Effects of dissolved oxygen probe lag on oxygen transfer parameter estimation

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ABSTRACT: Dissolved oxygen (DO) probes are widely used to collect concentration versus time data in non-steady-state reaeration tests that are used to estimate clean water oxygen transfer rates. Probe lag-induced error is known to alter the results of these tests. To estimate the magnitude of this error, a series of lab-scale reaeration experiments were performed using DO probes with various lag times. The experimental results were confirmed with a mathematical model that treats the probe lag as first order. The magnitude of the error in estimating oxygen transfer rate is less than 1% if the product of the volumetric oxygen transfer coefficient (K_La) and the probe time constant is less than 0.02. If low-end data truncation is performed, the product of probe lag and K_La can be increased to 0.05 without creating error in excess of 1%. *J. Water Pollut. Control Fed.*, **61**, 83 (1989).

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The American Society of Civil Engineers (ASCE) Clean Water Standard[1] for estimating oxygen transfer is finding widespread acceptance, and is frequently used by consultants as a method to ensure compliance and fairness among aeration equipment manufacturers. This standard requires frequent dissolved oxygen analysis in the reaeration test, which makes the DO probe method more practical than the time consuming Winkler wet chemical DO analysis. Furthermore, recent work[2] testing non-ideal reactor geometry, such as oxidation ditches, indicates that more frequent data collection is preferred.

Many consultants and manufacturers have been reluctant to use DO probes in the past. Part of this reluctance is because of the cost of meters and probes. Problems with probe drift, calibration, and electrical noise are also cited. A less well-known, but potentially very significant problem, is probe lag-induced error on oxygen transfer parameter estimation. The ASCE Standard recognizes this possibility, and makes certain recommendations to avoid it.

It is the objective of the research to better define the magnitude of probe lag-induced errors, and develop guidelines for their use. Low-end data truncation is shown to reduce probe lag-induced errors.

Background

Polarographic DO electrodes or DO probes are commonly used in the wastewater treatment field to measure dissolved oxygen. They are less susceptible to interferences than the Winkler procedure and more convenient when performing frequent or repetitive analyses. For most wastewater applications, the effect of lag in a probe's response to a changing DO concentration is not significant. For many applications, long lags are desirable because they provide smoothing, reducing the observed variation in probe response. This may be desirable because the noise may be electrical in origin and may not be a function of the actual variation in DO concentration.

Probe lag can result from a variety of sources. The meter can be designed to deliberately introduce lag, and it appears that some manufacturers introduce lag to avoid observable meter drift. Probe lag can also result from the internal voids in the electrodes. The oxygen concentration in these voids requires a finite length of time to change. The diffusional resistance of the membrane contributes to probe lag, and this lag has been described previously[3] as

$$t = \frac{b^2}{D_{o_2}} \qquad (1)$$

Where

t = probe lag,

b = membrane thickness, and

D_{o_2} = oxygen diffusivity.

Manufacturers often provide more than one membrane thickness. The difference between probe response with thin membranes (high sensitivity) and regular membranes is readily observable. High sensitivity membranes show more oscillation and variability, indicating a faster response time. A procedure has been developed to quantify probe lag from probe geometry and characteristics.[4]

Probe lag has a deleterious effect on oxygen transfer parameter estimation. Probes must respond instantaneously to introduce no error in estimating K_La, the volumetric oxygen transfer coefficient. Others[5] first suggested that probe lag could introduce errors in estimating K_La, and noted that it generally took 10 to 100 seconds for a probe to achieve 90% of the steady-state value. Elsewhere,[6] it was noted that it generally took 30 seconds for a probe to reach 99% of its final value, and it was shown mathematically that the presence of probe lag could reduce the estimates of K_La.

Probe lag effects on the estimates of K_La were quantified elsewhere.[7] The probe lag was modeled as first order.[7] At the time of the work,[7] the ASCE Standard did not exist, and the three popular methods for estimating K_La (log deficit, exponential, and differential methods) were used, showing that probe lag affects each technique differently. The ASCE Standard, in its advisory appendices, used these findings to recommend maximum permissible probe lags.

Experimental Procedures

Figure 1 shows the lag test apparatus. The objective of the probe lag test was to subject the probe to a nearly instantaneous change in DO concentration. The time required for the probe to respond to the change was then used to estimate the probe's time constant. The probe being tested was inserted into a 50-mL beaker that was mounted below the liquid level, as shown in Figure 1. The probe height was adjusted so that it was 2.5 cm below the tank liquid level.

After setting up the probe, the water in the 50-mL beaker was replaced with water having a much different DO concentration than the tank water. The probe was allowed to equilibrate with the beaker concentration. Next the beaker was quickly removed, which rapidly exposed the probe to the tank liquid with a different DO concentration. Tests were conducted in both directions—high DO water in the beaker with low DO water in the tank, and vice-versa. Generally, one liquid was saturated and the other was at near zero concentration. Test liquids were
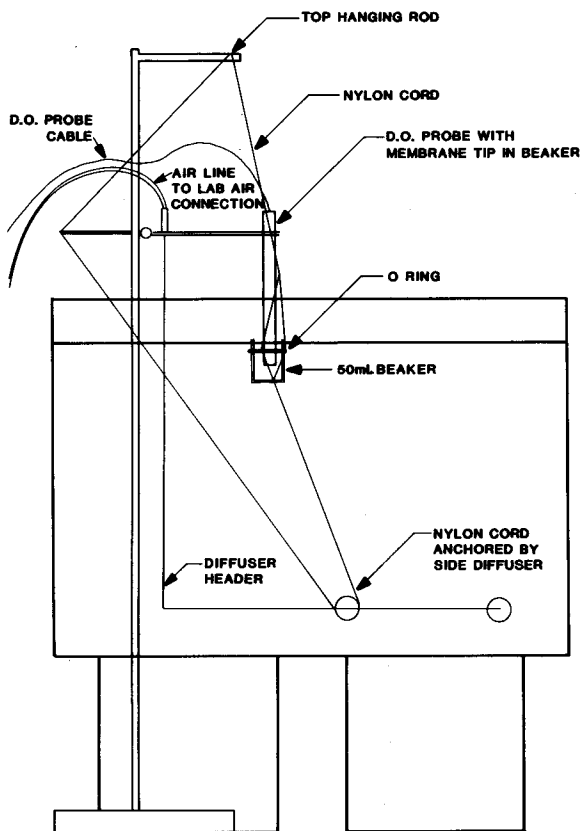

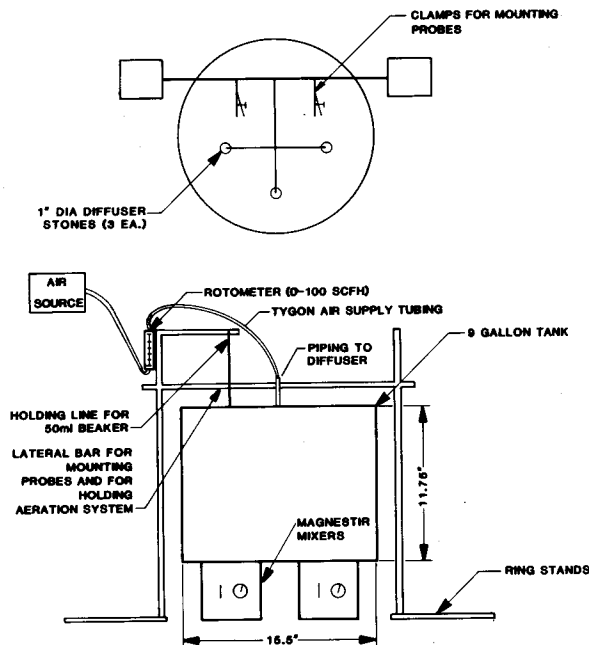Figure 1—Probe lag test apparatus.

Figure 2—Reaeration test apparatus.

deoxygenated with nitrogen gas to obtain low DO concentrations.

Data were collected using a personal computer equipped with a two-channel A to D converter. Dissolved oxygen concentration was recorded every second and the test duration was generally 200 seconds, or at least $4/K_La$. Different probe lags were achieved using different membrane thicknesses and combinations of membranes. In this way, it was possible to produce probe lag times over a wide range.

The reaeration test apparatus is shown in Figure 2. Two probes were used in reaeration testing—a fast probe that served as a control or reference, and a slow probe that served as the experiment. Probes were mounted in the tank at the same depth to insure equal hydrostatic pressure. In general, the ASCE[1] procedure was followed, except that nitrogen gas was used to deaerate the test liquid.

Probes were calibrated daily using the Winkler procedure. In general, probe lag tests were conducted consecutively with reaeration tests. This was necessary because each membrane or combination of membranes produced a slightly different lag, even for otherwise identical conditions. The procedures are described in detail elsewhere.[8]

Analysis and Discussion

Probe lag. Probe lag was modeled as a first-order lag as follows:

$$\frac{dC_p}{dt} = \frac{C - C_p}{\tau} \tag{2}$$

Where

C_p = DO indicated by the probe, mg/L;
C = actual DO concentration, mg/L; and
τ = probe lag constant, seconds.

The integrated form of Equation 2 becomes

$$C_p = C - (C - C_{po})e^{-t/\tau} \tag{3}$$

Where

C_{po} = initial probe indication, mg/L, (for example, 50-ml beaker DO concentration); and

C = tank DO concentration.

Equation 3 can be linearized as follows:

$$\ln\left|\frac{C - C_p}{C - C_{po}}\right| = \frac{-t}{\tau} \qquad (4)$$

By plotting this equation, the time constant τ can be estimated. Figure 3 shows a typical result. The early part of the test very precisely follows the first-order model. As the test proceeds, results deviate from the model, principally because of the difficulty in precisely measuring minutely different DO concentrations. The lag difference procedure shown in Equation 4 magnifies this error as the difference in C and C_p approaches zero.

The probe constant was also modeled as a second-order lag:

$$\frac{dC_p}{dt} = \frac{(C - C_p)^2}{\tau} \qquad (5)$$

The second-order lag did not describe the experimental results as well as a first-order lag, and was not pursued further.

The entire set of equations describing the two probes in the reaeration test is

$$\frac{dC}{dt} = K_L a(C_\infty^* - C) \qquad (6)$$

$$\frac{dC_{p1}}{dt} = \frac{C - C_{p1}}{\tau_1} \qquad (7)$$

$$\frac{dC_{p2}}{dt} = \frac{C - C_{p2}}{\tau_2} \qquad (8)$$

Where

C_{p1} and C_{p2} = observed DO concentration from probes;

C = actual DO concentration;

$K_L a$ = volumetric oxygen transfer coefficient, t^{-1};

C_∞^* = equilibrium DO concentration, mg/L; and
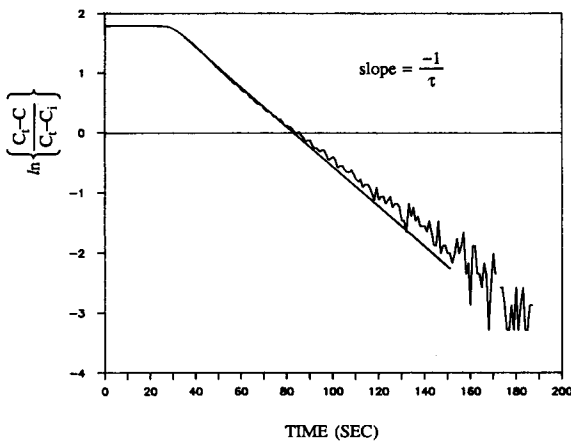
τ_1, τ_2 = probe lags, seconds.
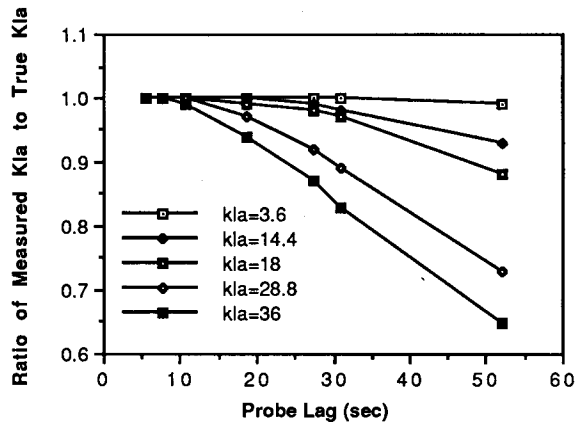

Figure 3—Typical probe lag results.

Figure 4—Simulation results for different probe lags.

Equations 6 through 8 were integrated numerically and results were then analyzed using the ASCE nonlinear least squares technique.

A wide range of $K_L a$, τ_1, and τ_2 values was experimentally evaluated. Generally, τ_1, the value for the control probe, was kept as small as possible so that $C = C_p$. Equations 4 through 6 were also solved for the experimentally determined values of τ and $K_L a$.

Figure 4 shows the results of the simulations. As the probe lag increases, the error in estimating $K_L a$ progressively increases. Figure 5 shows the simulated results and the experimental results, plotted as the ratio of the $K_L a$ containing probe lag-induced error to actual $K_L a$.

The experimental data and simulations were analyzed with varying amounts of low-end truncation. The ASCE Standard explicitly states that low-end truncation is allowed if the data in the early part of the test do not appear to conform to an exponential increase. The initial data in a reaeration test can be influenced by lingering sulfite or non-ideal mixing. Probe lags were investigated from 5 to 50 seconds, and $K_L a$ varied from 3 000 to 10 000 s^{-1} (0.833 to 2.8 h^{-1}). Figure 5 also shows the experimental and simulated results for data truncated at 20% of C_∞^*. Much
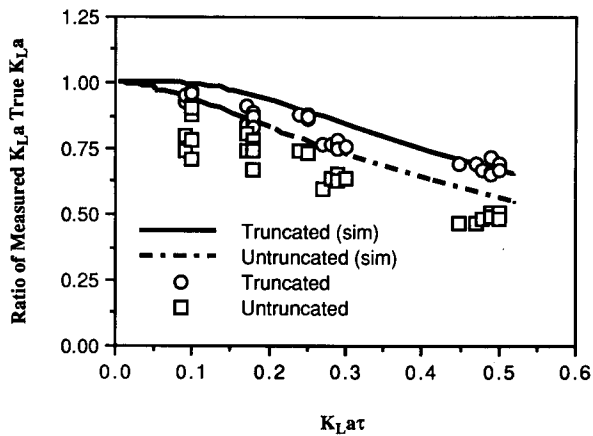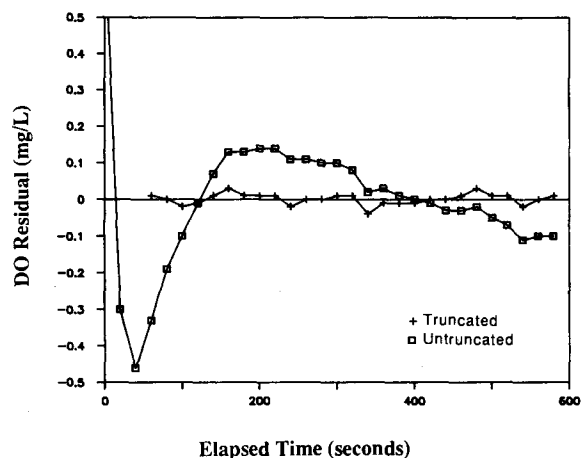

Figure 5—Ratios of measured $K_L a$ to actual $K_L a$ for varying probe lags and $K_L a$.

Figure 6—Residuals showing bias caused by probe lag.

greater probe lag can be tolerated if low-end truncation is performed.

Equations 6 through 8, which describe the reaeration tests, are linear. The results can be described by the dimensionless product of K_La and τ, shown previously.[7] By limiting the magnitude of τK_La, the effects of probe lag induced error can also be limited. To limit the error in K_La to less than 1%, the magnitude of τK_La should be less than 0.02. If low-end truncation is performed, this product can increase to 0.05, as shown in Figure 5.

The effects of probe lag can be observed from plotting the residuals (measured DO − calculated DO using the estimated parameters). Figure 6 shows two sets of biased residuals for large and small probe lags. It is useful to examine residuals to detect potential problems in test results. Other phenomena can also cause biased residuals as shown in Figure 6.

Summary and Conclusions

Lag time in polarographic dissolved oxygen probe response can bias estimates of K_La. This is shown over a wide range of K_La and probe lag time, and was confirmed experimentally. The dimensionless product of probe lag constant, approximated as a first-order lag, and K_La can be used to estimate the magnitude of probe lag-induced errors on K_La. The product of K_La and τ should be less

than 0.02 to limit the error in K_La to less than 1%. If the data are truncated on the low end at 20% of C_∞^*, the product of probe lag and K_La can increase to 0.05.

For the probes used in this study average time constants of 5 and 7.7 seconds were determined for high sensitivity and normal membranes, respectively. Using the previously stated criterion, these probes could be used in testing aeration systems with K_La as high as 14.4 and 9.3 h^{-1}, respectively. If truncation is performed for high sensitivity and normal membranes, this range extends to 36 and 23 h^{-1}. It is recommended that low-end truncation be routinely practiced in high rate aeration systems testing.

Acknowledgments

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