Dissolved Oxygen in Streams: Parameter estimation for the Delta method

Rajesh Srivastava

Associate Professor, Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India.

Abstract

The Delta method is one of the techniques used for estimating the reaeration coefficient, respiration rate, and production rate in streams from the diurnal dissolved oxygen (DO) profile. Recently, an approximate Delta method has been proposed which allows for approximate, but simpler, computation of these parameters. We suggest some modifications in the approximate Delta method to improve its accuracy. It is shown that the proposed method is more accurate for a wide range of parameter sets.

Introduction

Dissolved oxygen (DO) in a stream is a useful indicator of its water quality. Three main parameters which affect the diurnal DO variation are the reaeration coefficient, production rate, and respiration rate. Estimation of these parameters from measured DO profile has been the subject of many studies (e.g., Odum 1956, O’Connor and Di Toro 1970, Hornberger and Kelly 1972, Kelly et al. 1974, Hornberger and Kelly 1975, Chapra and Di Toro 1991). A recent and excellent review of various modelling techniques is provided by Cox (2003). Assuming negligible longitudinal oxygen gradients, constant stream temperature, and a primary production rate of the form of a half-sinusoid within the photoperiod, Chapra and Di Toro (1991) obtained a periodic analytical solution for the diurnal dissolved oxygen (DO) profile. The method was called the delta method, since an important parameter used in the analysis was the diurnal range of variation of the dissolved oxygen, denoted by $\Delta$. The method, though having its limitations (Chapra and Di Toro 1991, Cohen 1992, Erdmann 1992), has been widely used for analysing the DO profiles (e.g., Wilcock et al. 1995, Guasch et al. 1998, Wilcock et al. 1998, Jarvie et al. 2003, Wang et al. 2003, Kim and Je 2004). The form of the analytical solution, while allowing direct computation of the DO profile for given parameters (the stream reaeration coefficient, respiration rate, and average plant primary production rate), does not offer explicit closed form expressions for estimating the parameter values from the measured DO profile at a station. Chapra and Di Toro (1991) therefore used numerical techniques to obtain the parameters from characteristics of the measured DO profile and presented the results in graphical form. McBride (2002), noting that the shape of the graph relating the reaeration coefficient to the time lag between the DO maximum and solar noon is similar to that of a logistic curve, obtained an approximate equation for the same. This work was later extended by McBride and Chapra (2005) who proposed another approximate equation (again, based on the logistic curve) relating the daily average production rate to the diurnal variation range and the reaeration coefficient. This approximate delta method (ADM) was applied to a number of field measurements and was found to be reasonably accurate. However, the approximate equations were seen to have large errors for some combination of values. For example, the approximate equation for reaeration coefficient may overpredict the value by as much as 10% for time lag values of about 1 to 2 hours and also results in large errors when the lag is close to its theoretical maximum value. Similarly, the approximate equation for the production rate is not very accurate for aeration coefficient values larger than about 20 $d^{-1}$ and also for a photoperiod length of 8 h. This was
stated to be a mathematical curve fitting issue and better fits of simple form could not be obtained. McBride and Chapra (2005) also note that the ADM could predict negative DO values for some combination of parameter values and specified some constraints on the parameter values which would ensure the avoidance of such problems.

In this paper we analyse the accuracy of the approximate delta method and attempt to improve the accuracy by choosing a little more complex form of the approximation based on an analysis of the analytical expression. We also look closely at the issue of negative DO predictions and suggest an alternative way of computing the production rate.

**Mathematical Background**

The equation governing the variation of DO in a stream is

\[
\frac{dC}{dt} = k_a (C_{sat} - C) + P - R
\]

where, \( C = \text{DO (mg/L)}; \ t = \text{time (h)}; \ k_a = \text{first-order stream reaeration coefficient (h}^{-1}); \ C_{sat} = \text{saturated DO (mg/L)}; \ P = \text{plant primary production rate (mg/L/h)}; \) and \( R = \text{respiration rate (mg/L/h)}. \) Chapra and Di Toro (1991) worked with the DO deficit, \( D = C_{sat} - C \)

and assumed that the stream temperature is constant and the production rate is given by a half-sinusoid

\[
P = \frac{\pi T}{2f} P_{av} \sin \left( \frac{\pi t}{f} \right) \quad 0 \leq t \leq f
\]

\[
P = 0 \quad f \leq t \leq T
\]

where \( T \) is the period length (=24 h); \( f \) is the photoperiod length (h); \( P_{av} \) is the daily-average production rate (mg/L/h); and the time, \( t, \) is measured from sunrise. The analytical solution for the DO was obtained as (written in a slightly different form here since we use the DO rather than the DO deficit in this paper)

\[
C = C_{sat} - \frac{R}{k_a} + \frac{P_{av} T \sigma}{k_a} \left[ k_a f \sin \left( \frac{\pi t}{f} \right) - \cos \left( \frac{\pi t}{f} \right) + \gamma e^{-k_a t} \right] \quad 0 \leq t \leq f
\]

\[
C = C_{sat} - \frac{R}{k_a} + \frac{P_{av} T \sigma}{k_a} \left[ 1 + \gamma e^{-k_a f} \right] e^{-k_a (t-f)} \quad f \leq t \leq T
\]

where the dimensionless parameter groups, which are functions of \( k_a \) and \( f, \) are defined as

\[
\gamma = \left[ \frac{1 + e^{-k_a (T-f)}}{1 - e^{-k_a T}} \right], \quad \sigma = \frac{1}{2 \left[ \frac{k_a f}{\pi} \right]^2}
\]

From the analytical solution, it may be demonstrated that both the minimum and the maximum of the DO occur within the photoperiod and the time lag between the DO maximum and solar noon, \( \phi \) (see Fig. 1), could be obtained by solving (McBride 2002)

\[
\pi \cos \left( \frac{\pi \phi}{f} \right) - k_a f \sin \left( \frac{\pi \phi}{f} \right) - k_a f \gamma e^{-k_a (\phi+f/2)} = 0: \phi > 0
\]
From Eq. (6), it is seen that the reaeration coefficient, \( k_a \), is only a function of \( \phi \) and \( f \). Chapra and Di Toro (1991) numerically solved Eq. (6) and provided a graph which could be used for obtaining the value of \( k_a \) for a given \( \phi \) for a few selected values of \( f \) (Fig. 2). Waldon (1985) proposed a peak lag method and a modified form (Waldon 1992) for estimation of \( k_a \) as

\[
k_a = 24 \left[ \frac{0.2618}{\tan(0.2618\phi)} - (0.081 - 0.0049f)\phi - (0.38 - 0.06f + 0.0022f^2) \right]
\]

where, \( k_a \), from now onwards, is in the commonly used units of d\(^{-1}\). The accuracy of Eq. (7) was, however, found to be unacceptable for some parameter values (Chapra and Di Toro 1992).

McBride (2002) fitted a logistic curve to the plot of \( k_a \) versus \( \phi \) for \( f=14 \) h, and used a photoperiod correction factor for other values of \( f \) to obtain the following approximation:

\[
k_a = 7.5 \left( \frac{5.3\eta - \phi}{\eta \phi} \right)^{0.85}
\]

where \( \eta \) is the photoperiod correction factor given by

\[
\eta = \left( \frac{f}{14} \right)^{0.75}
\]

It was found that the approximation, Eq. (8), works well except for small \( k_a \) and large \( f \). McBride and Chapra (2005) extended this concept and proposed an approximate delta method which provided an additional logistic curve fit between the ratio of the diurnal DO range, \( \Delta = C_{\text{max}} - C_{\text{min}} \), to \( P_{av} \), and the reaeration coefficient, \( k_a \), as

\[
\frac{\Delta}{P_{av}} = \frac{16}{\eta \left( 33 + k_a^{1.5} \right)}
\]
with $P_{av}$ expressed in the more convenient units of mg/L/d. Thus once $k_a$ is known from Eq. (8), the average production rate could be obtained using Eq. (10). However, the approximation involved errors as large as 5% for $k_a$ values from 0.1 to 1 d$^{-1}$ and much higher for $k_a$ larger than 20 d$^{-1}$. The respiration rate, in mg/L/d, was then obtained from

$$R = P_{av} + k_a \left( C_{sat} - \bar{C} \right)$$

(11)

where $\bar{C}$ is the diurnal average DO (mg/L).

Wang et al. (2003) stated that the delta method could propagate computational errors since a computed parameter, which itself may be subjected to large errors, is subsequently used in the estimation of other parameters. For example, $k_a$ estimated from Eq. (8) is used to obtain $P_{av}$ through Eq. (10) and both these are used to estimate $R$ through Eq. (11). They proposed an extreme value method based on the fact that at the points of extremes of DO (or DO deficit), the slope of the DO curve is zero and, from Eq. (1),

$$R = P + k_a \left( C_{sat} - C \right)$$

for $t = t_{min}$ or $t_{max}$

(12)

Further, assuming that the minimum DO occurs during night when $P = 0$ (note that this assumption is in contradiction of the delta method solution which results in the minimum DO a little after sunrise), they obtained, for the respiration rate,

$$R = k_a \left( C_{sat} - C_{min} \right)$$

(13)

and, for the production rate,

$$P_{av} = \frac{R - k_a \left( C_{sat} - C_{max} \right)}{\pi T \cos \left( \frac{\pi \phi}{f} \right)}$$

(14)

Comparison with the delta method showed that the extreme value method produced similar results.

McBride and Chapra (2005) mention that the analytical solution of Chapra and Di Toro (1991) does not put a lower bound on the DO and it is possible, for certain combination of parameter values, to get negative DO values. They performed numerical experiments to suggest the following constraints to avoid these non-physical negative DO values:

$$R < 40e^{\frac{k_a}{2f}}, \quad k_a > 6d^{-1}$$

$$< 4.8e^{\frac{f}{2(1.8-0.32k_a)+0.4k_a}}, \quad k_a \leq 6d^{-1}$$

(15)

Analysis

Fig. 2 shows the percent error in prediction of $k_a$ using Eq. (8) and provided the motivation to arrive at a better fit which should be more accurate and may be of a little more complicated form than Eq. (8). The fitting philosophy used was that of matching the asymptotic behaviour and then tweaking some parameters to obtain a general improvement in the fit. Analysing Eq. (6), the following limiting cases were obtained (note that $\phi$ and $f$ are in h and $k_a$ in d$^{-1}$):

$$k_a \to 0: \quad \phi \to \frac{f}{\pi} \cos^{-1}\left( \frac{2f}{\pi T} \right)$$

$$k_a \to \infty: \quad \phi \to \frac{24}{k_a}$$

(16)
The form of Eq. (6) for small $k_a$ suggested a possible fitting function of the form

$$k_a = \frac{24}{f} \cos \left( \frac{\pi \phi}{f} \right) \frac{2f}{T} \sin \left( \frac{\pi \phi}{f} \right) - \frac{2\phi}{T} \right) \right)$$

which satisfies both the asymptotic conditions listed in Eq. (16). Data generated using values of $f$ equal to 8, 10, 12, 14, and 16 h and range of $k_a$ from 0.1 to 100 d$^{-1}$ was used to estimate the error in the approximate expression. Use of Eq. (15) produced a maximum error of about 12% and it was, therefore, modified as

$$k_a = \frac{12\pi}{f} \cos \left( \frac{\pi \phi}{f} \right) - \frac{1}{1 - 0.83 \sin \left( \frac{\pi \phi}{f} \right)} \right)$$

Fig. 3 shows the plot of $k_a$ obtained from Eq. (18) along with the analytical solution and Fig. 2 shows a comparison of the errors obtained from Eqs. (8) and (18). As seen from Fig. 3, for $k_a$ values of less than about 1 d$^{-1}$, a small difference in $\phi$ may cause a difference of about an order of magnitude in $k_a$ (Chapra and Di Toro 1991). Since the measurement of $\phi$ involves some uncertainties, it would probably not be prudent to come up with an approximation which is extremely accurate for small values of $k_a$. Therefore, in all the approximate expressions derived in this paper, we try to minimize the maximum error for the range 100 $\geq k_a \geq$ 1 and have a reasonable error for smaller $k_a$ values. It is seen that the performance of Eq. (18) is generally better with the maximum error for larger $k_a$ values being less than 4%. The additional complexity of Eq. (18) may be a drawback from the point of view of hand computations but should not be a factor in computer applications.
Figure 3. Comparison of the predicted and theoretical $k_a$ values. Solid line – Delta solution, Broken line – Eq. (18). Numbers near the curve are values of $f$.

Similarly, for the primary production rate, the following limiting values were obtained:

$$
k_a \rightarrow 0: \quad \frac{\Delta}{P_{av}} \rightarrow \sqrt{1 - \left(\frac{f}{12\pi}\right)^2 - \frac{f}{12\pi}\cos^{-1}\left(\frac{f}{12\pi}\right)}
$$

(19)

$$
\Delta P_{av} \rightarrow \frac{12\pi}{k_a f}
$$

where, $\frac{\Delta}{P_{av}}$ is in $d$, $k_a$ is in $d^{-1}$ and $f$ is in $h$. Chapra and Di Toro (1991) and Chapra and McBride (2005) expressed $\frac{\Delta}{P_{av}}$ as a function of $f$ and $k_a$. However, Wang et al. (2003) pointed that use of the derived parameter $k_a$, which is already approximate, may lead to accumulation of error in the prediction of $P_{av}$. We feel that Eq. (10) was fitted based on the approximate $k_a$ and not the exact value and therefore would not lead to propagation of error. In order to avoid ambiguity, however, we express $\frac{\Delta}{P_{av}}$ as a function of $f$ and $\phi$. Using the same philosophy as used for derivation of Eq. (18), we obtain the following approximation:

$$
\frac{\Delta}{P_{av}} = \frac{\pi}{2} \sin \left(\frac{\pi\phi}{f}\right) \left(\frac{\phi}{12}\right) \left(1 - \frac{\phi}{2\phi_m} - \frac{\phi^2}{2\phi_m^2}\right)
$$

(20)

in which $\phi_m$ is the maximum value of $\phi$ for any given $f$, as obtained from the small $k_a$ limit in Eq. (16). Fig. 4 shows a comparison of values obtained from Eq. (20) and those from the analytical solution and Fig. 5 compares the errors obtained from Eq. (20) and that from Eq. (10). The maximum error in the use of Eq. (20) is about 3%. The other alternative, Eq. (14), was not considered because the assumption made by Wang et al. (2003) of minimum DO occurring during night time is not consistent with the analytical solution and may lead to large errors (as shown in the next section) if the minimum DO occurs after sunrise (the time
of minimum DO may be as late as 2 hours after sunrise for a long photoperiod and small reaeration coefficient).

![Graph showing comparison of predicted and theoretical values of \( \frac{\Delta P}{\Delta t} \). Thick line – Delta solution, Thin line – Eq. (20). Numbers near the curve are values of \( f \).](image)

**Figure 4.** Comparison of the predicted and theoretical values of \( \frac{\Delta P}{\Delta t} \). Thick line – Delta solution, Thin line – Eq. (20). Numbers near the curve are values of \( f \).

![Graph showing percent error in predicted value of \( \frac{\Delta P}{\Delta t} \). Thick line – Eq. (10), Thin line – Eq. (20). Numbers near the curve are values of \( f \).](image)

**Figure 5.** Percent error in the predicted value of \( \frac{\Delta P}{\Delta t} \). Thick line – Eq. (10), Thin line – Eq. (20). Numbers near the curve are values of \( f \).

During the derivation of the approximate expressions for the production rate, the possibility of having a negative DO was not considered. Eq. (15) provides a criterion for predicting whether negative DO will occur. However, from an application point of view, it may not be as important to predict the conditions under which negative DO occurs as to suggest a method to estimate the parameters under these conditions. The observed DO profile in such cases will show zero value for some length of time. We may still assume the model to be valid with the modification that the negative values of DO predicted from the model are taken as zero. However, the diurnal DO range, \( \Delta \), would now be equal to \( C_{\text{max}} \) and Eqs. (10) and (20) would underpredict \( P_{\text{av}} \). Eq. (14) would be applicable but, as discussed earlier, the
assumption made in Eq. (13), of minimum DO occurring before sunrise, may lead to large errors. Making the assumption that the average DO would not be significantly affected by the presence of the zero DO segment, we propose below a modified delta method which uses the difference between the maximum and average DO as its parameter. Using the extreme value method of Wang et al. (2003) and the time averaged equation (11), it can be shown that

\[
P_{av} = \Delta_1 \frac{k_a}{\pi T} \cos \left( \frac{\pi \phi}{f} \right) - 1
\]

(21)

where \( \Delta_1 = C_{max} - C \) (see Fig. 1). Fig. 6 shows the theoretical graph relating \( \frac{\Delta_1}{P_{av}} \) to \( f \) and \( \phi \).

Using the approximate equation for \( k_a \), Eq. (18), and adjusting the coefficients to obtain minimum error for \( k_a > 1 \), we get

\[
\frac{\Delta_1}{P_{av}} = \frac{1}{2} \sin \left( \frac{\pi \phi}{f} \right) - \frac{\phi}{12} \left( 1 - 0.72 \sin \left( \frac{\pi \phi}{f} \right) \right)
\]

(22)

Fig. 6 shows the values predicted from Eq. (22) and Fig. 7 shows the relative error of prediction. The maximum error for larger reaeration coefficients is less than 4%. We believe that Eq. (22), which we call the modified delta method (MDM), would provide a better estimate of the production rate since the average DO would not be significantly affected by the “theoretically negative” DO values and \( \Delta_1 \) would be subjected to smaller errors compared to \( \Delta \). In the next section, we apply the modified delta method to synthetic and field data sets and show its improved accuracy.

**Figure 6.** Comparison of the predicted and theoretical values of \( \frac{\Delta_1}{P_{av}} \). Thick line – Delta solution, Thin line – Eq. (22). Numbers near the curve are values of \( f \).
Applications

Five cases have been considered for application of the modified delta method. Three of these are synthetically generated data and the other two are based on field measurements of diurnal DO profiles. Table 1 presents a summary of the key features of these cases. Note that the parameters listed for Mangaoronga are slightly different from those reported in McBride and Chapra (2005), because we obtained these parameters independently by using the features of the DO profile listed in Wilcock et al. (1998).

Table 1. Parameters used in various applications

<table>
<thead>
<tr>
<th>Data Set</th>
<th>$f$ (h)</th>
<th>$\phi$ (h)</th>
<th>$C_{max}$ (mg/L)</th>
<th>$C_{min}$ (mg/L)</th>
<th>$\bar{C}$ (mg/L)</th>
<th>$C_{sat}$ (mg/L)</th>
<th>$k_{aj}$ (d$^{-1}$)</th>
<th>$P_{av}$ (mg/L/d)</th>
<th>$R$ (mg/L/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic I</td>
<td>14</td>
<td>1.17</td>
<td>9.60</td>
<td>7.00</td>
<td>8.00</td>
<td>9.0</td>
<td>20</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Grand River</td>
<td>13</td>
<td>3.93</td>
<td>12.8</td>
<td>4.4</td>
<td>8.372</td>
<td>8.1</td>
<td>2.7</td>
<td>17.9</td>
<td>17.2</td>
</tr>
<tr>
<td>Mangaoronga Stream</td>
<td>12.5</td>
<td>1.44</td>
<td>9.5</td>
<td>6.1</td>
<td>7.4</td>
<td>9.1</td>
<td>15.7</td>
<td>18.8</td>
<td>46.1</td>
</tr>
<tr>
<td>Synthetic II</td>
<td>14</td>
<td>3.99</td>
<td>6.90</td>
<td>0</td>
<td>2.65</td>
<td>9.0</td>
<td>3</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Synthetic III</td>
<td>14</td>
<td>5.13</td>
<td>13.89</td>
<td>4.18</td>
<td>9.0</td>
<td>9.0</td>
<td>0.4</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Synthetic data set I

This application uses the DO profile generated from the analytical solution (Eq. 4) and compares the relative accuracy of parameters estimated from different methods. Table 2 lists the results and shows the improved accuracy of the proposed method. It is seen that the modified delta method, Eq. (22), results in a slightly larger error than that from Eq. (20) but both these approximations are significantly more accurate than the approximate delta method. Fig. 8 shows DO profiles from the delta method, approximate delta method, and the proposed method. Slight improvement is observed when the parameters obtained from the proposed method are used.
Table 2. Results for the data set Synthetic-I

<table>
<thead>
<tr>
<th>Method</th>
<th>(k_a) (d(^{-1}))</th>
<th>(P_{av}) (mg/L/d)</th>
<th>(R) (mg/L/d)</th>
<th>Percent Error in (k_a)</th>
<th>Percent Error in (P_{av})</th>
<th>Percent Error in (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta</td>
<td>20</td>
<td>20</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ADM (Eqs. 8, 10, &amp; 11)</td>
<td>21.91</td>
<td>22.03</td>
<td>43.94</td>
<td>9.55</td>
<td>10.15</td>
<td>9.85</td>
</tr>
<tr>
<td>Proposed (Eqs. 18, 20, &amp; 11)</td>
<td>19.46</td>
<td>19.80</td>
<td>39.25</td>
<td>2.72</td>
<td>1.02</td>
<td>1.87</td>
</tr>
<tr>
<td>MDM (Eqs. 18, 22, &amp; 11)</td>
<td>19.46</td>
<td>19.50</td>
<td>38.96</td>
<td>2.72</td>
<td>2.52</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Figure 8. Diurnal DO profile for the Synthetic-I data set. Symbols – Delta method, Solid line – Proposed method, Dashed line – ADM.

Grand River

The DO profile observed at Grand River, Michigan, have been analyzed in some earlier studies (Chapra and Di Toro 1991, McBride and Chapra 2005). Table 3 lists the results obtained using different schemes of parameter estimation. In this case, the modified delta method is a little more accurate than Eq. (20) and both of them are slightly better than the ADM. For this, and the next, application, it should be noted that the value of \(f\) is not one of the values used for generating the approximate expressions (i.e., 8, 10, 12, 14, and 16 h). The results, therefore, provide some confidence that the proposed approximations would work for other values of \(f\) also.
Table 3. Results for the Grand River data

<table>
<thead>
<tr>
<th>Method</th>
<th>( k_a ) (( d^{-1} ))</th>
<th>( P_{av} ) (mg/L/d)</th>
<th>( R ) (mg/L/d)</th>
<th>Percent Error in ( k_a )</th>
<th>Percent Error in ( P_{av} )</th>
<th>Percent Error in ( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta</td>
<td>2.7</td>
<td>17.9</td>
<td>17.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ADM (Eqs. 8, 10, &amp; 11)</td>
<td>2.63</td>
<td>18.51</td>
<td>17.79</td>
<td>2.60</td>
<td>3.39</td>
<td>3.44</td>
</tr>
<tr>
<td>Proposed (Eqs. 18, 20, &amp; 11)</td>
<td>2.69</td>
<td>18.33</td>
<td>17.60</td>
<td>0.34</td>
<td>2.39</td>
<td>2.3</td>
</tr>
<tr>
<td>MDM (Eqs. 18, 22, &amp; 11)</td>
<td>2.69</td>
<td>17.61</td>
<td>16.88</td>
<td>0.34</td>
<td>1.61</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Mangaoronga Stream

The DO profile observed at Mangaoronga stream, New Zealand, have been analyzed in some earlier studies (Wilcock et al. 1998, McBride and Chapra 2005). Table 4 lists the results obtained using different schemes of parameter estimation. The modified delta method has slightly more error than Eq. (20) but both of these are, again, more accurate than the ADM.

Table 4. Results for the Mangaoronga Stream

<table>
<thead>
<tr>
<th>Method</th>
<th>( k_a ) (( d^{-1} ))</th>
<th>( P_{av} ) (mg/L/d)</th>
<th>( R ) (mg/L/d)</th>
<th>Percent Error in ( k_a )</th>
<th>Percent Error in ( P_{av} )</th>
<th>Percent Error in ( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta</td>
<td>15.7</td>
<td>18.8</td>
<td>46.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ADM (Eqs. 8, 10, &amp; 11)</td>
<td>16.85</td>
<td>19.83</td>
<td>49.13</td>
<td>7.33</td>
<td>5.45</td>
<td>6.57</td>
</tr>
<tr>
<td>Proposed (Eqs. 18, 20, &amp; 11)</td>
<td>15.20</td>
<td>18.52</td>
<td>44.95</td>
<td>3.19</td>
<td>1.48</td>
<td>2.49</td>
</tr>
<tr>
<td>MDM (Eqs. 18, 22, &amp; 11)</td>
<td>15.20</td>
<td>18.26</td>
<td>44.69</td>
<td>3.19</td>
<td>2.87</td>
<td>3.05</td>
</tr>
</tbody>
</table>

Synthetic data set II

This application uses the DO profile generated from the analytical solution (Eq. 4) with the parameters chosen in such a way as to give a negative DO for some length of time. This negative DO was discarded and the profile was seen to have more than 7 hours of zero DO (Fig. 9). As discussed earlier, this will affect both the minimum and the average DO but it is expected that the average DO would not be as significantly affected as the minimum DO. Table 5 lists the results and shows the improved accuracy of the modified delta method. Note that the modified delta method also has a large error (about 9%) which is due to the truncation of the DO profile. However, it outperforms the other methods (Fig. 9), especially in the estimation of the average production rate. Using the extreme value method of Wang et al. (2003), Eqs. (13) and (14), with the exact \( k_a \) value of 3 \( d^{-1} \), we obtain \( R = 27.00 \) mg/L/d and \( P_{av} = 12.29 \) mg/L/d, which have errors of the order of 30%.
Table 5. Results for the data set Synthetic-II

<table>
<thead>
<tr>
<th>Method</th>
<th>$k_a$ (d$^{-1}$)</th>
<th>$P_{av}$ (mg/L/d)</th>
<th>$R$ (mg/L/d)</th>
<th>Percent Error in $k_a$</th>
<th>Percent Error in $P_{av}$</th>
<th>Percent Error in $R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta ADM (Eqs. 8, 10, &amp; 11)</td>
<td>3.91</td>
<td>16.37</td>
<td>34.84</td>
<td>3.00</td>
<td>18.14</td>
<td>12.90</td>
</tr>
<tr>
<td>Proposed ADM (Eqs. 18, 20, &amp; 11)</td>
<td>2.92</td>
<td>16.18</td>
<td>34.69</td>
<td>2.75</td>
<td>19.12</td>
<td>13.27</td>
</tr>
<tr>
<td>MDM (Eqs. 18, 22, &amp; 11)</td>
<td>2.92</td>
<td>18.18</td>
<td>36.70</td>
<td>2.75</td>
<td>9.09</td>
<td>8.26</td>
</tr>
</tbody>
</table>

Figure 9. Diurnal DO profile for the Synthetic-II data set. Symbols – Delta method, Solid line – Modified Delta method, Dashed line – ADM.

Synthetic data set III

As is clear from Fig. 2, for some combination of parameter values, the ADM would be more accurate than the proposed method. Here we present such a case. Table 6 lists the results and shows the better accuracy of the approximate delta method. However, the modified delta method still has acceptable errors. Using the extreme value method of Wang et al. (2003), Eqs. (13) and (14), with the exact $k_a$ value of 0.4 d$^{-1}$, we obtain $R = 1.93$ mg/L/d and $P_{av} = 3.54$ mg/L/d, which have errors of the order of 80%.
Table 6. Results for the data set Synthetic-III

<table>
<thead>
<tr>
<th>Method</th>
<th>$k_a$ $(d^{-1})$</th>
<th>$P_{av}$ (mg/L/d)</th>
<th>$R$ (mg/L/d)</th>
<th>Percent Error in $k_a$</th>
<th>Percent Error in $P_{av}$</th>
<th>Percent Error in $R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta ADM (Eqs. 8, 10, &amp; 11)</td>
<td>0.41</td>
<td>20.19</td>
<td>20.19</td>
<td>3.58</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>Proposed (Eqs. 18, 20, &amp; 11)</td>
<td>0.38</td>
<td>19.66</td>
<td>19.66</td>
<td>5.19</td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>MDM (Eqs. 18, 22, &amp; 11)</td>
<td>0.38</td>
<td>19.18</td>
<td>19.18</td>
<td>5.19</td>
<td>4.08</td>
<td>4.08</td>
</tr>
</tbody>
</table>

Summary and Conclusions

New approximations have been proposed for estimation of parameters using the delta method. Although of a little more complicated form than the previously proposed approximate delta method, these expressions lead to a significantly improved accuracy in the estimated value of the parameters. A modified delta method has been proposed for cases where the combination of parameter values would result in a negative DO from the analytical solution. For these cases, instead of using the diurnal range of DO variation, it is proposed that the deviation of the maximum DO from the mean be used in the estimation of production rate. Various data sets, some synthetic and some from the field observations, have been used to show the improvement in accuracy of parameter estimation.

References


