Figure 4.2: Effects of a +/- 20% Change in Rate Constant on DO Sag Curves for Three-Halves Order BOD Model.

4.6 Conclusions

1. Table 4.1 shows the three-halves order rate constant and ultimate BOD for seven analyses of BOD reaction data from five different rivers in New Jersey, USA and in Madrid, Spain. Unfortunately, in practice few data sets are published with enough readings distributed over time to determine how well they are described by BOD models of various orders. Instead, the five day BOD is usually the only value reported.
2. A DO sag equation developed for BOD consumption modeled as a three-halves order reaction is solved easily using the Laplace transform method and convolution. The DO sag equation contains exponential integrals which are evaluated from their series expressions. The exact series expression of an exponential integral may require summation of several hundred terms although 50 terms were adequate in the examples. The number of terms to include in an asymptotic expansion depends upon the magnitude of the argument. 14 terms were required in one example. An asymptotic expansion is not used to evaluate an exponential integral unless the argument is greater than five. The maximum error in the DO concentration was less than 0.79% on day 1.402 when comparing the two alternative methods of evaluating $Ei(x)$ when the argument was 9.661.
3. The minimum value of the DO concentration occurs at the critical time, t_c , which may be 0 if the reaeration rate is greater than or equal to the DO consumption rate, otherwise $t_c > 0$. t_c is calculated numerically from the DO sag equation by a root finding method. As the rate constant, $k_{3/2}$, increases both the minimum DO and t_c become smaller.
4. It is recommended that river BOD data be collected at daily intervals for 5 to 10 days, then with less frequency, say 7 to 10 days, to obtain sufficient values of DO consumed versus time to allow for evaluation of the rate constant as well as determination of which

BOD model is appropriate. Also, the duration of the BOD test should be extended to larger values of time such as 30 days to identify the appropriate BOD reaction order.

5. The user now has a model available with which to describe the DO sag curve when the three-halves order BOD reaction equation is applicable. Field testing following the methods used by the authors cited in Table 4.1 would show the frequency of application of the three-halves order BOD equation and DO sag curve.

CHAPTER 5. TREATMENT AND DISSOLVED OXYGEN MODEL FOR LOGGING DEBRIS IMPACT ON STREAMS

5.1 Introduction

Water quality in relation to forestry practices refers to a few specific attributes including suspended sediment, bedload sediment, temperature, nutrient levels, and toxins. A significant change in, or addition of, any of these biodegradable items to the stream system changes the dissolved oxygen concentration, and so, the stream's health and function. Also, logging activities can potentially impact stream ecosystem through altered input of organic matter such as leaves, needle fragments, debris and large wood debris. These inputs may reduce stream oxygen levels and alter microhabitat conditions necessary for the survival, breeding, foraging or resting activities of many organisms.

Leaves exert an oxygen demand on stream water as they decay. Slack and Feltz (1968) noted that the dissolved oxygen (DO) concentration in North Fork Quantico Creek in Virginia decreased from approximately 8 g/m³ to less than 1 g/m³ during the month of October, the month with peak leaf fall, before recovering to approximately 8 g/m³ the next month. Only limited information is available on the biochemical oxygen demand (BOD) reaction kinetics of decay of tree leaves and needles. A study of the oxygen consuming characteristics in water of dead maple and oak leaves and pine needles in Massachusetts was reported by Chase and Ferullo (1957). They conducted a modified long term biochemical oxygen demand (BOD) test of the leaves and needles, using tap water rather than BOD dilution water while conducting the test for 386 days at room temperature which varied between 20° and 29°C, rather than in an incubator at 20°C. They did not report genus and species. They found the leaves and needles consumed

oxygen over the entire 386 day period although at a diminished rate as time elapsed. After 140 days the oxygen consumption was approximately 650 mg/g of leaves (maple), 360 mg/g of leaves (oak), and 330 mg/g of needles (pine). The original leaf and needle loadings in g of leaf (or needles) per m³ of water were reported which facilitated BOD calculations. They noted that data for maple leaves may have been influenced by algal growth which was first observed at 140 days. The corresponding 140 day BOD values were: 34.3 g/m³ (maple), 19.0 g/m³ (oak) and 17.4 g/m³ (pine). By contrast the 386 day BOD values were: 39.1 g/m³ (maple), 26.4 g/m³ (oak) and 25.9 g/m³ (pine). Indeed, the authors calculated that the leaves and needles had exerted during the test period an oxygen demand equivalent to 75% (maple), and 50% (oak and pine needles), of their dry weight. The leaves and needles were still consuming oxygen at the end of the 386 day test period.

An unfortunate shortcoming of BOD measurements is that the amount of oxygen consumed in a sample in the first five days of a test, called the 5 day BOD, or BOD₅, is meaningful in domestic wastewater treatment, but provides little information about the BOD decay characteristics of leaves and logging debris which may decay slowly for a year, or even more. For example, de Hoop *et al.* (1997 and 1998) measured the BOD₅ as varying between 0 and 48.4 g/m³ of samples of storm water runoff from a log storage and handling facility in Louisiana. By contrast, they found the Chemical Oxygen Demand (COD) varied from 0 to 14,724 g/m³ for the same samples, suggesting that BOD measurements taken over a longer period of time would have produced higher results. Instead, de Hoop *et al.* (1998) concluded that only 1% to 13% of the COD was biodegradable, but this conclusion is questionable as it was based on 5 day BOD tests.

Ponce (1974) measured the BOD of logging debris over a 90 day period. His measurements included BOD of Douglas Fir, Red Alder and Western Hemlock.

5.2 Objectives

The objective of this paper was to develop a DO model for a stream which would take into account the BOD exerted on the stream water by the decomposition characteristics of logging debris in water. The BOD was to be expressed through two models: a classical model expressing the BOD as a first order reaction, and an alternative approach expressing the BOD as a second order reaction. Loss of solids which contain BOD from the stream water was to be incorporated into each model. In addition, an objective was to propose a treatment system, applying the second order BOD and DO models to treat the logging debris water in order to meet the water quality standards before release to a stream.

5.3 Model Formulation for BOD

The classical first order BOD reaction equation has been expressed at least since 1909 (Phelps, 1909; Baird and Smith, 2003) in the form

$$\frac{dL}{dt} = -k_1 L \quad (5.1)$$

in which L is BOD, g/m^3 ; k_1 is a rate constant, day^{-1} ; and t is time, day. Equation (5.1) is solved to yield

$$L(t) = L_0 e^{-k_1 t} \quad (5.2)$$

in which L_0 is the BOD of a wastewater at time zero. The amount of oxygen consumed is

measured in the BOD test rather than the BOD, although they are related, as $y(t) = L_0 - L(t)$, where $y(t)$ is the dissolved oxygen consumed. Thus, equation (5.2) is expressed as

$$y(t) = L_0(1 - e^{-k_1 t}) \quad (5.3)$$

The majority of applications of the previous equations have been to domestic wastewaters flowing into and from municipal wastewater treatment plants which discharge to a receiving water. In a stream some of the solids which contain BOD are removed from the stream water by sedimentation. This phenomena is accounted for by the Thomas (1948) modification to equation (5.1), so the BOD reaction when sedimentation occurs is expressed as

$$\frac{dL}{dt} = -k_1 L - k_r L \quad (5.4)$$

where k_r is a sedimentation rate constant with units day^{-1} . Equation (5.4) integrates to

$$L(t) = L_0 e^{-(k_1 + k_r)t} \quad (5.5)$$

Several investigators have explored alternative forms of the BOD reaction equation, with considerable attention directed to the second order form

$$\frac{dL}{dt} = -k_2 L^2 \quad (5.6)$$

in which k_2 is the second order rate constant, $\text{m}^3/(\text{g day})$ (see references in Adrian and Sanders, 1998). When sedimentation is included the BOD equation becomes

$$\frac{dL}{dt} = -k_2 L^2 - k_r L \quad (5.7)$$

The integrated form of equation (5.6) is

$$L(t) = \frac{L_0}{1 + k_2 L_0 t} \quad (5.8)$$

while equation (5.7), which accounts for sedimentation, integrates to

$$L(t) = \frac{k_r L_0 e^{-k_r t}}{k_2 \left[L_0 (1 - e^{-k_r t}) + \frac{k_r}{k_2} \right]} \quad (5.9)$$

5.4 Estimation of BOD Equation Parameters

This example analyzes BOD data in Table 5.1 for Douglas Fir, Red Alder and Western Hemlock logging debris published by Ponce (1974), using root mean squared error to measure how well data fit the models.

Table 5.1. BOD Data from Douglas Fir Needles of Ponce (1974) and Predicted BOD Concentration. Each Value of Oxygen Consumed is the Mean of Four Measurements.

Time day	Oxygen Consumed g/m ³	Predicted by First Order BOD Model ¹ g/m ³	Predicted by Second Order BOD Model ² g/m ³
0	0	0	0
5	252	225	248
10	312	335	327
20	408	415	390
45	432	440	436
60	440	440	446
90	460	440	457

¹First order model parameters:

$$k_1 = 0.143 \text{ day}^{-1}, L_0 = 440.5 \text{ g/m}^3, \text{ RMSE} = 15.83 \text{ g/m}^3$$

²Second order model parameters:

$$k_2 = 0.000,440,2 \text{ m}^3/(\text{g day}), L_0 = 481.4 \text{ g/m}^3, \text{ RMSE} = 9.62 \text{ g/m}^3$$

RMSE is calculated from the equation

$$RMSE = \sqrt{\frac{1}{DOF} \sum_{i=1}^{i=N} [y_p(t_i) - y_m(t_i)]^2} \quad (5.10)$$

where $y_p(t_i)$ is obtained from combining the expression $y(t) = L_0 - L(t)$ with equation (5.2) for a first order model or equation (5.8) for a second order model on day t_i . The measured value is $y_m(t_i)$, and DOF is the degree of freedom. $DOF = N - 2$ or $N - 3$, depending on whether no sedimentation or with sedimentation included in second order model, where N is the number of measurements. The fit between model and data is measured by equation (5.10). Analyzing the three data sets from Ponce (1974) in Table 5.1 with first order and the second order BOD models results in RMSE values which are lower in two cases, Douglas Fir and Red Alder, for the second order model (respectively, $RMSE = 9.62 \text{ g/m}^3$, and 18.16 g/m^3) than they are for the first order model (respectively, $RMSE = 15.83 \text{ g/m}^3$, 34.21 g/m^3), while the reverse holds true for Western Hemlock which had $RMSE = 17.22 \text{ g/m}^3$ for first order BOD decay and $RMSE = 28.91 \text{ g/m}^3$ for second order. The two models predict different rate constants as their units are different. Footnotes of Table 5.1 note the second order model predicts a larger value of the ultimate BOD than the first order model, as discussed by others (Young and Clark, 1965; Tebbutt and Berkun, 1976). Berthouex and Brown (2002) illustrate that collecting BOD data over longer periods improves prediction of k_1 , k_2 , L_0 , and the reaction order. Indeed, Borsuk and Stow (2000) measured BOD data for periods that extended to 140 days. Their data gave unconventional BOD reaction orders of 1.3, 1.7, 2.4 and 4.0 for three wastewaters and a river sample. Footnotes of Table 5.1 show the second order BOD model had the best fit to the data from Table 5.1.

Rodriguez (1999) analyzed BOD data by an equation similar to the square of equation (5.11), called the average quadratic difference, to calculate unconventional reaction orders of 1.632 (paper recycling effluent), 1.515 (river sample), and 1.224 (textile dyeing plant effluent), finding two of the three BOD reaction orders closer to a second order reaction than to a first order reaction.

5.5 Model Formulation for Dissolved Oxygen When Sedimentation Occurs

The DO balance in a stream is developed from mass balance considerations for a first order BOD reaction equation to yield the differential equation (Streeter and Phelps, 1925; Rich, 1973)

$$\frac{dC}{dt} + k_s C = k_s C_s - k_1 L_0 e^{-(k_1+k_r)t} \quad (5.11)$$

in which C is the DO concentration, g/m^3 ; k_s is the reaeration rate constant, day^{-1} ; and C_s is the DO concentration at saturation, g/m^3 . Equation (5.11) integrates to

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) - \frac{k_1 L_0}{k_s - k_1 - k_r} \left[e^{-(k_1+k_r)t} - e^{-k_s t} \right] \quad (5.12)$$

in which C_0 is the DO concentration at $t = 0$. When the sedimentation rate constant is zero Equation (5.12) reduces to the venerable Streeter Phelps (1925) model.

When the BOD reaction is second order and sedimentation is present the differential equation for DO is modified from an equation presented by Adrian and Sanders (1998) so it incorporates Equation (5.9) to become

$$\frac{dC}{dt} + k_s C = k_s C_s - \frac{k_r^2 e^{-2k_r t}}{k_2 (A - e^{-k_r t})^2} \quad (5.13)$$

in which $A = 1 + k_r / (k_2 L_0)$. An integrating factor, $e^{k_s t}$, is applied, followed by integration to obtain the DO concentration

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) + \frac{k_r e^{-k_s t}}{k_2} \int_1^{e^{-k_r t}} X^m (A - X)^{-2} dX \quad (5.14)$$

where $m = 1 - k_s / k_r$, is called the Phelps-Thomas index to honor E.B. Phelps who introduced the BOD equation (Phelps, 1909) and H.B. Thomas who introduced sedimentation loss of BOD (Thomas, 1948) and the second order BOD model (Thomas, 1957). Equation (5.13), the dissolved oxygen equation which includes a second order BOD reaction and loss of BOD by sedimentation, becomes for m positive or negative

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) + \frac{k_r e^{-k_s t}}{k_2} \sum_{k=0}^{\infty} \frac{k+1}{k+m+1} A^{-(k+2)} (e^{-(k+m+1)k_r t} - 1) \quad (5.15)$$

in which $m = 1 - k_s / k_r$ and $A = 1 + k_r / (k_2 L_0)$. An apparent indeterminate form arises in the special case with m negative in which $k + m + 1 = 0$ as both numerator and denominator become zero, but application of L'Hospital's rule shows that the numerator approaches zero more rapidly than the denominator so no problem occurs.

When $m = 0$, which means $k_s = k_r$, the DO model becomes

$$C(t) = C_0 e^{-k_s t} + C_s (1 - e^{-k_s t}) + \frac{k_r e^{-k_s t}}{k_2} \left(\frac{1}{A - e^{-k_r t}} - \frac{1}{A - 1} \right) \quad (5.16)$$

5.5.1 Magnitude of Phelps-Thomas Index

The range of values for the reaeration rate coefficient, k_s , is available in Table 5.2 as presented in Tchobanoglous and Schroeder (1985). The values of k_r depend upon sediment characteristics including particle size and density as well as stream temperature

and turbulence, but obviously $k_r = 0$ is a lower limit while a negative k_r signifies benthic solids are scouring from the stream bottom. Thomann (1972) has stated that the sedimentation rate coefficient, k_r , may vary from 0.1 day^{-1} to 0.2 day^{-1} , values which are based on municipal and industrial wastewater impacted streams. These values are for streams in which removal of BOD by sedimentation has a noticeable effect on the BOD and DO concentration. With this range in values of k_r , one can calculate the range of the Phelps-Thomas index, m , for several categories of streams as shown in Table 5.2. From the table one can see that m may be smaller than -10.50 or as large as 0.50.

Table 5.2. Reaeration Rate Constants And Sedimentation Exponents For Water Bodies (Adapted from Thomann (1972) and Tchobanoglous and Schroeder (1985)).

Water Body	Ranges of k_s , day^{-1} at 20°C	Ranges of k_s/k_r for $k_r = 0.10$ to $k_r = 0.20 \text{ day}^{-1}$	Ranges of $m = 1 - k_s/k_r$
Small ponds and backwaters	0.10 to 0.23	0.50 to 2.30	-1.30 to 0.50
Sluggish streams and large lakes	0.23 to 0.35	1.15 to 3.50	- 2.5 to - 0.15
Large streams of low velocity	0.35 to 0.46	1.75 to 4.60	- 3.60 to - 0.75
Large streams of normal velocity	0.46 to 0.69	2.30 to 6.90	- 5.90 to -1.30
Swift streams	0.69 to 1.15	3.45 to 11.50	-10.50 to - 2.45
Rapids and waterfalls	>1.15	> 5.75 to > 11.50	< -10.50 to < - 4.75

5.6 Treatment System Design for Logging Debris Wastewater Treatment

A small treatment system design is proposed in this section to treat wastewater disposed from a logging operation manufacturer. For the sake of simplification, the design is considering only one set of data for a particular type of trees, Douglas fir, which is the most dominant timber specie in North Pacific area where Ponce (1974) had studied and collected the data. Thus, this design is based on the second order model for biochemical oxygen demand decay reactions. Figure 5.1 presents a schematic treatment train for the treatment system.

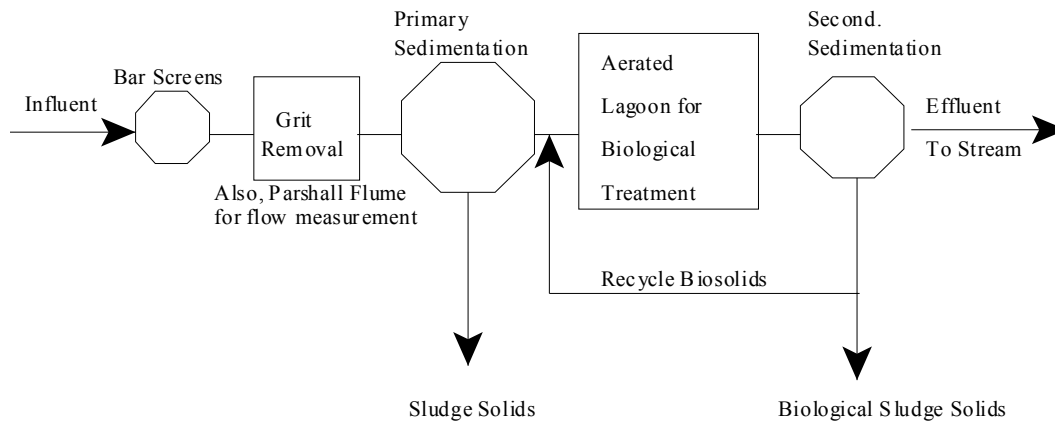


Figure 5.1: Schematic Diagram For The Treatment System

The design is based on some main characteristics of the influent and effluent of logging debris wastewater under consideration for treatment as shown below:

- Influent Characteristics of Logging Debris:

Average flow rate, $Q_{\text{avg}} = 4000 \text{ m}^3/\text{d}$

Maximum flow rate, $Q_{\text{max}} = 10,000 \text{ m}^3/\text{d}$

SS = $2000 \text{ g}/\text{m}^3$

Ultimate BOD, $L_0 = 400 \text{ g}/\text{m}^3$

- Effluent standards applicable to effluent entering a stream:

$$\text{BOD} = 30 \text{ g/m}_3$$

$$\text{SS} = 30 \text{ g/m}^3$$

$$\text{pH} = 6.5 \text{ to } 8.5$$

$$\text{Effluent dissolved oxygen (DO) concentration} \geq 6 \text{ g/m}^3$$

Each process in the treatment system is discussed in sections 5.6.1 through 5.6.4.

5.6.1 Bar Screens

A manually cleaned bar screen chamber is designed as the first unit treatment process in this treatment system. It was designed to remove larger material such as branches, twigs, large barks, and solids that could otherwise damage or interfere with downstream operations. The unit consists of 10 bars with width of 6.4 mm and bars depth of 50.8 mm. Spacing of bars are 31.9 mm and openings of 25.4 mm with the bars set 30° from the vertical to ease cleaning. Velocity at average flow is 0.305 m/s and will remain constant because the depth varies with the flow, controlled by the Parshall flume.

Below are some calculations:

$$\text{Width of channel} = W_c = [\text{number of bars} + 1 \text{ extra space}] \times \text{Open space} + [\text{number of bars} \times \text{Width}] = 0.343 \text{ m}$$

$$\text{Width of screen} = W_s = [\text{number of bars} + 1 \text{ Extra space}] \times \text{Open space} = 0.28 \text{ m}$$

$$\text{Max. length of screen} = L_{\text{max}} = Q_{\text{max}} / [W_s \times V_{\text{avg}}] = 1.36 \text{ m}$$

$$\text{Max. depth of channel} = L_{\text{max}} \times \sin 30 = 0.68 \text{ m}$$

$$\text{Max. velocity of channel} = Q_{\text{max}} / [\text{width} \times \text{max. depth}] = 0.496 \text{ m/s}$$

Screenings are manually raked from the screen onto a perforated plate where they drain before removal for disposal. Screens must be cleaned frequently to avoid backwater caused by the buildup of debris between cleanings, which may cause flow surges when the screens are cleaned. These high-velocity surges can reduce the solids-capture efficiency of downstream units.

5.6.2 Grit Removal

A horizontal-flow grit chamber is designed to remove grit particle sizes larger than 0.21mm with a specific gravity of 2.65 as suggested by U.S. EPA (1987). A single grit removal unit with a bypass channel around the unit will suffice for the purpose of this small treatment system. The design is capable of removing up to 75% of 0.15 mm material. This grit chamber is designed for an average flow of 4000 m³/d and a peaking factor of 2.5. The throat width of the flume (W) = 152 mm, horizontal velocity = 0.3 m/s, particle settling velocity (v_s) = 7 mm/s, channel width of float tube = 330 mm, depth of 0.52 m, and the chamber length safety factor = 1.2. Calculations yield cross-sectional area of 0.38 m², width = 1.096 m. Settling time in the grit chamber is determined as $t = \text{depth}/v_s = 69.3$ second, and length = horizontal velocity $\times t = 20.8$ m. The design length is $12 \times 20.8 = 25$ m.

Parshall flume operates to vary the flow depth and keeps the velocity of the flow stream constant at 0.3 m/s. Operational experience has shown that this velocity allows heavier grit particles to settle while lighter organic particles remain suspended and are carried out of the channel.

5.6.3 Primary Sedimentation

Primary treatment equalizes raw wastewater quality and flow to a limited degree, thereby protecting downstream unit processes from unexpected surges in flow. Raw wastewater contains suspended particulates heavier than water; these particles settle by gravity under quiescent conditions. A typical rectangular primary settling tank, which normally ranges from 15 to 90 m in length and 3 to 24 m in width, and depths should exceed 2 m (WPCF, 1985). However, a system of two rectangular lagoons is considered for the primary settling in this particular logging debris wastewater treatment system. It is designed for detention time at average flow of two days, width of 4 m, and the length to width ratio is 8:1. Again, average flow rate is 4000 m³/d and peaking factor of 2.5. For these designed parameters, the dimensions of the lagoons can be determined as follows: Total volume, $V_{\text{tot}} = t_{\text{avg}} \times Q_{\text{avg}} = 8,000\text{m}^3$; surface area of each lagoon = $4000/(2 \times 4) = 1000 \text{ m}^2$, from which the length and width are calculated to be 89.6 m and 11.2 m, respectively. Detention time at peak flow is 0.8 day.

In practice, the linear flow-through velocity, or scour velocity, should be kept sufficiently low to avoid resuspension of settled solids (Metcalf and Eddie, 2003). The critical scour velocity may be calculated from equation (Camp, 1946), $v_s = \left[\frac{8k(s-1)gd}{f} \right]^{0.5}$, where $k = 0.04$ = constant for type of scoured particles; $s = 1.2$ = specific gravity; $d = 0.2 \text{ mm}$ = diameter of scoured particles; $f = 0.025$ = Darcy-Weisbach friction factor. Substituting values into this equation yields v_s to be 0.016 m/s. Since critical scour velocity is much greater than peak flow horizontal velocity, which is calculated by dividing the peak flow by the cross-sectional area of the lagoons, yielding

0.00058 m/s, the design is adequate. Expected BOD and SS removal can be estimated using the equation developed by Crites and Tchobanoglous (1998), $R = t/(a + bt)$, where $a = 0.018$, $b = 0.014$ for BOD removal, and $a = 0.0075$, $b = 0.014$ for SS removal, t is the detention time. Thus, BOD removal at average and peak flow are 49% and 47%, respectively, and SS removal at average and peak flows are 70% and 69.5%, respectively. Therefore, at average flow, 784 kg/d BOD is removed, and primary effluent BOD reduces to 204 g/m³. Primary-sludge production can be estimated in SI units as $S_M = (Q \times SS \times R)/1000$, where Q is influent to settling lagoons (m³/d), SS is incoming suspended solids concentration (mg/L), and R is efficiency of SS removal. For this design, SS removal is calculated to be 5.6 tons/day. A scum removing unit, which may be as simple as a net, is necessary to follow the primary sedimentation lagoons and is placed before the biological treatment unit to capture any floatable solids to prevent these materials from entering the biological treatment lagoon.

5.6.4 Biological Treatment

Figure 5.2 presents a general schematic of a typical flow-through activated-sludge system and its modifications. Wastewater and biological solids are first combined, mixed, and aerated in an aeration tank (an aeration lagoon in this design). From the aeration lagoon the mixed liquor goes to the secondary settling lagoon to allow gravity separation of the suspended solids from the treated wastewater. Settled SS are then recycled to the aeration lagoon to maintain a concentrated microbial population for degradation of influent wastewater constituents, known as return activated sludge.

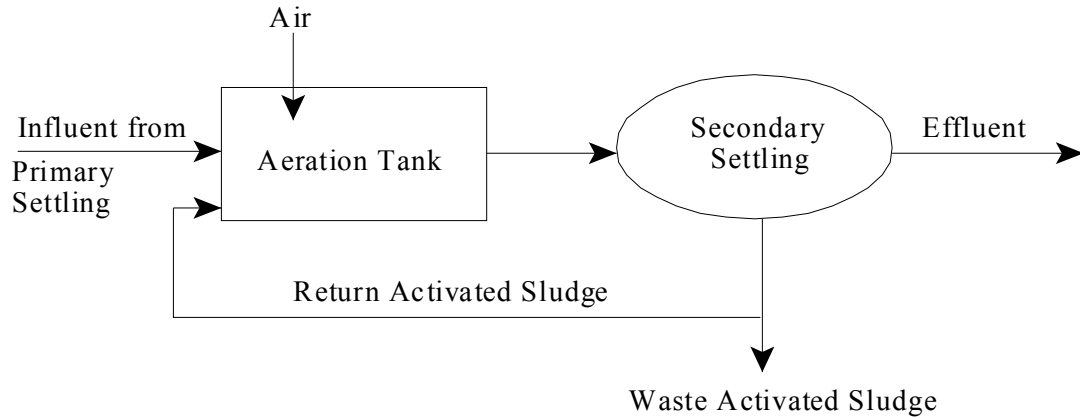


Figure 5.2. The Activated-Sludge Process

5.6.5 Aerated Lagoons

An aerated system of lagoons is used for the biological treatment process. Aerated lagoons accept higher biochemical oxygen demand (BOD) loadings than facultative lagoons, are less susceptible to odors, and require less land. Typical depth for this type of lagoon ranges from 3 to 6 m, with hydraulic detention times ranging from 5 to 30 days. For the purpose of this study, 2 completely mixed lagoons are used. Design parameters include: average influent flow of 4000 m³/d, detention time of 5 days, depth of 6 m. Influent BOD and SS are the primary effluent BOD and SS, which are 204 g/m³ and 600 g/m³, respectively. Calculations for lagoons dimensions result in total volume of 20,000 m³, and thus each lagoon has surface area of 1,667 m² or diameter of about 50 m if round shape lagoons are used. The decomposition process of the material in this process will follow the second order BOD model, as described in Equation (5.8), in which k_2 (value of 4.402×10^{-4} m³/g/d) is the second order reaction rate constant, L_0 is the primary effluent BOD, and t is the detention time of the aerated lagoon.

Mechanical surface aerators are needed to provide adequate oxygen supply, which is about 1.5 kgO₂/kg of BOD loading. The number of aerators needed is determined as follow:

$$\text{BOD loading} = 4,000 \text{ m}^3/\text{d} \times 204 \text{ g/m}^3 = 816,0000 \text{ g/d} = 816 \text{ kg/d}$$

$$\text{Oxygen needed} = (1.5 \text{ kg O}_2/\text{kg BOD loading}) \times (816 \text{ kg/d}) = 1,224 \text{ kg/d}$$

1 surface aerator will supply, say, 4 lb O₂/HP/d

$$\text{Oxygen supply} = (4 \text{ lb O}_2/\text{HP/d}) \times (24 \text{ hr/d}) = 96 \text{ lb O}_2/\text{HP/d} \approx 44 \text{ kg O}_2/\text{HP/d}$$

$$\text{Amount of horsepower needed} = (1,224 \text{ kg O}_2/\text{d}) / (44 \text{ kg O}_2/\text{HP/d}) \approx 28 \text{ HP}$$

Thus, six 5HP-aerators provide adequate oxygen supply for this aerated lagoon system.

5.6.5 Secondary Settling Lagoon

Aerated lagoons are followed by a settling lagoon, which is 2 m in depth, to reduce suspended solids before discharge to stream. In secondary clarification, mixed liquor is fed to the clarifier and the SS settle, forming a sludge blanket with an overlying clear water zone. This lagoon is designed to reduce BOD to approximately 30 mg/L or 30 g/m³. Influent suspended solids are removed by sedimentation. The detention time and dimension of this lagoon are calculated as shown below:

Assume that the settling velocity of critical particle, v_s , is 0.5 mm/s

$$\text{Detention time} = 2\text{m}/0.00005 \text{ m/s} = 40,000 \text{ s} \approx 0.46 \text{ days}$$

$$\text{Volume} = 4,000 \text{ m}^3/\text{d} \times 0.46 \text{ d} = 1840 \text{ m}^3$$

$$\text{Area} = 1840 \text{ m}^3 / 2 \text{ m} = 920 \text{ m}^2$$

Therefore, the surface area of the lagoon needed is 920 m², or 34.2 m diameter if a round shape lagoon is used.

To prevent erosion and desiccation of clay or bentonite liners, interior slopes of the lagoon should have soil cover and riprap. Within the clear water zone, discrete floc particles settle, resulting in a clarified effluent. In the lower zone, the blanket of SS thickens before withdrawal as clarifier underflow. Secondary clarifier process failure can involve either clarification or thickening stages; thus, proper design must consider both.

5.7 Conclusions

Hewitt et al. (1979) carried out BOD measurements from samples collected from eight New Jersey streams with measurement durations of 9 to 21 days and found samples fit reaction orders that ranged from 1st order to 4th order. Rodriguez (1999) carried out BOD tests of duration 20, 25, and 40 days to calculate unconventional reaction orders that ranged from 1.224 to 1.632. Borsuk and Stow (2000) carried out BOD tests of duration 140 to 180 days while calculating unconventional reaction orders 1.3, 1.7, 2.4 and 4.0. Clearly, BOD data may be represented in some cases by unconventional reaction orders, including second order.

The rate constants for data collected over a 90 day duration by Ponce (1974) for Douglas Fir needles were $k_2 = 4.402 \times 10^{-4}$. The data fit a second order BOD reaction better than they fit a first order BOD reaction using RMSE criteria.

BOD tests that are carried out for longer durations than the traditional five days are needed to discern reaction orders, especially for slowly decaying wastewaters such as those containing logging debris. Clearly, BOD data may be represented in some cases by unconventional reaction orders, including second order.

Stream sampling protocols should be encouraged in which sedimentation data are collected in addition to BOD data. Thomann (1972) provides sedimentation rate constants of 0, 0.1 and 0.2 day⁻¹, but additional values of rate constants which are related to wastewater type and stream conditions would be beneficial.

The proposed design is based on the unconventional second reaction order, based on Douglas fir data. It serves as a basic structure and focuses on only BOD and SS treatment. For practical purpose, more details such as removal efficiencies in each process, the different flow conditions such as peak hour flow, peak monthly flow need to be considered more carefully and thoroughly.

CHAPTER 6. DILUTIONS OF GLUCOSE AND GLUTAMIC ACID ANALYZED AS MULTI-ORDER BOD REACTIONS

6.1 Introduction

Reining (1967) analyzed the BOD kinetics of a 1:1 mixture which at full strength contained 175 g/m^3 of glucose and 175 g/m^3 of glutamic acid in a Hach Model 191 Manometric BOD apparatus (Hach Chemical Co., Ames, IA). The samples were prepared according to Standard Methods (1965) with the modification that the glutamic acid was neutralized with 1 N potassium hydroxide as suggested by Tom (1951). This mixture had a theoretical oxygen demand of 357.5 g/m^3 . Reining's results consisted of values of oxygen consumed at daily intervals for five days. The mixture of glucose and glutamic acid was prepared in ten different strengths, respectively, 100%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, and 10% of full strength. Ten replications of each strength of sample were prepared. Reining's major objective was to determine how closely the 5 day BOD for each strength of sample compared with the theoretical oxygen demand. He also applied a first order BOD reaction model in which the ultimate BOD was equated to the theoretical oxygen demand while the 10 measured values collected on day five yielded the mean of the 5 day BOD as 220.1 g/m^3 . These two data points enabled him to calculate a first order reaction rate coefficient of 0.191 day^{-1} . However, there were large deviations between the daily BOD predictions from the first order model and the BOD values that were measured on days 1, 2, 3 and 4, but there was, of course, close agreement between the measured and predicted 5 day BOD values.

Tangpanichdee (unpublished special project report, 1977) analyzed an aggregation of Reining's data in which the mean of the oxygen consumed values for each

strength of sample were calculated on days 1, 2, 3, 4 and 5. Then these mean values were analyzed. Tangpanichdee found that when the sample strength was 50% or greater, it was described better by a half order BOD equation rather than by a first order model, while the first order BOD model described the 10, 20, 30, and 40 percent strengths better as measured by the root mean squared error. The results of this analysis are shown in Table 6.1. The first order BOD model had smaller mean squared errors in four cases out of ten, for the samples having 10%, 20%, 30 % and 40% strength, while the half order model had lower mean squared error for the remaining six higher strength samples. The mean of the mean squared error for all of the data was smaller for the half order model. The half order model predicted a consistent value for the ultimate BOD with a mean across all of the tests of 221.7 g/m^3 , in which there was a narrow range of values from 219.5 to 224.7 g/m^3 . By contrast the first order model predicted a mean ultimate BOD of 245.7 g/m^3 , but the predictions showed a trend of increasing ultimate BOD's with the increasing strength of the sample so that the values ranged from a low of 211.6 g/m^3 to a high of 276.0 g/m^3 . Both the first order and the half order rate constants exhibited a trend with the sample strength. The first order model resulted in a mean rate constant of 0.55 day^{-1} with values ranging from 1.00 day^{-1} to 0.34 day^{-1} . The half order model resulted in a mean rate constant of $4.70 \text{ (g/m}^3)^{1/2}/\text{day}$ and a range in values from $2.50 \text{ (g/m}^3)^{1/2}/\text{day}$ to $5.90 \text{ (g/m}^3)^{1/2}/\text{day}$. Thus, the half order model fit the entire data set better than the first order model whether one compared the rate constant, the ultimate BOD or the mean squared error. Adrian and Sanders (1992-1993) applied a graphical method based on linearizing the half-order BOD model to estimate the rate constant and the ultimate BOD from part of Reining's data, but a least squares approach is recognized as having a

sounder statistical basis than the graphical and linearized equation approach (Berthouex and Brown, 2002).

Table 6.1. Kinetic Characteristics of First Order and Half Order BOD Models When Applied to the Mean Values of Oxygen Uptake for Each Sample Strength (After Tangpanichdee, 1977).

Strength of Sample	First Order Kinetics			Half Order Kinetics		
Percent	k_1 day ⁻¹	L_0^1 (g/m ³)	MSE ² (g/m ³) ²	$k_{1/2}$ (g/m ³) ^{1/2} /d	L_0^1 (g/m ³)	MSE ² (g/m ³) ²
10	1.00	211.6	0.53	2.50	224.7	2.23
20	0.61	230.3	0.72	3.10	219.5	2.24
30	0.67	228.7	1.60	4.00	223.1	2.99
40	0.59	237.5	3.80	4.50	223.7	3.82
50	0.53	246.1	7.09	5.00	224.7	5.68
60	0.42	256.7	6.56	4.80	219.8	5.47
70	0.50	245.1	7.93	5.60	219.5	6.67
80	0.45	252.1	7.01	5.80	220.2	4.73
90	0.37	273.0	13.80	5.80	221.9	11.49
100	0.34	276.0	17.08	5.90	219.4	15.35
Mean	0.55	245.7	6.61	4.70	221.6	6.07
Standard Deviation	0.19	19.95	5.46	1.19	2.23	4.24

¹Ultimate BOD has been adjusted to the value projected for full strength

²MSE = Mean squared error between the model and the data.

6.2 Purpose

The purpose of this investigation was to examine all of Reining's (1967) disaggregated data set in which the BOD data would be modeled as:

1. a first order model, or
2. a half order model, or
3. an order n model.

The root mean squared error was to be the criterion by which model fit to the data were evaluated.

6.3 Model Formulation

The multi-order BOD model was formulated by Hewitt *et al.* (1979) in differential form as

$$\frac{dL}{dt} = -k_n L^n \quad (6.1)$$

where L is the BOD exerted, g/m^3 , t is time, day, n is the dimensionless reaction order, and k_n is the rate constant, $\text{g}^{1-n} \text{m}^{3(n-1)} \text{day}^{-1}$. Equation (6.1) integrates to

$$L(t) = \left[L_0^{1-n} - k_n (1-n)t \right]^{\frac{1}{1-n}} \quad (6.2)$$

for $n \neq 1$. When $n=1$, equation (6.1) integrates to

$$L(t) = L_0 e^{-k_1 t} \quad (6.3)$$

where L_0 is the BOD remaining at $t = 0$. In the BOD test the amount of oxygen consumed, $y(t)$, g/m^3 , is measured rather than the BOD remaining, $L(t)$, but the terms are related as $y(t) = L_0 - L(t)$. Equation (6.3) becomes the familiar first order BOD model

$$y(t) = L_0 (1 - e^{-k_1 t}) \quad (6.4)$$

while equation (6.2) for $n \neq 1$ becomes

$$y(t) = L_0 - \left[L_0^{1-n} - k_n(1-n)t \right]^{\frac{1}{1-n}} \quad (6.5)$$

When $n = \frac{1}{2}$ for the half order reaction, equation (6.5) becomes

$$y(t) = L_0 - \left[L_0^{1/2} - \frac{k_{1/2}t}{2} \right]^2 \quad (6.6)$$

Where $k_{1/2}$ is the rate constant, $g^{1/2} m^{-3/2} d^{-1}$.

6.4 Parameter Estimation and Model Evaluation

The parameter k_n , L_0 , and n were evaluated from the experimental data and the first order, half order, or order n BOD model by using the root mean squared error criterion (Berthouex and Brown, 2002)

$$RMSE = \sqrt{\frac{\sum_{i=1}^M [y(t_i) - \hat{y}(t_i)]^2}{DOF_n}} \quad (6.7)$$

where $y(t_i)$ is the measured oxygen uptake value on day t_i , $\hat{y}(t_i)$ is the predicted oxygen uptake value on day t_i calculated from equations 6.4, 6.5 or 6.6, depending on the reaction order, M is the number of data points, and DOF_n is the number of degrees of freedom for each reaction order, with $DOF_1 = 3$, $DOF_{1/2} = 3$, and $DOF_n = 2$. Equation (6.7) was applicable to most of the data, but when $n < 1$ a special condition may arise in which all of the BOD is consumed prior to $t = 5$ days so that equation (6.7) has to be modified.

When $n < 1$ equation (6.5) is no longer applicable after a critical time which occurs when all of the BOD has been consumed. The critical time, t_c , occurs in equation (6.5) when the term $L_0^{1-n} - k_n(1-n)t_c = 0$, which yields

$$t_c = \frac{L_0^{1-n}}{k_n(1-n)} \quad (6.8)$$

For $n = 1$, $t_c = \infty$, but when $n < 1$, t_c has a finite value. t_c is meaningless for $n > 1$. The critical time is important in evaluating BOD parameters and models as equation (6.5) requires

$$y(t) = L_0 \quad \text{for } t > t_c \quad (6.9)$$

The root mean squared error equation for $t > t_c$ is modified to

$$RMSE = \left[\frac{1}{DOF_n} \left\{ \sum_{i=1}^N [y(t_i) - \hat{y}(t_i)]^2 + \sum_{M-N}^M [y(t_i) - L_0]^2 \right\} \right]^{1/2} \quad (6.10)$$

where N is the number of data points for which $t_i \leq t_c$. Adrian and Sanders (1992-1993) suggested that t_c be calculated by estimating the parameters using all of the data in equation (6.7), then estimating t_c from equation (6.8), and noting whether t_c was larger than the time corresponding to the last measured data point. If it was larger, then it had no role in the analysis and equation (6.7) did not have to be modified to equation (6.10). However, if the calculated t_c was less than the time for the last data point, then the data set would be divided and equation (6.10) would be applied to calculate a new set of k_n , L_0 and n . These values would be applied in equation (6.8) and equation (6.10) would be reapplied. A few iteration are expected to suffice to calculate parameters k_n , L_0 , and n which are consistent with t_c .

6.5 Applications

The data from Reining (1967) were analyzed as described previously. The DOF_n was set equal to $M - 2$ for the first and half order BOD models, and to $M - 3$ for the order n model. In some cases a preliminary value of t_c was estimated from the data as one would see that $y(t_4) = y(t_5)$, or $y(t_3) = y(t_4) = y(t_5)$. In these cases t_c was estimated as $t_c = t_4$ or $t_c = t_3$, respectively. After the values of k_n , L_0 and n were available, t_c was calculated from equation (6.8) to determine whether equation (6.10) had been applied correctly.

The results of the calculations of the parameters k_1 , L_0 ; $k_{1/2}$, L_0 ; and k_n , L_0 , n , are shown in Table 6.2 as well as the corresponding RMSE values. The most appropriate model had the smallest RMSE.

6.6 Results

Table 6.2 lists the results obtained when all of the BOD data collected for each of the ten strengths of samples were analyzed for L_0 , k_n , RMSE, and reaction order n . Each strength of sample also was analyzed for the above parameters measured from the mean values of BOD recorded each day. Table 6.3 summarizes the results tabulated in Table 6.2 by showing the number of times the first order, half order, and order n BOD models had the best fit to the data for each strength of sample. Of the 100 BOD samples which were analyzed, 10 BOD samples for each strength, 22% fit the first order BOD model best, 56% fit the half order model best, and 22% fit the order n BOD model best, with

Table 6.2. BOD Parameters Calculated from the Ten Sets of Sample Data

Run #	Parameters	10% Strength			20% Strength			30% Strength		
		1st Order	n order	Half order	1st Order	n order	Half order	1st Order	n Order	Half order
1	n	1	1.851	0.5	1	1.114	0.5	1	1.14	0.5
	L ₀	22.463	24.589	24.672	41	41	41	64.338	65.202	63.999
	k	1.326	0.131	2.608	0.724	0.493	3.889	1.08	0.649	5.972
	RMS	1.602	1.355	3.803	1.583 E-7	1.828 E-7	2.018 E-7	1.83	1.967	3.928
2	n	1	1.117	0.5	1	1.848	0.5	1	1.409	0.5
	L ₀	17.60	17.86	17.836	37.368	40.504	41.794	45.714	47.751	47.861
	k	1.856	1.413	5.013	1.527	0.105	3.605	2.285	0.615	8.57
	RMS	9.19 E-7	1.34 E-6	0.035	1.201	0.62	6.101	0.033	0.127	0.105
3	n	1	0.834	0.5	1	0.729	0.5	1	0.76	0.5
	L ₀	19.334	19.085	20.979	49.079	46.724	48.287	63.769	61.577	64.589
	k	1.152	1.716	2.539	0.698	1.858	3.582	0.788	1.95	4.247
	RMS	0.52	0.544	2.244	4.123	4.225	3.868	4.182	4.127	4.621
4	n	1	0.625	0.5	1	0.749	0.5	1	0.677	0.5
	L ₀	23.875	22.458	22.61	61.79	57.226	56.597	72.352	66.928	67.774
	k	0.974	2.776	3.707	0.524	1.455	3.361	0.584	2.149	4.076
	RMS	0.566	0.3	0.146	4.553	5.196	5.085	6.507	6.567	5.232
5	n	1	0.502	0.5	1	0.712	0.5	1	0.469	0.5
	L ₀	22.516	19.686	19.679	54.122	47.914	45.174	85.579	65.093	65.675
	k	0.692	2.924	2.951	0.38	0.712	2.641	0.296	3.25	2.883
	RMS	0.629	0.374	0.32	2.349	2.624	2.374	5.72	6.302	5.462
6	n	1	0.047	0.5	1	0.784	0.5	1	0.321	0.5
	L ₀	25.93	22.11	22.274	53.975	50.56	49.618	82.813	66.448	66.54
	k	0.631	9.194	2.936	0.529	1.238	3.148	0.502	8.669	4.511
	RMS	1.865	0.728	1.545	2.063	2.382	2.89	4.01	3.033	3.393
7	n	1	1.557	0.5	1	1.506	0.5	1	0.42	0.5
	L ₀	21.03	22.407	22.987	38.816	40.844	42.943	120.105	82.833	86.241
	k	1.263	0.286	2.585	1.372	0.272	3.612	0.234	4.06	2.87
	RMS	1.019	1.027	3.253	1.417	0.962	5.778	4.642	4.916	4.32
8	n	1	2.082	0.5	1	0.468	0.5	1	0.221	0.5
	L ₀	19.78	21.562	22.437	55.259	43.319	44.101	75.002	65.395	65.494
	k	1.893	0.135	2.629	0.308	2.564	2.269	0.498	11.253	3.989
	RMS	1.068	0.867	3.932	3.392	4.064	3.508	3.41	1.83	2.556

Table 6.2 continued.

9	n	1	1.35	0.5	1	0.557	0.5	1	1.434	0.5
	L ₀	18.967	20.371	19.2	44.992	33.491	35.256	63.332	65.748	67.037
	k	0.785	0.289	2.156	0.238	1.441	1.068	0.997	0.209	4.116
	RMS	0.712	0.696	1.798	2.302	2.884	2.495	4.561	4.366	8.885
10	n	1	1.813	0.5	1	0.773	0.5	1	1.434	0.5
	L ₀	24.768	28.741	25.487	51.115	47.794	46.944	71.238	65.748	73.583
	k	0.821	0.063	2.35	0.529	1.268	3.075	0.869	0.209	4.289
	RMS	2.218	2.006	3.504	2.21	2.614	2.679	2.968	4.336	7.823
Mean	n	1	1.326	0.5	1	0.878	0.5	1	0.723	0.5
	L ₀	21.059	22.036	22.498	45.854	44.539	44.024	68.848	65.247	66.993
	k	1.059	0.435	2.528	0.625	0.98	3.13	0.666	1.995	4.026
	RMS	0.581	0.57	2.507	0.883	1.096	2.561	1.758	1.597	3.337

Run #	Parameters	40% Strength			50% Strength			60% Strength		
		1st Order	n Order	Half Order	1st Order	n Order	Half Order	1st Order	n Order	Half Order
1	n	1	0.832	0.5	1	0.755	0.5	1	0.743	0.5
	L ₀	75.501	74.754	83.017	112.477	108.691	114.678	121.121	117.12	123.905
	k	1.246	2.302	5.165	0.812	2.353	5.678	0.823	2.542	5.943
	RMS	1.708	1.336	8.899	7.354	7.347	8.892	6.77	6.169	8.096
2	n	1	1.934	0.5	1	1.445	0.5	1	1.442	0.5
	L ₀	82.608	88.062	94.285	93.898	96.439	106.757	122.317	127.283	136.295
	k	2.115	0.063	5.363	1.782	0.33	5.945	1.489	0.224	6.435
	RMS	5.559	4.958	17.357	1.643	1.229	16.323	4.953	4.06	20.261
3	n	1	0.446	0.5	1	0.607	0.5	1	0.583	0.5
	L ₀	124.64	85.191	85.448	121.169	107.796	108.122	141.617	120.97	119.875
	k	0.392	6.495	5.27	0.499	3.162	4.909	0.429	3.41	4.975
	RMS	7.559	7.885	7.041	12.805	13.167	10.922	19.356	20.721	17.439
4	n	1	0.411	0.5	1	0.161	0.5	1	0.529	0.5
	L ₀	121.855	104.584	103.814	313.951	121	122.581	219.076	170.486	162.014
	k	0.436	2.4	4.639	0.146	19.615	4.567	0.224	2.989	3.6
	RMS	14.188	15.184	12.273	15.004	16.598	17.024	18.904	20.948	18.051
5	n	1	0.505	0.5	1	0.613	0.5	1	0.561	0.5
	L ₀	119.56	92.092	91.792	144.529	119.56	114.597	160.03	127.891	123.238
	k	0.299	3.364	3.446	0.338	2.447	4.152	0.28	2.874	3.913
	RMS	8.531	9.38	8.119	10.847	11.799	9.966	11.212	12.223	10.435

Table 6.2 continued.

6	n	1	0.551	0.5	1	0.652	0.5	1	0.525	0.5
	L ₀	104.726	89.225	89.067	126.321	110.526	107.501	184.945	144.629	142.602
	k	0.415	3.259	3.958	0.423	2.301	4.47	0.85	3.935	4.479
	RMS	7.322	7.879	6.874	10.071	10.757	8.971	13.699	14.605	12.554
7	n	1	1.32	0.5	1	0.686	0.5	1	0.741	0.5
	L ₀	76.01	79.591	77.301	141.22	121.895	120.603	218.503	191.161	169.686
	k	1.122	0.321	6.469	0.574	2.84	6.265	0.85	1.222	4.327
	RMS	2.875	2.94	5.683	2.703	2.46	2.461	8.243	9.623	8.497
8	n	1	0.648	0.5	1	0.756	0.5	1	0.601	0.5
	L ₀	105.212	96.151	96.345	125.801	121.087	126.193	217.707	169.864	158.65
	k	0.531	2.557	4.511	0.755	2.248	5.888	0.85	2.221	3.784
	RMS	2.149	0.618	1.518	6.629	5.968	6.552	6.813	7.55	6.44
9	n	1	0.668	0.5	1	0.593	0.5	1	0.777	0.5
	L ₀	97.307	88.633	88.304	107.296	94.564	94.415	122.627	115.09	112.609
	k	0.523	2.296	4.437	0.471	3.035	4.385	0.531	1.52	4.8
	RMS	6.678	6.518	4.968	7.017	6.715	5.563	2.849	3.048	4.435
10	n	1	0.595	0.5	1	0.282	0.5	1	0.664	0.5
	L ₀	124.254	99.398	94.417	207.508	111.856	112.576	164.585	142.417	136.093
	k	0.307	2.348	3.704	0.221	10.991	4.41	0.391	2.225	4.935
	RMS	10.218	11.011	9.185	11.189	12.144	12.483	16.895	18.577	15.477
Mean	n	1	0.71	0.5	1	0.754	0.5	1	0.537	0.5
	L ₀	95.705	89.246	89.916	122.039	113.951	112.088	157.702	133.517	133.061
	k	0.585	2.081	4.541	0.544	1.729	5.041	0.407	4.088	4.827
	RMS	4.216	3.973	3.989	8.014	8.243	6.235	7.394	6.73	5.693

Run #	Parameters	70% Strength			80% Strength			90% Strength		
		1st Order	n Order	Half Order	1st Order	n Order	Half Order	1st Order	n Order	Half Order
1	n	1	0.661	0.5	1	0.641	0.5	1	0.669	0.5
	L ₀	164.353	146.456	143.486	189.72	174.551	177.394	197.482	184.016	188.804
	k	0.46	2.556	5.362	0.579	3.533	6.512	0.627	3.348	6.867
	RMS	9.155	8.679	6.168	13.626	12.835	10.55	17.512	17.874	15.814
2	n	1	0.881	0.5	1	1.131	0.5	1	0.501	0.5
	L ₀	158.027	155.34	163.276	175.696	178.233	190.23	297.097	218.117	216.934
	k	0.872	1.525	6.662	1.15	0.621	7.529	0.266	5.036	5.117
	RMS	3.25	3.76	13.338	3.94	4.354	21.59	19.436	20.512	17.15

Table 6.2 continued.

3	n	1	0.593	0.5	1	0.542	0.5	1	0.243	0.5
	L ₀	185.627	159.629	158.082	224.572	184.582	183.156	350.99	189.336	189.517
	k	0.433	3.648	5.657	0.381	4.656	5.751	0.188	17.077	4.8
	RMS	21.609	22.918	19.204	27.98	30.247	25.921	15.95	17.253	16.254
4	n	1	0.54	0.5	1	0.583	0.5	1	0.551	0.5
	L ₀	222.78	182.524	180.451	242.041	206.117	202.325	260.409	218.049	215.807
	k	0.362	4.432	5.412	0.387	3.776	5.715	0.396	4.833	6.303
	RMS	11.31	10.178	8.387	12.017	12.998	10.965	18.417	17.144	13.918
5	n	1	0.63	0.5	1	0.556	0.5	1	0.549	0.5
	L ₀	179.796	159.138	157.919	229.279	179.157	174.068	296.516	224.244	217.499
	k	0.458	3.044	5.431	0.311	3.801	5.174	0.253	3.647	4.79
	RMS	11.221	12.279	11.108	26.765	29.374	25.093	14.386	15.739	13.513
6	n	1	0.666	0.5	1	0.499	0.5	1	0.696	0.5
	L ₀	193.326	179.212	182.416	251.605	197.548	196.864	227.053	215.531	224.372
	k	0.595	3.21	6.539	0.333	5.509	5.531	0.709	3.369	7.82
	RMS	11.685	11.536	10.968	20.945	21.615	18.72	20.091	19.971	17.576
7	n	1	0.718	0.5	1	0.544	0.5	1	0.583	0.5
	L ₀	158.555	149.603	152.582	236.996	186.222	182.083	220.998	193.049	193.187
	k	0.637	2.447	6.002	0.317	4.109	5.227	0.458	4.196	6.139
	RMS	3.616	3.068	6.518	18.571	19.305	16.322	17.92	19.004	16.533
8	n	1	0.722	0.5	1	0.567	0.5	1	0.414	0.5
	L ₀	155.792	146.467	148.613	283.698	214.953	199.547	270.091	205.84	215.107
	k	0.616	2.359	5.845	0.188	2.415	3.589	0.286	7.439	4.709
	RMS	4.845	4.883	7.227	11.734	12.878	10.988	14.596	13.246	12.325
9	n	1	0.636	0.5	1	0.544	0.5	1	0.56	0.5
	L ₀	179.559	143.549	131.732	188.229	151.505	149.231	220.948	177.029	173.112
	k	0.243	1.777	3.549	0.34	3.855	4.785	0.31	3.5	4.717
	RMS	3.29	3.357	2.704	15.836	17.063	14.623	8.474	9.092	7.843
10	n	1	0.62	0.5	1	0.535	0.5	1	0.449	0.5
	L ₀	161.802	141.692	140.045	289.282	203.415	193.897	313.422	213.387	219.35
	k	0.453	3.104	5.363	0.193	3.159	3.922	0.225	6.052	4.599
	RMS	16.031	16.792	13.83	20.162	22.394	19.257	14.892	15.251	13.535
Mean	n	1	0.619	0.5	1	0.578	0.5	1	0.531	0.5
	L ₀	171.664	153.674	153.739	202.291	176.951	176.391	244.711	201.129	199.662
	k	0.495	3.339	5.615	0.452	4.04	5.792	0.371	4.911	5.767
	RMS	8.862	8.478	7.429	7.867	6.444	5.361	15.397	15.062	12.794

Table 6.2 continued.

Run #	Parameters	100%			Run No.	Parameters	100%		
		1st Order	n Order	Half Order			1st Order	n Order	Half Order
1	n	1	0.715	0.5	7	n	1	0.533	0.5
	L ₀	213.565	203.824	213.256		L ₀	293.826	232.359	229.47
	k	0.742	3.118	7.557		k	0.325	4.866	5.82
	RMS	13.577	13.309	15.171		RMS	26.21	28.491	24.505
2	n	1	0.609	0.5	8	n	1	0.447	0.5
	L ₀	263.176	234.736	235.619		L ₀	324.816	237.426	241.994
	k	0.502	4.239	7.195		k	0.272	7.034	5.322
	RMS	24.306	24.695	20.53		RMS	13.737	13.41	11.951
3	n	1	0.62	0.5	9	n	1	0.406	0.5
	L ₀	224.859	201.876	203.249		L ₀	296.352	199.804	208.956
	k	0.52	3.915	6.855		k	0.23	7.431	4.54
	RMS	25.86	26.904	22.309		RMS	18.647	19.868	17.645
4	n	1	0.566	0.5	10	n	1	0.509	0.5
	L ₀	369.454	271.152	256.492		L ₀	292.851	227.831	226.466
	k	0.234	3.554	5.283		k	0.299	5.056	5.318
	RMS	27.841	30.645	26.09		RMS	7.249	6.215	5.333
5	n	1	0.509	0.5	Mean	n	1	0.527	0.5
	L ₀	364.588	244.558	239.733		L ₀	275.475	222.896	220.731
	k	0.194	4.222	4.526		k	0.35	5.084	5.879
	RMS	27.314	30.492	26.363		RMS	19.06	19.722	16.908
6	n	1	0.598	0.5					
	L ₀	308.724	246.097	234.188					
	k	0.281	3.035	5.248					
	RMS	14.4	15.795	13.463					

best fit evaluated by the root mean squared error criterion. When the models that fit the mean values of BOD data for each strength of sample were tabulated, 10% fit the first order model best, 60% fit the half order model best, and 30% fit the order n model best.

Table 6.3. Summary to Show How Frequently the Data Fit a BOD Model.

Strength of Samples, %	Number of Times Samples Had a Best Fit for the Models, Including Mean		
	First Order	Half Order	n Order
10	3	2	5, M ¹
20	7, M	1	2
30	3	3	4, M
40	1	6	3, M
50	2	4, M	4
60	2	6, M	2
70	2	7, M	1
80	1	9, M	0
90	1	9, M	0
100	0	9, M	1
Sum	22, 1M	56, 7M	22, 3M

¹M signifies the mean values of BOD data fit this model best as measured by RMSE criterion.

It is apparent that the first order and the half order BOD models tend to have their best fit for different parts of the sample strength range. For example, the first order model tends to fit the data more frequently for the lower strength samples and less

frequently as the sample strength increases. The half order model tends to fit the data frequently for all strengths of samples, but it fits most frequently as the sample strength increases. The order n BOD model is always a second or third place contender for the best fit to the data across all sample strengths, where it is associated with the 40% strength and lower samples, although it ranked second for the 100% strength samples.

Fewer calculations are involved in fitting a model when the mean values of the BOD data are analyzed rather than all data for each sample, so it is of interest to determine how frequently the model which fit the mean values corresponded to the model that fit the individual data sets. Table 6.3 shows that for 90% of the sample strengths there was agreement between the most frequently found BOD model and the model found from the mean values. At 30% strength of sample the first order or the half order model fit all of the data, but the analysis of the mean values indicated an order n model had the best fit. Interestingly enough, examination of Table 6.2 shows that the order n model selected $n = 0.782$ as the reaction order that had the best fit. This value of n is nearly the mean value of the first order and half order reaction orders.

Table 6.4 shows the critical times that were calculated for each sample. Critical time has a meaning only when the reaction order, n, is less than 1. When the reaction order is 1 or greater an infinite amount of time is required for all of the BOD to be consumed. The frequency with which various reaction order occurred are tabulated in Table 6.5.

Table 6.4. Critical Time, t_c , vs Sample Strength.

Strength of Samples, %	Run No.	Half Order $n = 0.5$	n Order	
			n	t_c , day
10	1	3.803	1.851	∞
	2	1.686	1.117	∞
	3	3.442	0.834	5.734
	4	2.557	0.625	3.085
	5	3.007	0.502	3.029
	6	3.204	0.047	2.084
	7	3.662	1.557	∞
	8	3.532	2.082	∞
	9	4.186	1.350	∞
	10	4.563	1.813	∞
	Mean	3.714	1.326	∞
20	1	3.293	1.114	∞
	2	3.531	1.848	∞
	3	3.817	0.729	5.630
	4	4.502	0.749	7.565
	5	5.242	0.712	8.589
	6	4.517	0.748	8.726
	7	3.539	1.506	∞
	8	5.802	0.468	5.446
	9	7.196	0.557	7.422
	10	4.496	0.773	8.357
	Mean	4.265	0.878	13.304
30	1	2.704	1.140	∞
	2	1.613	1.409	∞
	3	3.696	0.760	5.743
	4	4.014	0.677	5.487
	5	5.597	0.469	5.320
	6	3.614	0.321	2.923
	7	6.343	0.420	5.497
	8	4.054	0.221	2.961
	9	3.940	1.434	∞
	10	4.037	1.299	∞
	Mean	4.013	0.723	5.759

Table 6.4 continued

40	1	3.348	0.832	5.322
	2	3.50	1.934	∞
	3	3.503	0.446	3.262
	4	4.409	0.411	3.923
	5	5.569	0.505	5.633
	6	4.774	0.551	5.138
	7	2.760	1.320	∞
	8	4.347	0.648	5.546
	9	4.243	0.668	5.581
	10	5.383	0.595	6.765
	Mean	4.161	0.710	6.098
50	1	3.675	0.755	5.470
	2	3.304	1.445	∞
	3	4.230	0.607	5.067
	4	4.817	0.161	3.392
	5	5.267	0.613	6.724
	6	4.704	0.652	6.420
	7	3.525	0.686	5.064
	8	3.738	0.756	5.875
	9	4.435	0.593	5.157
	10	4.796	0.282	3.743
	Mean	4.235	0.754	7.536
60	1	3.642	0.743	5.207
	2	3.506	1.442	∞
	3	4.422	0.583	5.198
	4	7.253	0.529	7.993
	5	5.781	0.561	6.661
	6	5.370	0.525	5.685
	7	6.390	0.741	12.311
	8	6.889	0.601	8.766
	9	4.470	0.777	8.502
	10	4.837	0.664	6.988
	Mean	4.788	0.537	5.089
70	1	4.514	0.661	6.237
	2	3.742	0.881	10.042
	3	4.467	0.593	5.311
	4	4.992	0.540	5.387
	5	4.646	0.630	5.790
	6	4.094	0.666	5.274
	7	4.075	0.718	5.879
	8	4.141	0.722	6.104
	9	6.754	0.636	9.432
	10	4.439	0.620	5.575
	Mean	4.415	0.619	5.347

Table 6.4 continued

80	1	4.058	0.641	5.034
	2	3.546	1.131	∞
	3	4.724	0.542	5.122
	4	5.025	0.583	5.864
	5	5.201	0.556	5.927
	6	5.082	0.599	5.116
	7	5.221	0.544	5.778
	8	8.171	0.567	9.789
	9	5.145	0.544	5.614
	10	7.272	0.535	8.066
	Mean	4.593	0.578	5.204
90	1	3.951	0.669	5.067
	2	5.772	0.501	5.838
	3	5.733	0.243	4.090
	4	4.686	0.551	5.174
	5	6.252	0.549	6.979
	6	3.755	0.696	5.002
	7	4.527	0.583	5.127
	8	6.094	0.414	5.202
	9	5.642	0.560	6.342
	10	6.353	0.449	5.768
	Mean	4.919	0.531	5.219
100	1	3.779	0.715	5.120
	2	4.259	0.609	5.092
	3	4.146	0.620	5.050
	4	6.553	0.566	7.385
	5	6.910	0.509	7.169
	6	5.979	0.598	7.442
	7	5.238	0.533	5.604
	8	5.790	0.447	5.290
	9	6.226	0.406	5.271
	10	5.677	0.509	5.792
	Mean	5.079	0.527	5.360

Table 6.5. Summary to Show How Frequently the Data Fit a BOD Model of Various Reaction Orders.

Strength of Samples, %	Number of Times Samples Had Reaction Order in This Range, Including Mean		
	n = 1	0.5 < n < 1	n < 0.5
10	6, M	3	1
20	3	6, M	1
30	4	2, M	4
40	2	6, M	2
50	1	7, M	2
60	1	9, M	0
70	0	10, M	0
80	1	9, M	0
90	0	7, M	3
100	0	8, M	2
Sum	18, 1M	67, 9M	15

Figures 6.1 and 6.2 show the behavior of the first order BOD model parameters, including the rate constant, as a function of sample strength. Similarly, Figures 6.3 and 6.4 show the behavior of the half order BOD model parameters, including the rate constant, as a function of sample strength. The half order model shows less variation than the first order model when ultimate BOD is compared with sample strength in Figures 6.1 and 6.3. The rate constants k_1 and $k_{1/2}$ show considerable variation with sample strength in Figures 6.2 and 6.4.

First Order Model

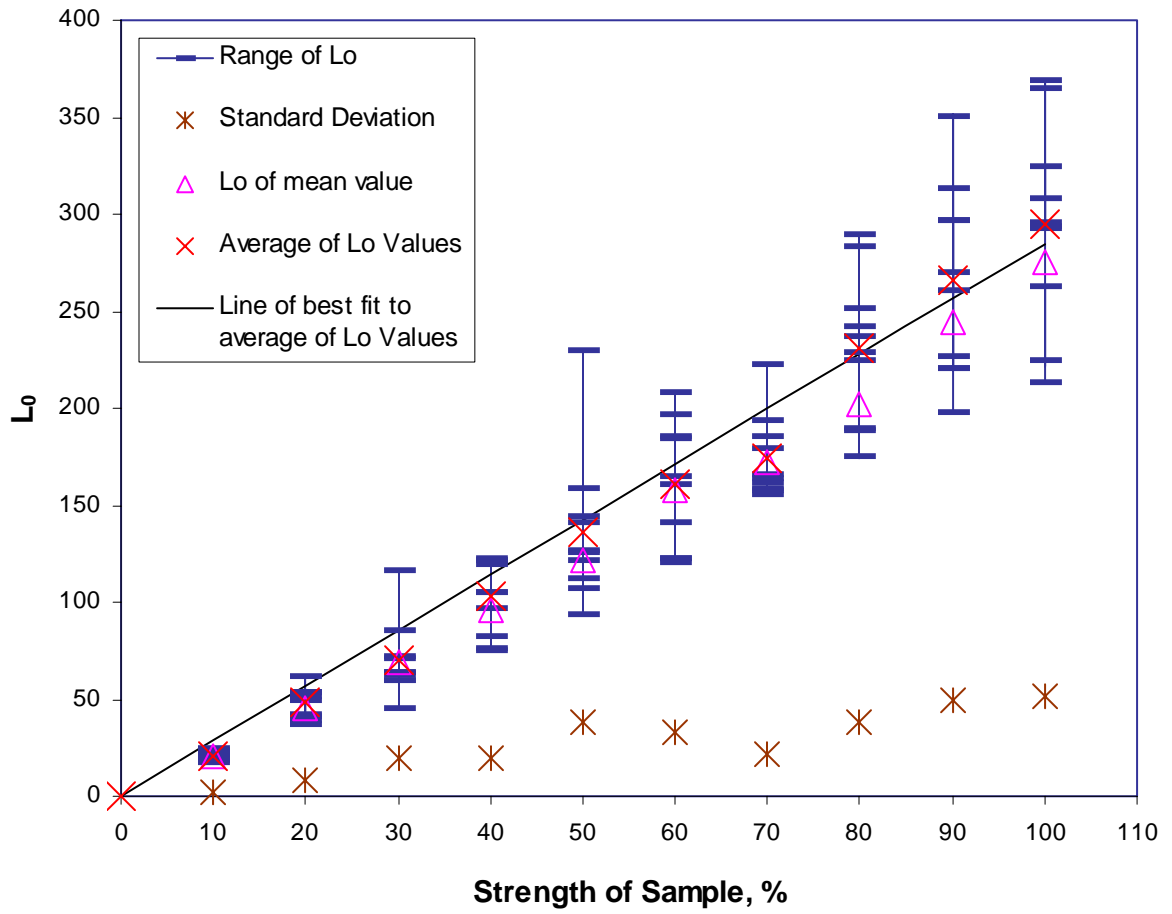


Figure 6.1. Behavior of First Order BOD Model Parameters as a Function of Sample Strength.

First Order Model

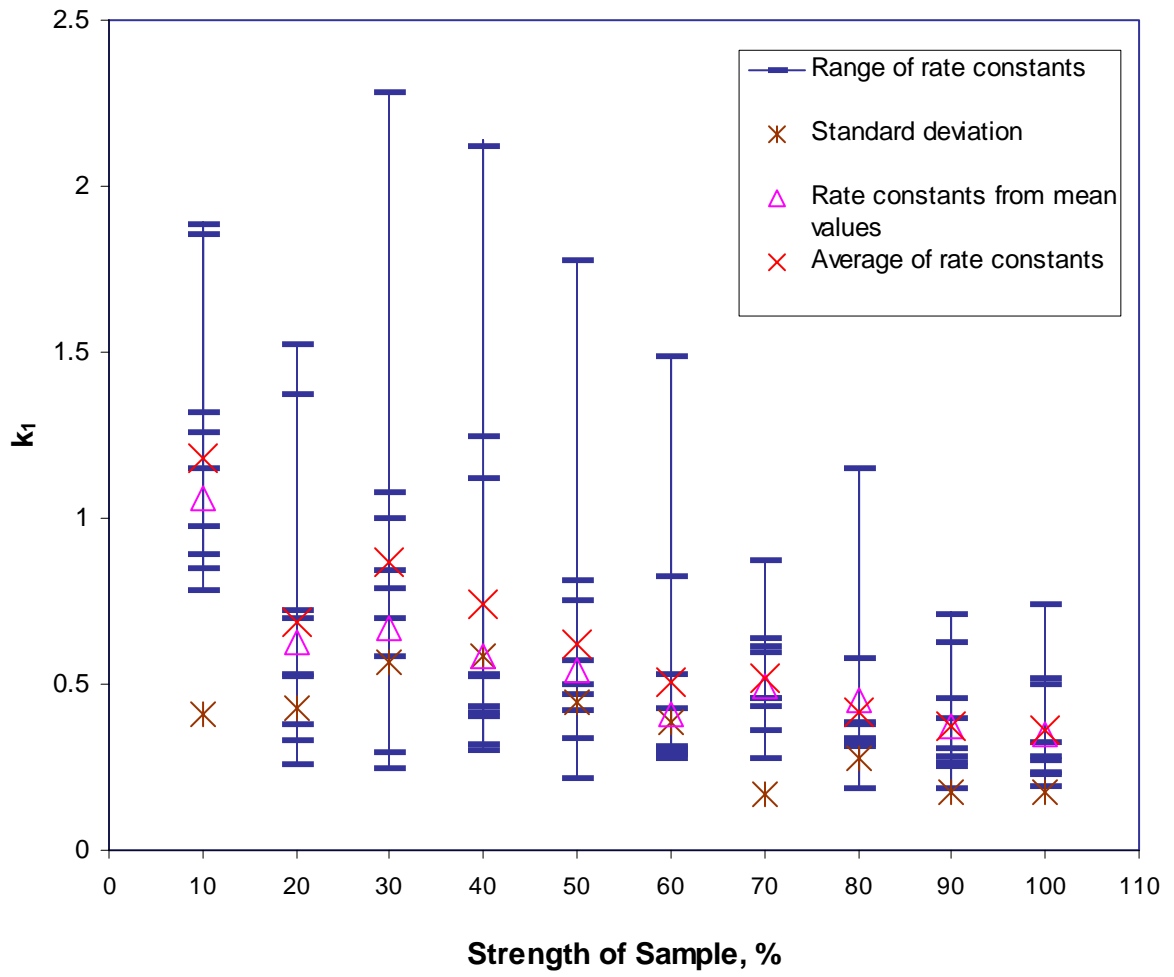


Figure 6.2. Behavior of First Order BOD Model Rate Constant as a Function Of Sample Strength.

Half Order Model

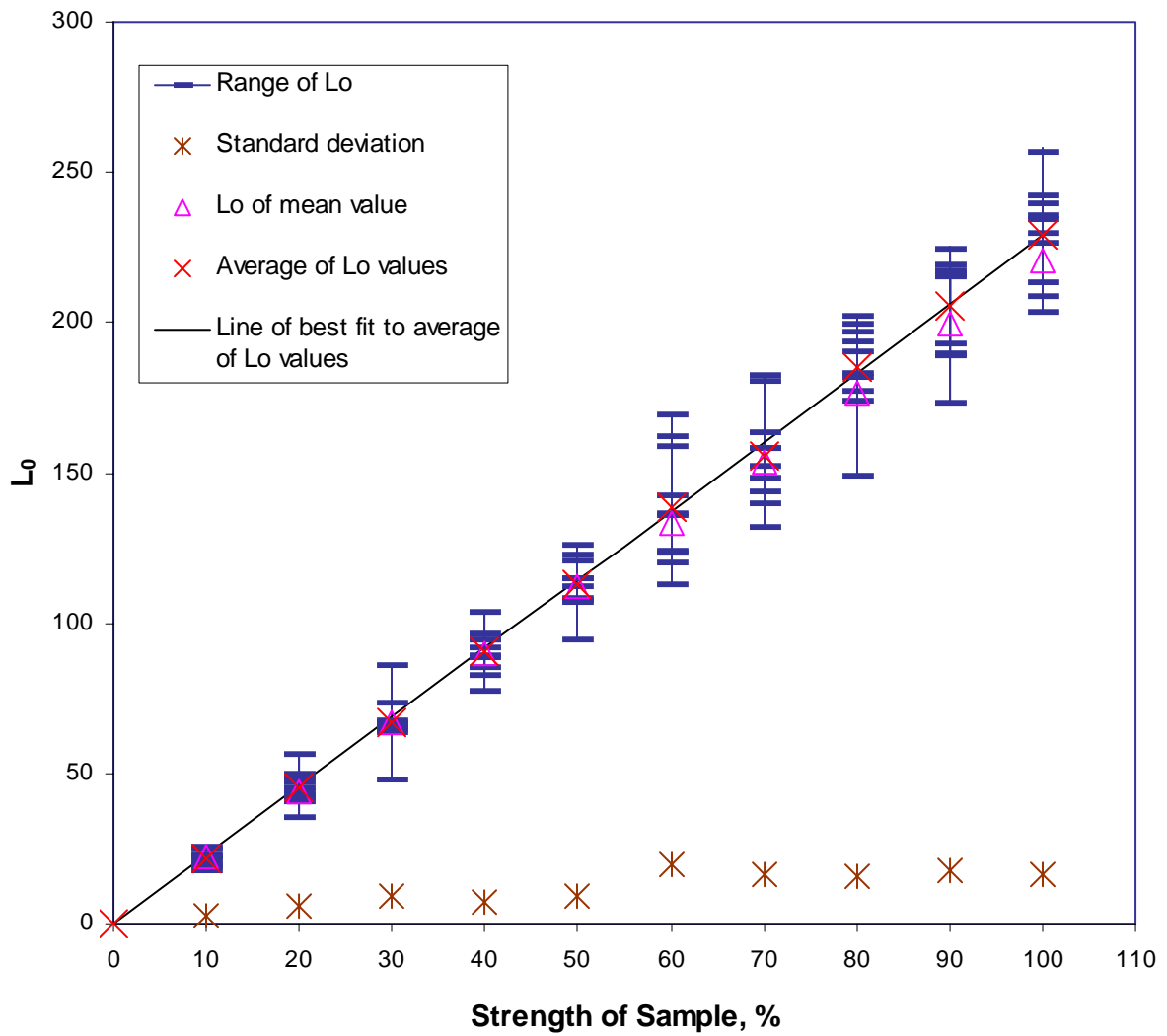


Figure 6.3. Behavior of Half Order BOD Model Parameters as a Function of Sample Strength.

Half Order Model

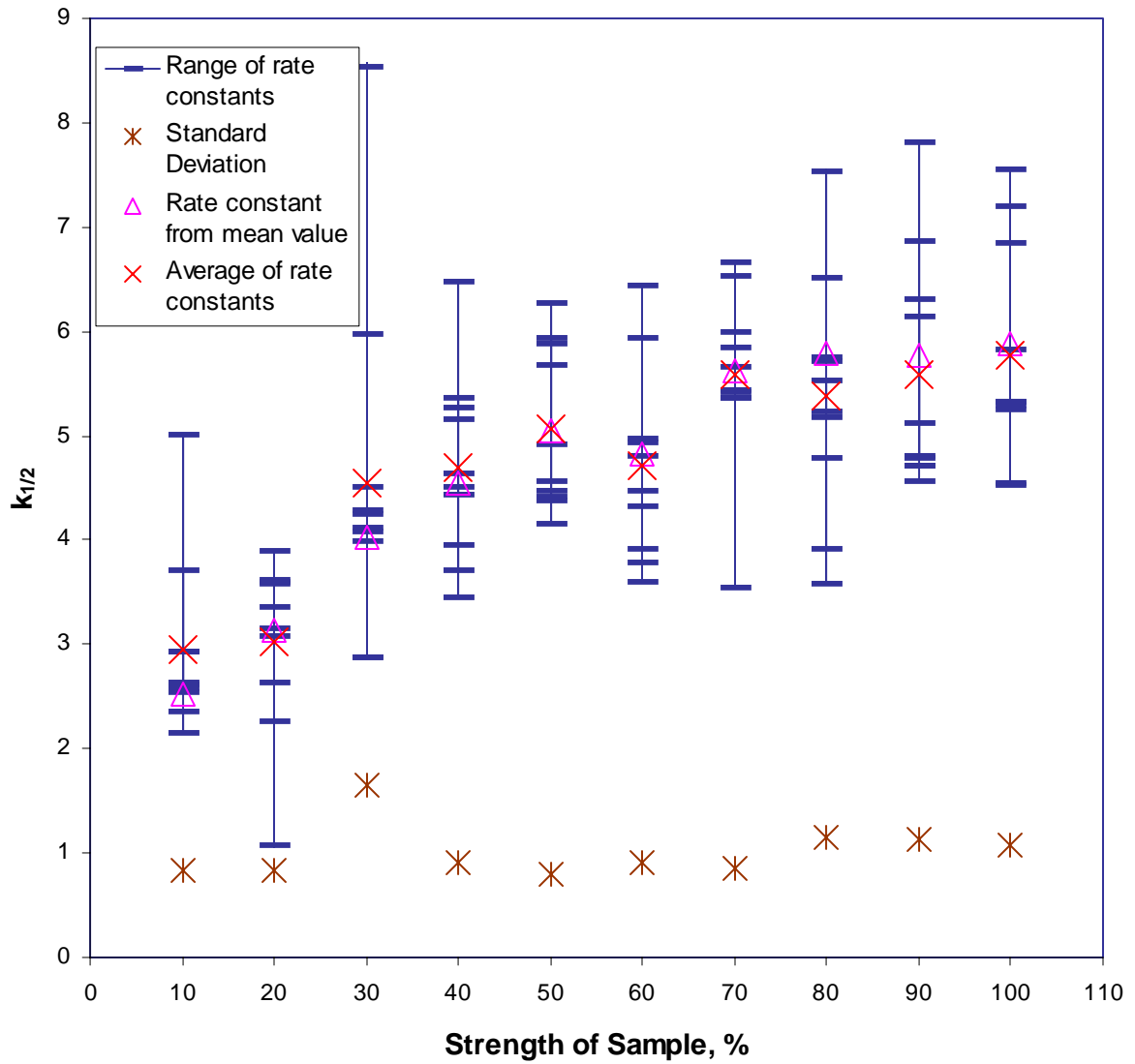


Figure 6.4. Behavior of Half Order BOD Model Rate Constant as a Function Of Sample Strength.

6.7 Conclusions

1. 22% of the samples fit the first order BOD model best, 56% fit the half order BOD model best, and 22% fit the order n model best when using the root mean squared error criterion as the measure of best fit.
2. Only five BOD measurements were available on a sample, so the number of degrees of freedom had a large effect on the calculated root mean squared error. The number of degrees of freedom make it more likely that the first and half order BOD models would fit the data better than the order n BOD model.
3. The ultimate BOD predicted from the half order model showed a smaller variation across the range of dilutions than the prediction from the first order model.
4. The first order BOD model fit the data best for 10% and 20% strength samples, while the half order BOD model fit the data best for all other strength samples.
5. The half order BOD model showed 65 % of the samples had t_c values which indicated all of the BOD was consumed in less than five days, while 100 % of the samples' BOD was consumed in less than 8.171 days.

CHAPTER 7. CONCLUSIONS

A DO sag equation for a stream has been developed in which the biochemical oxygen demand is evaluated as a second order reaction. The differential equation for the DO sag model was solved by applying the Laplace transform method. The DO sag model, equation (3.10), contains exponential integrals which are evaluated by either an exact series or an approximate asymptotic series. The location of the minimum DO concentration is found by calculating the time at which $dC/dt = 0$ in equation (3.18). Other simulations have shown the asymptotic series should not be used to calculate the DO concentration in equation (3.10) or the critical time in equation (3.18) at which the minimum DO occurs if the values of M or N from equations (3.15) and (3.16) are less than five. Also, other simulations have shown that when N is less than 7 a plot of equation (3.14) may produce a rough appearing DO sag curve which may have a jump or a sudden change in slope each time N takes on a different integer value in equation (3.16). It has been recommended that equation (3.14) not be used for M or N less than 5. The example presented in this study in which Douglas Fir needles produced BOD, showed that the DO sag model which incorporated an asymptotic series was virtually identical in its predictions with $M = 14$ and N ranging from 14 to 18 to predictions using the exact series. It is necessary to experiment with equation (3.12), the exact series for the exponential integral, to find the number of terms to sum. 150 terms were used in the calculations in this paper, although more terms may have been needed for calculations at larger times. Thus, the DO sag equation for second order BOD is not suitable for calculation without a computer. Figure 1 shows that the small value of the BOD reaction

rate constant results in the stream being able to carry a large BOD concentration from Douglas Fir needles without having the DO concentration being exhausted. The result is of interest in TMDL studies involving waste load allocation to streams.

A DO sag equation developed for BOD consumption modeled as a three-halves order reaction is solved easily using the Laplace transform method and convolution. The DO sag equation contains exponential integrals which are evaluated from their series expressions. The exact series expression of an exponential integral may require summation of several hundred terms although 50 terms were adequate in the examples. The number of terms to include in an asymptotic expansion depends upon the magnitude of the argument. 14 terms were required in one example. An asymptotic expansion is not used to evaluate an exponential integral unless the argument is greater than five. The maximum error in the DO concentration was less than 0.79% on day 1.402 when comparing the two alternative methods of evaluating $Ei(x)$ when the argument was 9.661.

The minimum value of the DO concentration occurs at the critical time, t_c , which may be 0 if the reaeration rate is greater than or equal to the DO consumption rate, otherwise $t_c > 0$. t_c is calculated numerically from the DO sag equation by a root finding method. As the rate constant, $k_{3/2}$, increases both the minimum DO and t_c become smaller.

It is recommended that river BOD data be collected at daily intervals for 5 to 10 days, then with less frequency, say 7 to 10 days, to obtain sufficient values of DO consumed versus time to allow for evaluation of the rate constant as well as determination of which BOD model is appropriate. Also, the duration of the BOD test

should be extended to larger values of time such as 30 days to identify the appropriate BOD reaction order.

The user now has a model available with which to describe the DO sag curve when the three-halves order BOD reaction equation is applicable. Field testing following the methods used by the authors cited in Table 4.1 would show the frequency of application of the three-halves order BOD equation and DO sag curve.

A dissolved oxygen model for a stream was developed for BOD reduction by decay, described as a second order reaction, and sedimentation, while sediment oxygen demand was present. In addition, a DO model for a stream when scour of benthic solids occurs is developed. Removal of BOD containing solids by sedimentation reduces the dissolved oxygen consumption rate.

One hundred glucose and glutamic acid data sets were modeled as first order, half order, and order BOD models. 22% of the samples fit the first order BOD model best, 56% fit the half order BOD model best, and 22% fit the order n model best when using the root mean squared error criterion as the measure of best fit.

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