

WATER QUALITY MODEL INCORPORATES UNCONVENTIONAL BOD REDUCTION*

EMERALD M. ROIDER

TRIEU V. LE

DONALD DEAN ADRIAN

Louisiana State University, Baton Rouge

THOMAS G. SANDERS

Colorado State University, Fort Collins

ABSTRACT

Biochemical Oxygen Demand (BOD) reduction through the joint action of BOD decay expressed as an unconventional second order reaction and sedimentation is incorporated into a dissolved oxygen (DO) sag model for a river. A term named the Phelps-Thomas index, which is a function of the reaeration and sedimentation rate constants, is introduced and presented as a composite measure of river and wastewater rejuvenation characteristics. Calculations using ranges of reaeration and sedimentation rates show the Phelps-Thomas index has values between -2 and 10 or larger, with large values associated with rapid recovery of DO. The time at which the minimum DO occurs is calculated numerically. Examples apply the DO sag model to logging debris in a stream.

INTRODUCTION

For decades, the pioneering work of Streeter and Phelps served as a basis for water quality modeling in a river [1]. Their classic dissolved oxygen sag model

*Financial support was provided by the Louisiana Transportation Research Center, Louisiana Water Resources Institute, and a sabbatical leave for Adrian.

related stabilization of an organic waste measured by the biochemical oxygen demand (BOD) and the dissolved oxygen (DO) resources of the river. Thomas accounted for settleable BOD in the DO sag equation [2]. The effect of dispersion on BOD and DO in small rivers has been found to be negligible [3].

The BOD reaction model is an empirical expression chosen on the basis of convenience to describe the complex transformations that take place as BOD stabilizes in a water body. A first order BOD decay equation has been widely applied to describe the deoxygenation rate of most municipal wastewaters, although an unconventional second order rather than a first order model was introduced by Thomas [4] prior to being applied by many investigators [5-11]. Conventional practice treats the BOD reaction as being first order; however, in this investigation the term *unconventional reaction order* designates a BOD reaction that is other than first order. Streams are subject to many sources of BOD loadings in addition to municipal wastewaters; this study draws upon the BOD characteristics of logging debris as measured by Ponce [12]. Rigorous statistical bases for deciding whether a first order or an unconventional second order BOD model provided a better fit to data are available [7, 13]. An analytical DO sag equation that incorporated second order reaction kinetics to describe BOD decay was not available until one was developed in 1998 [10], simplified in 2003 [11], and generalized in 2004 [14]. A notable deficiency of these BOD and DO models was that they did not include loss of BOD by sedimentation. As a result, an analytical DO sag model is not currently available that incorporates BOD decay as a second order reaction while also including loss of BOD by sedimentation.

The primary objective of this study was to develop a methodology for including BOD loss through sedimentation in a DO sag model which included BOD decay expressed as a second order reaction. In addition, an expression was to be developed with which to calculate the time to reach the minimum dissolved oxygen concentration. A secondary objective was to show through examples how to determine the BOD rate constant and the ultimate BOD from logging debris data. Additional examples were to demonstrate the effect of sedimentation rates on the DO behavior of streams in which BOD decays by a second order reaction.

SECOND ORDER BOD MODEL

The second order BOD decay model applied to a moving plug flow reactor or a moving Lagrangian control volume as proposed in [4] is

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

in which $L(t)$ = BOD remaining at time t , g/m^3 , L_0 = BOD at time zero, t = elapsed time or flow time, day, and k_2 = BOD deoxygenation reaction rate

constant, $\text{m}^3/(\text{g day})$. BOD represented by $L(t)$ is not measured directly in the laboratory; instead, $y(t)$, the DO consumed in the BOD test in g/m^3 is measured. The relationship between $y(t)$, $L(t)$, and L_0 is $y(t) = L_0 - L(t)$ so equation (1) becomes

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

which is applied to calculate the parameters k_2 and L_0 from laboratory measurements of DO consumed as a function of time in the BOD test (for examples see [7, 10, 11, 15]).

BOD loss through sedimentation in a river is incorporated into a BOD decay model using the method introduced by Thomas [2]:

$$\frac{dL}{dt} = -k_2 L^2 - k_r L \quad (3)$$

where k_r is the net rate of BOD loss by sedimentation, with units of day^{-1} . Equation (3) is integrated and rearranged to

$$L(t) = \frac{k_r L_0}{(k_2 L_0 + k_r) e^{k_r t} - k_2 L_0} \quad (4)$$

which will be incorporated in the DO sag equation. $k_r = 0.1 \text{ day}^{-1}$ to 0.2 day^{-1} represents a range of sedimentation rate constants from Thomann [19], while $k_r = 0$ is applicable with equation (2).

EXAMPLE OF BOD DATA ANALYSIS

This example analyzes BOD data in Table 1 for Douglas Fir and Red Alder logging debris [12], using root mean squared error to measure how well data fit the models. RMSE is calculated from the equation

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{i=N} [y_p(t_i) - y_m(t_i)]^2} \quad (5)$$

where $y_p(t_i)$ is obtained from equation (2) for a second order model on day t_i . The measured value is $Y_m(t_i)$, and N is the number of measurements. The data for Douglas Fir and Red Alder are also analyzed using a first order BOD model. The fit between model and data is measured by equation (5) in which a smaller RMSE signals a better fit of model and data than a larger RMSE. Analyzing the two data sets in Table 1 with first order and the second order BOD models results in RMSE values which are lower 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). The two models predict different rate constants as their units are different. Although both the second order and the first order models appear to fit the data extremely well (Figure 1), the fit of the second order model was better. Footnotes of Table 1 note that the second order model predicts a larger value of the ultimate BOD than the first order model, as discussed by others [5, 9]. Berthouex and Brown illustrate that collecting BOD data over longer periods improves prediction of k_2 , L_0 , and the reaction order [16]. Indeed, Borsuk and Stow measured BOD data for periods that extended to 140 days and 180 days [17]. Their data gave unconventional BOD reaction orders of 1.3, 1.7, 2.4, and 4.0 for three wastewaters and a river sample.

Rodriguez analyzed BOD data by an equation similar to the square of equation (5), 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 [18].

Table 1. BOD Data from Douglas Fir Needles and Red Alder Leaves of Ponce [12] and Predicted BOD Concentration^a

Time day	Oxygen consumed g/m^3		Predicted by first order BOD model* g/m^3		Predicted by second order BOD model** g/m^3	
	Douglas Fir	Red Alder	Douglas Fir	Red Alder	Douglas Fir	Red Alder
0	0	0	0	0	0	0
5	252	316	225	264	248	299
10	312	504	335	466	327	439
20	408	696	415	740	390	729
45	432	992	440	1028	436	922
60	440	1096	440	1085	446	1070
90	460	1148	440	1122	457	1160

^aEach value of oxygen consumed is the mean of four measurements.

*First order model parameters:

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

Red Alder: $k_1 = 0.053 \text{ day}^{-1}$, $L_0 = 1,132 \text{ g/m}^3$, $RMSE = 34.21 \text{ g/m}^3$

**Second order model parameters:

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

Red Alder: $k_2 = 0.000,039,11 \text{ m}^3/(\text{g day})$, $L_0 = 1,396 \text{ g/m}^3$, $RMSE = 18.16 \text{ g/m}^3$

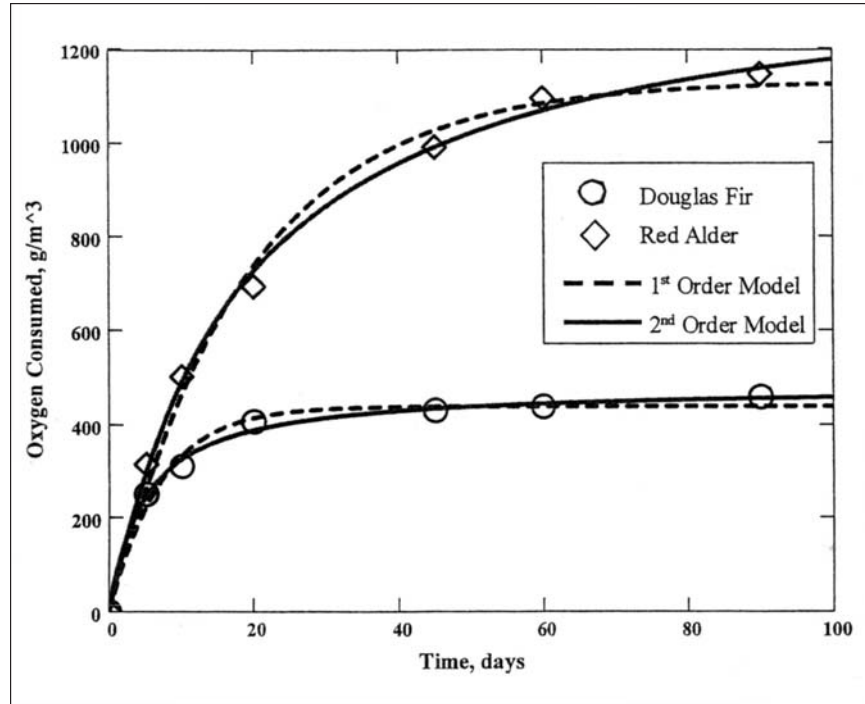


Figure 1. Oxygen consumption data from Table 1 with a first order and a second order BOD reaction model for Red Alder and for Douglas Fir logging debris. The rate constants and RMSE values are in the footnotes to Table 1.

DO SAG EQUATION FOR SECOND ORDER BOD DECAY WITH SEDIMENTATION

The DO sag equation for a control volume moving with the river flow when the BOD decay reaction is second order and there is loss of BOD by sedimentation, equation (4), is modified from [10]:

$$\frac{dC}{dt} = k_s (C_s - C) - k_2 \left(\frac{k_r L_0}{(k_2 L_0 + k_r) e^{k_r t} - k_2 L_0} \right)^2 \quad (6)$$

where C is the dissolved oxygen concentration, g/m³, k_s is the reaeration coefficient, day⁻¹, and C_s is the saturation concentration of dissolved oxygen, g/m³. This equation integrates to

$$C(t) = C_s - (C_s - C_0) e^{-k_s t} - k_2 k_r^2 L_0^2 e^{-k_s t} \int_0^t \frac{e^{k_s t}}{(A e^{k_r t} - k_2 L_0)^2} dt \quad (7)$$

where $A = k_2 L_0 + k_r$ and C_0 is the initial DO concentration (see Appendix I).

A new parameter, $m = (k_s/k_r) - 2$, which is restricted to integer values, is introduced. The term m is named the Phelps-Thomas index in honor of E. B. Phelps who presented the first order BOD equation in 1909 and H. A. Thomas who accounted for BOD removal by sedimentation in 1948 and also introduced the second order BOD model in 1957. The Phelps-Thomas index (PTI) is shown later to range from -2 to about 10. Appendix I shows that equation (7) has a different integral for each of the cases: $m = -2$, $m = -1$, $m = 0$, and $m \geq 1$. A common case is for $m \geq 1$, for which equation (7) integrates to

$$C(t) = C_s - (C_s - C_0) e^{-k_s t} - a k_r L_0 e^{-k_s t} \left(\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} \right) \quad (8)$$

$$- \frac{a(k_s - k_r)L_0 e^{-k_s t}}{A} \left[\frac{e^{k_r m t} - 1}{m} + \frac{a(e^{k_r(m-1)t} - 1)}{m-1} + \frac{a^2(e^{k_r(m-2)t} - 1)}{m-2} + \dots + a^m \ln \left(\frac{e^{k_r t} - a}{1-a} \right) \right]$$

where $m = (k_s/k_r) - 2$, which is restricted to integer values, while $a = k_2 L_0/A$. It appears one would eventually divide by zero as $n = 0, 1, \dots, m-1$ when evaluating the terms with the form $a^n \{ \exp[k_r(m-n)t] - 1 \} / (m-n)$. However, the series is truncated when the denominator term $m-n$ reaches 1. The final term in equation (8) is a logarithmic term which is always retained and is added to the truncated series. Thus, if $m = 1$, the series is truncated after the term $(\exp[k_r m t] - 1)/m$ and one retains the logarithmic term.

In Appendix I, the PTI was restricted to integer values, so one should evaluate the Phelps-Thomas Index, $m = (k_s/k_r) - 2$, then round to the nearest integer before substituting it in equation (8). Three cases yield PTI values for which equation (8) is not applicable. For example, $k_s = 0$ corresponds to $m = -2$, which represents the rare case of no reaeration, a situation that may occur in an ice covered river or when a small stream is diverted through a closed conduit that flows full. Another case is for $k_s = k_r$ which yields $m = -1$, while $k_s = 2k_r$ yields $m = 0$. As the reaeration rate constant increases, or the sedimentation rate constant decreases, PTI becomes a larger positive constant as is shown in Table 2 where integer values of the index range from -2 to at least 10.

The Phelps-Thomas index, $m = (k_s/k_r) - 2$, incorporates two desirable restorative features of a river: reaeration and sedimentation. The reaeration rate constant relates to physical features of the river, including its depth, velocity, and temperature. Higher reaeration rates assist a river's rejuvenation while DO is consumed by decaying wastewaters. Sedimentation describes another mechanism for rivers to become less burdened by particulate BOD. The sedimentation rate is a function of characteristics of the river's waste load as well as the degree of mixing

Table 2. Reaeration Rate Constants and Sedimentation Exponents for Water Bodies

Water body	Ranges of k_s , day ⁻¹ at 20°C	Ranges of k_s/k_r for $k_r = 0.10$ to $k_r = 0.20$ day ⁻¹	Ranges of m before rounding to integers
Small ponds and backwaters	0.10 to 0.23	0.50 to 2.30	-1.50 to 0.30
Sluggish streams and large lakes	0.23 to 0.35	1.15 to 3.50	-0.85 to 1.50
Large streams of low velocity	0.35 to 0.46	1.75 to 4.60	-0.25 to 2.60
Large streams of normal velocity	0.46 to 0.69	2.30 to 6.90	0.30 to 4.90
Swift streams	0.69 to 1.15	3.45 to 11.50	1.45 to 9.50
Rapids and waterfalls	>1.15	>5.75 to >11.50	>3.75 to >9.50

Source: Adapted from [19, 20].

and turbulence. The nature of the waste load relates to particle size, shape, and density, all of which influence the magnitude of the sedimentation rate while greater mixing and turbulence reduces sedimentation rate. For example, for a given degree of mixing and turbulence the sedimentation rate constant may have different values for municipal wastewater, agricultural plant material in runoff, and logging debris. In sum, the PTI is a composite of river and wastewater characteristics.

The equations for DO concentration are stated for PTI = -2, -1, and 0. For PTI = -2, the DO concentration from equations (A1)-(A3) in the Appendix is

$$C(t) = C_s - (C_s - C_0)e^{-k_s t} - a k_r L_0 e^{-k_s t} \left[\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - K_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{k_s - k_r}{a A k_r} \left[e^{-k_r t} - 1 + \frac{1}{a} \ln \left(\frac{e^{k_r t} - a}{(1-a)e^{k_r t}} \right) \right] \right] \quad (9)$$

while the equation for PTI = -1 is

$$C(t) = C_s - (C_s - C_0)e^{-k_s t} - a k_r L_0 e^{-k_s t} \left[\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{k_s - k_r}{a A k_r} \ln \left(\frac{e^{k_r t} - a}{(1-a)e^{k_r t}} \right) \right] \quad (10)$$

and the equation for PTI = 0 is

$$C(t) = C_s - (C_s - C_0) e^{-k_s t} - a k_r L_0 e^{-k_s t} \left[\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{k_s - k_r}{k_r A} \ln \left(\frac{e^{k_r t} - a}{1 - a} \right) \right] \quad (11)$$

An Eulerian rather than a Lagrangian viewpoint can be adopted by substituting $t = x/U$ in the DO equations with $x =$ distance downstream and $U =$ velocity of the river. The Eulerian viewpoint references DO concentration to distance along the river and is favored in applications for locating the minimum DO value as it determines the precise location in the river system of the minimum oxygen content.

TIME TO REACH THE MINIMUM DO

The minimum DO concentration is found by calculating the critical time, t_c , at which $dC/dt = 0$ in equations (8), (10), and (11). The minimum DO for equation (9), the ice covered river case, is zero or a constant concentration as the DO will decline either continuously to zero due to there being no reaeration, or to some constant DO concentration after exhausting all the initial BOD. Cases $m = -1, 0$, and $m \geq 1$ will have $t_c = 0$ or the critical time will occur when $dC/dt = 0$. The derivatives are called $f_{-1}(t)$, $f_0(t)$, and $f_m(t)$, for the cases $m = -1, 0$, and $m \geq 1$, respectively.

The derivative of equation (10) for PTI = -1 is

$$f_{-1}(t) = k_s(C_s - C_0) + a k_s k_r L_0 \left[\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{k_s - k_r}{a A k_r} \ln \left[\frac{e^{k_r t} - a}{(1 - a) e^{k_r t}} \right] \right] - a k_r L_0 \left[\frac{A k_r e^{k_s t}}{(A e^{k_r t} - k_2 L_0)^2} - \frac{(k_s - k_r) e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{k_s - k_r}{A(1 - a) e^{k_r t}} \right] \quad (12)$$

When PTI = 0 the derivative for equation (11) is

$$f_0(t) = k_s(C_s - C_0) + a k_s k_r L_0 \left[\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{k_s - k_r}{k_r A} \ln \left(\frac{e^{k_r t} - a}{1 - a} \right) \right] - a k_r L_0 \left[\frac{k_r A e^{k_s t}}{(A e^{k_r t} - k_2 L_0)^2} - \frac{(k_s - k_r) e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} + \frac{(k_s - k_r) e^{k_r t}}{A(e^{k_r t} - a)} \right] \quad (13)$$

The derivative of equation (8) in which PTI ≥ 1 is

$$f_m(t) = T_1 + T_2 + T_3 + T_4 \quad (14)$$

where

$$T_1 = k_s (C_s - C_0) + a k_s k_r L_0 \left[\frac{1}{A - k_2 L_0} - \frac{e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} \right] \quad (14a)$$

$$T_2 = \frac{a k_s L_0 (k_s - k_r)}{A} \left(\frac{e^{k_r m t} - 1}{m} + \frac{a(e^{k_r(m-1)t} - 1)}{m-1} + \frac{a^2(e^{k_r(m-2)t} - 1)}{m-2} + \dots + a^m \ln \left[\frac{e^{k_r t} - a}{1-a} \right] \right) \quad (14b)$$

$$T_3 = a k_r L_0 \left[\frac{k_r A e^{k_s t}}{(A e^{k_r t} - k_2 L_0)^2} - \frac{(k_s - k_r) e^{(k_s - k_r)t}}{A e^{k_r t} - k_2 L_0} \right] \quad (14c)$$

$$T_4 = -\frac{a k_r L_0 (k_s - k_r)}{A} \left(e^{k_r m t} + a e^{k_r(m-1)t} + a^2 e^{k_r(m-2)t} + \dots + \frac{a^m e^{k_r t}}{e^{k_r t} - a} \right) \quad (14d)$$

Equations (12), (13), and (14) for $f_{-1}(t)$, $f_0(t)$, and $f_m(t)$ are solved for the critical time, t_c , which makes the respective equation equal to zero. All three equations are complicated enough to encourage finding the value of t_c by applying a software program such as Mathcad™, TableCurve™, or Maple™. The value of t_c found from the appropriate equation is the flow time to reach the minimum dissolved oxygen concentration. An alternative method to find t_c and the minimum DO concentration is to evaluate the appropriate DO equation (8), (9), (10), or (11) for a series of values of time, tabulate and graph the results, then pick the value of t_c and the minimum DO concentration in the tabulation or graph. This alternative method is only feasible when using a suitable software program for calculating the DO concentration. Both methods work in the following example.

APPLICATION OF THE OXYGEN SAG EQUATION

This example applies the DO sag equation which incorporates a second order BOD reaction while including loss of BOD by sedimentation. A BOD rate constant, $k_2 = 4 \times 10^{-4} \text{ m}^3/(\text{g day})$, with $L_0 = 100 \text{ g/m}^3$ was used in equations (10), (11), and (8) for a sluggish stream typical of Gulf Coast Louisiana having PTI = -1, 0, and 2 (Table 2) to generate the DO sag curves in Figure 2. Site specific measurements are necessary to find rate constants appropriate for Gulf Coast logging debris but in their absence, Table 1 values serve as proxies. The curve for PTI = -1 is developed using $k_s = 0.23 \text{ day}^{-1}$ and $k_r = 0.2 \text{ day}^{-1}$ to give $m = -0.85$, or $m = -1$ as the nearest integer. The curve for PTI = 0 is developed using $k_s = 0.35 \text{ day}^{-1}$ and $k_r = 0.2 \text{ day}^{-1}$ to give $m = -0.25$ with $m = 0$ as the nearest integer.

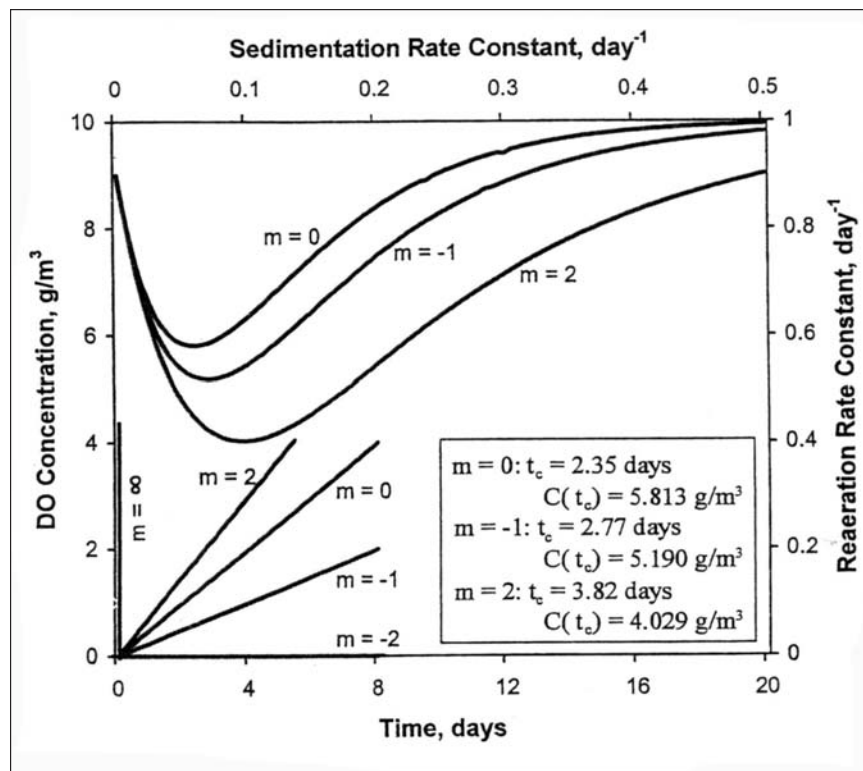


Figure 2. DO sag curves for a stream for Phelps-Thomas indices of $-1, 0$, and 2 (left and bottom axes). Parameters include $C_0 = 9 \text{ g/m}^3$, $C_s = 10 \text{ g/m}^3$ with second order BOD parameters $L_0 = 100 \text{ g/m}^3$ and $k_2 = 0.000,4 \text{ m}^3/(\text{g day})$. Insert shows combinations of reaeration and sedimentation rate constants to give constant m values (right and top axes).

The curve for $\text{PTI} = 2$ is developed with $k_s = 0.35 \text{ day}^{-1}$ and $k_r = 0.1 \text{ day}^{-1}$ to yield $m = 1.50$, which is arbitrarily rounded to $m = 2$ (although it could have been rounded arbitrarily to 1). The example shows that the combination of a large BOD load, $L_0 = 100 \text{ g/m}^3$, and a small BOD rate constant, $k_2 = 4 \times 10^{-4} \text{ m}^3/(\text{g day})$, produces DO sag curves that decline to a minimum before recovering as BOD reacts and is removed by sedimentation. The DO sag curves are similar yet depend on the complex interaction of decay and sedimentation as shown in the insert to Figure 2. The insert shows that a constant Phelps-Thomas index may represent different combinations of reaeration rates and sedimentation rates.

CONCLUSIONS

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. Hewitt et al. carried out BOD measurements using 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 [15]. Rodriguez carried out BOD tests of duration 20, 25, and 40 days to calculate unconventional reaction orders that ranged from 1.224 to 1.632 [18]. Borsuk and Stow carried out BOD tests of duration 140 to 180 days while calculating unconventional reaction orders 1.3, 1.7, 2.4, and 4.0 [17]. Clearly, BOD data may be represented in some cases by unconventional reaction orders, including second order.

The BOD deoxygenation rate constants for data collected over a 90 day duration for Douglas Fir needles and Red Alder leaves [12] were $k_2 = 4.402 \times 10^{-4}$ and $0.3911 \times 10^{-4} \text{ m}^3/(\text{g day})$, respectively. The data fit a second order BOD reaction model better than a first order BOD reaction model using RMSE criteria.

A DO equation for a stream has been developed which incorporates BOD decay as a second order reaction and BOD loss by sedimentation. Loss of BOD by sedimentation speeds recovery of the DO in a stream. The location of the minimum DO concentration ordinarily is found by calculating the time at which $dC/dt = 0$, but the calculations are sufficiently arduous to encourage use of a software program such as Mathcad™.

Stream sampling protocols should be encouraged in which sedimentation data were collected in addition to BOD data. Thomann provides sedimentation rate constants of 0, 0.1, and 0.2 day^{-1} [19], but additional values of rate constants which are related to wastewater type and stream conditions would be beneficial.

The Phelps-Thomas index, $m = (k_s/k_r) - 2$, is a new index of a river's rejuvenation capacity which combines physical properties of the river with properties of the settleable BOD. Yet the index should be interpreted with caution while relying on the fundamental reaeration rate and sedimentation rate components, as illustrated in Figure 2. A mountain stream is expected to have a larger PTI than a languid flow through a Gulf Coast swamp, even when both waters are subject to the same wastewater load. But there are subtle interrelated behaviors incorporated in PTI as the mountain stream's turbulence can keep waste load settleable solids suspended in contrast to the limited settleable solids holding capacity of the languid swamp stream.

ACKNOWLEDGMENTS

Ben Hill and Sherly Hartono provided valuable assistance.

APPENDIX I: Evaluation of DO Sag Equation

Equation (7) is the DO sag equation

$$C(t) = C_s - (C_s - C_0) e^{-k_s t} - k_2 k_r^2 L_0^2 e^{-k_s t} \int_0^t \frac{e^{k_s t}}{(A e^{k_r t} - k_2 L_0)^2} dt \quad (A1)$$

where $A = k_2 L_0 + k_r$. Integration by parts with dummy variable u yields

$$\int_0^t \frac{e^{k_s u}}{(A e^{k_r u} - k_2 L_0)^2} du = \frac{1}{k_r A (A - k_2 L_0)} - \frac{e^{(k_s - k_r)t}}{k_r A (A e^{k_r t} - k_2 L_0)} + \frac{k_s - k_r}{k_r A} \int_0^t \frac{e^{(k_s - k_r)u}}{A e^{k_r u} - k_2 L_0} du \quad (A2)$$

Change in variable $e^{k_r u} = x$ in the integral yields

$$\int_1^{e^{k_r t}} \frac{x^{\frac{k_s}{k_r} - 2}}{x - \frac{k_2 L_0}{A}} dx = \int_1^{e^{k_r t}} \frac{x^m}{x - a} dx \quad (A3)$$

where $m = (k_s/k_r) - 2$ and $a = k_2 L_0/A$.

Practical cases restrict m to integers $m = -2, -1, 0$, and $m \geq 1$. When $m = -2$, or -1 , the integrand is expressed as the sum of partial fractions and integrated. For $m = 0$ equation (A3) can be integrated directly. For $m \geq 1$ the integrand is a polynomial and a remainder

$$\frac{x^m}{x - a} = x^{m-1} + a x^{m-2} + a^2 x^{m-3} + \dots + a^{m-2} x + a^{m-1} + \frac{a^m}{x - a} \quad (A4)$$

One truncates the polynomial when the exponent on x , $m - n = 0$, where $n = 1, 2, 3, \dots$ represents the first, second, etc. term of the polynomial, then one adds the final term $a^m/(x - a)$. Equation (A1) is evaluated as

$$C(t) = C_s - (C_s - C_0) e^{-k_s t} - \frac{a k_r L_0 e^{-k_s t}}{A} \left(\frac{1}{1-a} - \frac{e^{(k_s - k_r)t}}{e^{k_r t} - a} \right) - \frac{a L_0 (k_s - k_r) e^{-k_s t}}{A} \left[\frac{e^{k_r m t} - 1}{m} + \frac{a(e^{k_r(m-1)t} - 1)}{m-1} + \frac{a^2(e^{k_r(m-2)t} - 1)}{m-2} + \dots + a^m \ln \left(\frac{e^{k_r t} - a}{1-a} \right) \right] \quad (A5)$$

where $A = k_2 L_0 + k_r$, $m = (k_s - 2k_r)$, and $a = k_2 L_0/A$, with the restrictions that $m \geq 1$ and $k_r \neq 0$.

REFERENCES

1. H. W. Streeter and E. B. Phelps, *A Study of the Pollution and Natural Purification of the Ohio River, III. Factors Concerned in the Phenomena of Oxidation and Reaeration*, U.S. Public Health Service, Bulletin 146, 1925.
2. H. A. Thomas, The Pollution Load Capacity of Streams, *Water and Sewage Works*, 95, pp. 409-413, 1948.
3. S. C. McCutcheon, *Water Quality Modeling, Vol. I: Transport and Surface Exchange in Rivers*, CRC Press, Boca Raton, Florida, 1989.
4. H. A. Thomas, *Hydrology and Oxygen Economy in Stream Purification*, seminar on Waste Water Treatment and Disposal, Boston Society of Civil Engineers, Boston, Massachusetts, 1957.
5. J. C. Young and J. W. Clark, Second Order Equation for BOD, *Journal of the Sanitary Engineering Division Proceedings of the American Society of Civil Engineering*, 91:SA1, pp. 43-57, 1965.
6. T. A. Butts and V. Kothandaraman, Fitting First and Second Order BOD Reaction Equations to Stream Data, *Water and Sewage Works*, 117:8, pp. 276-278, 1970.
7. D. M. Marske and L. B. Polkowski, Evaluation of Methods for Estimating Biochemical Oxygen Demand Parameters, *Journal of Water Pollution Control Federation*, 44:10, pp. 1987-1999, 1972.
8. N. L. Nemerow, *Scientific Stream Pollution Analysis*, McGraw-Hill, New York, 1974.
9. T. H. Y. Tebbutt and M. Berkun, Respirometric Determination of BOD, *Water Research*, 10, pp. 613-617, 1976.
10. D. D. Adrian and T. G. Sanders, Oxygen Sag Equation for Second Order BOD Kinetics, *Water Research*, 32:3, pp. 840-848, 1998.
11. T. V. Le, E. M. Roider, and D. D. Adrian, Simplified Development of Oxygen Sag Model, *Journal of Environmental Systems*, 30:2, pp. 135-145, 2003.
12. S. L. Ponce, The Biochemical Oxygen Demand of Finely Divided Logging Debris in Stream Water, *Water Resources Research*, 10:5, pp. 983-988, 1974.
13. D. M. Bates and D. G. Watts, *Nonlinear Regression Analysis and Its Applications*, John Wiley and Sons, Inc., New York, 1988.
14. D. D. Adrian, E. M. Roider, and T. G. Sanders, Oxygen Sag Models for Multiorder Biochemical Oxygen Demand Reactions, *Journal of Environmental Engineering*, 130:7, pp. 784-791, 2004.
15. J. Hewitt, J. V. Hunter, and D. Lockwood, A Multiorder Approach to BOD Kinetics, *Water Research*, 13, pp. 325-329, 1979.
16. P. M. Berthouex and L. C. Brown, *Statistics for Environmental Engineers* (2nd Edition), Lewis Publishers, Boca Raton, Florida, pp. 388-396, 2002.
17. M. E. Borsuk and C. A. Stow, Bayesian Parameter Estimation in a Mixed-Order Model of BOD Decay, *Water Research*, 34:6, pp. 1830-1836, 2000.
18. M. G. Rodriguez, Calculus of the Biochemical Oxygen Demand of Effluents with Xenobiotics, *Journal of Environmental Science and Health, Part a: Toxic/Hazardous Substances & Environmental Engineering*, 34:4, pp. 879-897, 1999.
19. T. V. Thomann, *Systems Analysis and Water Quality Management*, McGraw-Hill, New York, 1972.

20. G. Tchobanoglous and E. D. Schroeder, *Water Quality: Characteristic, Modeling, Modification*, Addison-Wesley Publishing Co., Reading, Massachusetts, 1985.

Direct reprint requests to:

Donald Dean Adrian
Rubicon Professor and Effie C. & Donald M. Hardy
Professor of Civil and Environmental Engineering
Louisiana State University
Baton Rouge, LA 70803
e-mail: dadrian@lsu.edu