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PROPOSED MODIFICATIONS OF K_2-TEMPERATURE RELATION

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INTRODUCTION

The technical note by Howe (5) serves as a good example of the pitfalls associated with an inadequate analysis of aeration data. Howe (5) presents experimental data from two unsteady aeration tests (see Table 1). These data are used to show that the reaeration coefficient varies inversely with temperature. This finding is counter to the accepted temperature dependence of K_2. It is well recognized in the literature that oxygen transfer coefficients increase with increasing temperature, other factors remaining constant (2).

The writers believe that Howe's (5) conclusion is unfounded and that it is the result of an inadequate statistical analysis of data from poorly designed experiments. The analysis suffers from at least three deficiencies: (1) An inappropriate method for determining the value of the mass transfer coefficient, K_2; (2) a lack of data taken during the unsteady aeration tests; and (3) an oversight in not computing the precision of the estimated values of K_2. An explanation of these deficiencies and a reanalysis of the data follows.

COMPARISON OF DATA ANALYSIS TECHNIQUES

A variety of graphical and numerical procedures have been proposed for the analysis of unsteady-state oxygen transfer data. A general review of these procedures has been given by Brown (4). They are conveniently grouped into three categories, i.e., the exponential, log deficit, and direct methods, and they will be summarized herein. The methods derive their name from the form of the equation used to fit the data. The basic oxygen transfer model can be expressed in three forms; first the direct or differential form:

$$\frac{dC_t}{dt} = K_2(C_s - C_t) \qquad (1)$$

Second, the log deficit form:

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$$\ln (C_s - C_t) = \ln (C_s - C_o) - K_2 t \qquad (2)$$

And third, the exponential form:

$$C_t = C_s - (C_s - C_o) \exp (-K_2 t) \qquad (3)$$

in which C_t = the dissolved oxygen concentration at time t; K_2 = the reaeration (oxygen transfer) coefficient; C_s = the equilibrium (steady-state) dissolved oxygen concentration; and C_o = the dissolved oxygen concentration at time zero. The notation used in Eqs. 1, 2, and 3 is consistent with that of Howe (5).

The exponential form of the oxygen transfer model, Eq. 3, is best suited for the analysis of unsteady-state oxygen transfer data (3,6). It requires a nonlinear least squares regression technique to estimate the values of C_o, C_s, and K_2, but has the following advantages. It provides the least squares estimates and precision of these estimates for all three parameters directly from the data; it works directly with the observed dissolved oxygen concentration, C_t, rather than with a calculated log dissolved oxygen deficit, or with an approximation to the time rate of change of oxygen concentration; it does not require the truncation of observed data as the dissolved oxygen concentration approaches saturation; and it provides parameter estimates that are more precise than those given by other commonly-used methods.

TABLE 1.—Comparison of Parameter Estimates

Parameter (1)	Set I—20.5*C* Howe's data[a] (2)	Set I—20.5*C* Writer's data[b] (3)	Set II—30*C* Howe's data[a] (4)	Set II—30*C* Writer's data[b] (5)
K_2, per hour	1.221	1.016 ± 18%	1.085	1.011 ± 2.9%
C_s, in milligrams per liter	9.75	10.36 ± 6.4%	7.75[c]	7.81 ± 0.7%
C_o, in milligrams per liter	0.00[c]	−0.048 ± 0.45	0.00[c]	0.004 ± 0.06

[a] Howe's method—log deficit.
[b] Writer's method—exponential.
[c] Assumed value.

While the nonlinear regression method using Eq. 3 is recommended for parameter estimation, methods employing graphical, or linear least squares numerical techniques, or both, may be useful for obtaining approximate values for the parameters. The log deficit method using a measured value of C_s to compute the deficits has the advantage of being linear in K_2. The disadvantage is that the value of C_s must be assumed, and thus, the estimate of K_2 will be biased to the extent that C_s is selected incorrectly. Furthermore, the method does not yield estimates of the precision of C_s, and often requires truncation of the data in the vicinity of saturation.

The direct method is another useful approximate method and has the advantage of not requiring that C_s be specified in order to estimate K_2. However, the differentiation inherent in the direct method produces a variable dC_t/dt, having a larger error than the error in C_t. The larger error in dC_t/dt causes the error in the parameter estimates, C_s and K_2, to be larger than those from other methods.

It appears from the data and calculations in Table 1 of Howe's work (5), that he used the log deficit method for estimating the reaeration coefficient. It is not clear how the values of C_s used in the calculations were selected. A value of C_s larger than the best fit value (in a least square sense) will result in a negative bias to the estimated mass transfer coefficient. To avoid this problem, the writers have used the exponential method to fit Eq. 3 to Howe's data. A comparison of the results of the two estimation procedures is given in Table 1.

For data set I (20.5*C*), the least squares estimate of K_2 by the exponential method is 16% lower than that reported by Howe. Correspondingly, the estimate of C_s is 6% higher than the value assumed by him. For data set II (30*C*), the least squares estimates of K_2 and C_s by the exponential method are 7% lower and 1% higher, respectively, than the values reported by Howe. Two important observations can be made from this comparison. First, the estimates of K_2 by the two estimation methods differ for both sets of data. Second, using the exponential method, the estimates of K_2 for set I (20.5*C*) differ from that for set II (30*C*) by less than 1%.

Another disturbing feature in the analysis is the manner in which Howe uses the zero-zero concentration-time pair. From inspection of his Figs. 1, 2, and 3, and the fitted equations he reports, it appears that Howe forces the equation through the origin. It is the writers' experience in unsteady aeration testing that it is practically impossible to define the precise point in time at which the dissolved oxygen concentration changes from zero to steadily increasing values. Time zero is usually established arbitrarily near the point in a test where the reaeration curve begins to increase. Thus, the value of concentration at time zero should be treated similarly to any other observation, subject to experimental error. Forcing the model through the origin potentially biases the other parameter estimates.

EXPERIMENTAL DESIGN

According to Berthouex and Hunter (1), parameter estimation is most efficient if care is taken in selecting the times at which observations of the dependent variable are made. For models of the type of Eq. 3, it can be shown that the important observation times are zero, $1/K_2$, and times approaching infinity. These times correspond to the maximum sensitivity of C_o, K_2, and C_s, respectively. Thus, an efficient experimental design should reflect these sensitivities. The regression analysis with Eq. 3 therefore should be based on a minimum of 10–15 data values. Approximately two-thirds of these values should be evenly distributed over the time period of $0/K_2$–$2/K_2$ (or approx 0%–86% equilibrium dissolved oxygen concentration). The remaining one-third of the values should be evenly distributed over the time period of $2/K_2$–$4/K_2$ (or 86%–98% equilibrium). If there is considerable uncertainty about the anticipated value of K_2, then the test should be conducted for as long a period of time as possible to insure a length of at least $4/K_2$.

Howe's table 1 shows that only 5 and 6 observations for data sets I and

II, respectively, were used in the analysis. Although the division of data values above and below $2/K_2$ is probably acceptable, clearly there are too few observations in each region for good parameter estimation. Especially important are more data at the beginning of each experiment (the dissolved oxygen range from 0 mg/l–5 mg/l), because the estimate of K_2 is sensitive to values in this region. In addition, data set I was not carried out for a sufficient length of time (for this set $4/K_2$ is about 4 h). It is unfortunate that Howe does not fully report his experimental procedures. For example, it is not reported how the test water was deaerated, or if normally accepted methods were used. Numerous investigators have reported spurious results in determining K_2, which were produced by faulty deaeration techniques. Also, Howe does not indicate how power input was measured to insure that equal power was used for both test temperatures. At the Reynolds number used in these two experiments, small changes in fluid viscosity should not change power input; however this should be confirmed experimentally and not assumed. A small change in power input could produce a change in K_2 much greater than the Howe's proposed temperature effect.

Precision of Parameter Estimates

In addition to the least squares estimates, the standard deviations or relative standard deviations of the parameter estimates should be calculated and reported. The parameter standard deviations reflect the degree of scatter in the data and should be small (say less than 5% of the least squares estimate) for a good experiment. The standard deviations are also useful in comparing the least squares parameter estimates from one experiment to another.

The precision of the parameter estimates by the exponential method for data sets I and II are presented in Table 1 as relative standard deviations. For data set I they are high, 18.6% for K_2 and 6.4% for C_s, while for data set II they are low, 2.9% and 0.7%, respectively. The reason for the better precision in data set II is probably because the data are less noisy than in set I and because the experiment in set II was carried out for a longer period of time.

A statistical test of the hypothesis comparing the reaeration coefficient from set I (20.5C) with that from set II (30C) shows no significant difference between the parameter estimates from the two sets at a 95% confidence level. Although the estimate of K_2 is lower at 30C than at 20.5C, the difference between the two values is easily attributable to experimental error, rather than to a potential temperature effect.

Summary

The precise estimation of reaeration coefficients from unsteady-state oxygen transfer data is not a trivial exercise. It requires an unambiguous estimation technique and an adequate set of observed values of concentration versus time. In addition, many unsteady aeration tests performed over a wide range of temperatures are required to verify a postulated temperature dependence of the reaeration coefficient. The data reported by Howe (5) do not provide any support for a "new theory" of an inverse temperature dependence for the reaeration coefficient.

Appendix.—References

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