Temporal-moment matching for truncated breakthrough curves for step or step-pulse injection

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Abstract

The method of temporal moments is an efficient approach for analyzing breakthrough curves (BTCs). By matching the moments of the BTCs computed through parametric transfer-function models or one-dimensional transport models to those of the data, one can estimate the parameters characterizing the transfer function or apparent transport parameters. The classical method of moments presumes infinite duration. However, the measurement of BTCs is usually terminated prematurely, before the concentration has reached zero. Unless this truncation of the BTCs has been taken into account, the estimates of the parameters may be in error. Truncated measured BTCs are sometimes extrapolated assuming exponential decay. In this study, we use the concept of moments of the truncated impulse–response function [Jawitz JW. Moments of truncated continuous univariate distributions. Adv Water Res 2004;27:269–81] in the analysis of truncated BTCs corresponding to the commonly encountered step and step-pulse injection modes. The method is straightforward, based on the relation, which we derive, between truncated moments of the impulse–response function and the measured BTC. It is practical to apply and does not require the extrapolation of the measured BTC. The method is also accurate. In a numerical study we discuss how short a step-pulse injection may be so that we can approximate it as instantaneous. Finally, we apply the method to the analysis of a field-scale tracer test.

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1. Introduction

The method of temporal moments is an efficient way for analyzing breakthrough curves (BTCs) in order to evaluate transport and mixing mechanisms in groundwater. By matching the moments of the data to those of transport models, such as the advective–dispersive equation (ADE) with constant parameters, one computes apparent transport parameters. This technique is useful in quantifying key features of transport between the injection and observation points and is a computationally efficient, and sometime more stable alternative to least-squares fitting of all measurements.

inputs in a two-layer aquifer by integrating complementary concentrations over time. Yu et al. [17] presented a method to calculate temporal moments for step inputs. For reactive transport, Das and Kluitenberg [2] considered first-order degradation in the mobile aqueous phase for Dirac and step-pulse inputs. The latter expressions were used to analyze experimental data by Pang et al. [9]. A variety of researchers have used temporal moments for parameter inference in heterogeneous media (e.g., [1,10,12]).

The classical methods for estimation of parameters from temporal moments, however, require complete time series of data. For a pulse injection, this implies that the concentrations must be measured until the initial value of zero has been reached again. In practice, unfortunately, complete data sets are generally unavailable because measurements are terminated too early due to time constraints or because concentrations are below detection limits [16]. Data truncation is very common in column and field experiments, especially in systems characterized by strong dilution or kinetic mass transfer, resulting in BTCs with a long tail. Inferring transport mechanisms besides advection and dispersion [11]. The travel-time distributions, evaluated by taking derivatives of the BTCs of step inputs, typically, show much stronger fluctuations than the cumulative BTCs [15]. Additionally, for time-invariant linear transport systems [14], the time for BTCs of Dirac inputs to reach zero is equivalent to the time for BTCs of unit step inputs to reach the input concentration. Thus, for long-tail BTCs, using step inputs may not improve the estimation of moment-derived parameters significantly.

The accurate way of estimating moment-derived parameters is to match the truncated moments (i.e., temporal moments of truncated BTC data) instead of using expressions related to complete moments. Jawitz [4] derived truncated moment expressions for several continuous univariate distributions, and suggested to evaluate complete moments of truncated BTCs for solute transport by completing the BTCs following an exponential distribution. His approach used several points at late time to estimate the missing data, thus required accurate measurements of late-time BTCs. In addition, the approach considered only the BTCs of Dirac inputs.

In the present study, we first show how the truncated moments for step and step-pulse inputs, the most commonly used injection modes, are related to those of the transfer function. The transfer function, also known as the impulse–response function, is the BTC corresponding to Dirac delta inputs. The transfer function fully describes a time-invariant linear system. Then, for the identification of the transfer function and transport parameters, we present a procedure that is advantageous compared to both the method of deconvolution and methods of moments that assume complete data series. This procedure utilizes the moments of the truncated data and also the analytical relations between truncated moments of the transfer function and parameters that were developed by Jawitz [4].

2. Temporal moments

The complete $k$th temporal moment $m_k$ of a BTC obtained at location $x$ is defined as

$$m_k = \int_0^\infty t^k c(x,t) \, dt$$

in which $t$ is time and $c$ is the concentration of the BTC. The normalized $k$th moment is

$$\mu_k = \frac{m_k}{m_0} = \frac{\int_0^\infty t^k c(x,t) \, dt}{\int_0^\infty c(x,t) \, dt}$$

and the second-central moments are defined by

$$m_{2c} = \int_0^\infty (t - \mu_1)^2 c(x,t) \, dt = m_2 - \frac{m_1^2}{m_0}$$

$$\mu_{2c} = \frac{m_{2c}}{m_0} = \mu_2 - \mu_1^2$$

$\mu_1$ and $\mu_{2c}$ are the mean and variance of travel times at the location of measurements.

Consider a BTC subject to upper truncation at time $T$ (i.e., data are available in the interval $0 \leq t \leq T$). The $k$th truncated temporal moment, $\tilde{m}_k$ and $\tilde{\mu}_k$ are defined by

$$\tilde{m}_k(T) = \int_0^T t^k c(x,t) \, dt$$

$$\tilde{\mu}_k(T) = \frac{\tilde{m}_k(T)}{\tilde{m}_0(T)} = \frac{\int_0^T t^k c(x,t) \, dt}{\int_0^T c(x,t) \, dt}$$

The second-central moments are

$$\tilde{m}_{2c}(T) = \int_0^T (t - \tilde{\mu}_1)^2 c(x,t) \, dt = \tilde{m}_2 - \left(\frac{\tilde{m}_1}{\tilde{m}_0}\right)^2$$

$$\tilde{\mu}_{2c}(T) = \frac{\tilde{m}_{2c}}{\tilde{m}_0} = \tilde{\mu}_2 - (\tilde{\mu}_1)^2$$
3. Mathematical derivation

3.1. Complete moments

For a time-invariant linear system, the response of the system can be computed by convolution:

\[ c_{\text{out}}(t) = \int_0^t c_{\text{in}}(t - \tau) h(\tau) \, d\tau \tag{6} \]

where \( c_{\text{in}} \) and \( c_{\text{out}} \) represent the input and response function, respectively, and \( h \) is the transfer function (i.e., the response function corresponding to an instantaneous unit pulse, or Dirac delta function, introduced at time zero). The following well-known moment relationship can be derived for complete BTCs (e.g., [13]):

\[ m^c_k = \sum_{j=0}^k \binom{k}{j} m^c_j m^c_{k-j} \tag{7} \]

where the superscript indicates the function to be evaluated. Thus, if the moments of the input and transfer functions are known, we can compute the moments of the output BTC. Inversely, the moments of the transfer function \( h \) can be derived from the moments of the input and output functions, \( c_{\text{in}} \) and \( c_{\text{out}} \). For certain parametric distributions and transport models, the relationship between moments of the transfer function and the parameters are known (e.g., [5]). Thus, we can infer the coefficients of the parametric transfer functions and transport parameters from experiments with arbitrary input function via computing the moments of the transfer function.

For unit step inputs, i.e., \( c_{\text{in}} = 1 \) starting at time 0, Eq. (6) can be simplified to

\[ c_{\text{out}}(t) = \int_0^t h(\tau) \, d\tau \tag{8} \]

Differentiation with respect to time yields [17]

\[ h(t) = \frac{d c_{\text{out}}}{d t} \tag{9} \]

Thus, the relationship of the complete temporal moments between \( h \) and \( c_{\text{out}} \) is [18]

\[ m^h_k = t^k - km^c_{k-1} \tag{10} \]

3.2. Truncated moments

For truncated BTCs, Eq. (7) does not hold. In fact, theoretically, provided that the input and response concentrations to a truncation time are known, the truncated transfer function can be evaluated by deconvolution. However, deconvolution is challenging in practice because of noisy data. It requires regularization or smoothing, and the non-negativity of the transfer function is not guaranteed without enforcing constraints. In the following, we consider the most commonly used input modes: step inputs and step-pulse inputs, and show how one can evaluate the truncated moments of the transfer function directly from the measured BTCs, thus avoiding deconvolution.

3.2.1. Step input

The step input function is defined by

\[ c_{\text{in}}(t) = \begin{cases} 1 & 0 \leq t \leq t_0 \\ 0 & \text{otherwise} \end{cases} \tag{11} \]

where all concentrations are normalized by dividing the constant input concentration. Thus, convolution becomes a simple integration (see Eq. (8)), and differentiation with respect to time yields Eq. (9).

The zeroth truncated moment is given by

\[ \hat{m}^c_0(T) = \int_0^T \frac{d c_{\text{out}}}{d t} \, d t = c_{\text{out}}(T) - c_{\text{out}}(0) \tag{12} \]

Generally, \( c_{\text{out}}(0) \) is assumed to be zero. Then,

\[ \hat{m}^c_0(T) = c_{\text{out}}(T) \tag{13} \]

For \( k \geq 1 \), the truncated moments are given by

\[ \hat{m}^c_k(T) = \int_0^T t^k h(t) \, d t = \int_0^T t \frac{d c_{\text{out}}}{d t} \, d t 
\]

\[ = [t^k c_{\text{out}}]_0^T - k \int_0^T t^{k-1} c_{\text{out}} \, d t \]

\[ = T^k c_{\text{out}}(T) - k \hat{m}^c_{k-1}(T) \tag{14} \]

Eq. (14) states that the \( k \)th truncated moment of the transfer function depends on the \((k - 1)\)th truncated moment of the BTC, the final concentration and the truncation time. Eq. (14) enables determining the truncated moments of the transfer function from truncated BTCs resulting from step inputs. Explicitly, the first and second-central moments are

\[ \hat{m}^h_1(T) = T c_{\text{out}}(T) - \hat{m}^c_0(T) \tag{15} \]

\[ \hat{m}^h_2(T) = T^2 c_{\text{out}}(T) - 2 \hat{m}^c_1(T) - [\hat{m}^c_0(T)]^2 \tag{16} \]

Assume \( T_0 \) is the time at which \( c_{\text{out}} \) stabilizes at its final value. If the truncation time \( T \) is larger than \( T_0 \), the observed breakthrough is complete and no truncation error occurs. Otherwise, we must account for the effect of truncation.

3.2.2. Step-pulse input

For step-pulse inputs, after normalization, the input function is defined by

\[ c_{\text{in}}(t) = \begin{cases} 1 & 0 \leq t \leq t_0 \\ 0 & \text{otherwise} \end{cases} \tag{17} \]

The superposition principle yields

\[ c_{\text{out}}(t) = \begin{cases} \int_0^t h(\tau) \, d \tau & 0 \leq t \leq t_0 \\ \int_0^t h(\tau) \, d \tau - \int_0^{t-t_0} h(\tau) \, d \tau & t \geq t_0 \end{cases} \tag{18} \]
and differentiation gives
\[
\frac{d c_{\text{out}}}{d t} = \begin{cases} h(t) & 0 \leq t \leq t_0 \\ h(t) - h(t - t_0) & t > t_0 \end{cases}
\]  
(19)

If the truncation time \( T \) is smaller than the duration \( t_0 \) of the pulse, the truncated BTC does not differ from the case of a step input. In the case that the truncation time \( T \) is larger than the duration \( t_0 \) of the pulse, \( h(t) \) is the sum of the time derivative \( \frac{d c_{\text{out}}}{d t} \) and \( h(t - t_0) \). This leads to the following expression for the transfer function:

\[
h(t) = \frac{d c_{\text{out}}(t)}{d t} + h(t - t_0)
\]
\[
= \frac{d c_{\text{out}}(t)}{d t} + \frac{d c_{\text{out}}(t - t_0)}{d t} + h(t - 2t_0) = \cdots
\]
\[
= \sum_{i=0}^{n} \frac{d c_{\text{out}}(t - it_0)}{d t}, \quad \text{where } n = \text{int}(t/t_0)
\]  
(20)
in which \( n \) is the largest integer value smaller than or equal to \( t/t_0 \). Eq. (20) demonstrates that, in theory, we can derive the truncated transfer function using the truncated BTC. This procedure is not recommended, however, because it relies on the evaluation of derivatives, which is prone to errors for noisy data.

If we are just interested in the truncated moments of the transfer function, we do not have to evaluate derivatives:

\[
\hat{m}_k^t(T) = \int_0^T t^k h(t) dt = \sum_{i=0}^{n} \int_{it_0}^{(i+1)t_0} t^k \frac{d c_{\text{out}}(t - it_0)}{d t} dt
\]
\[
= \sum_{i=0}^{n} \left( [t^k c_{\text{out}}(t - it_0)]_{t_0}^{(i+1)t_0} - k \int_{it_0}^{(i+1)t_0} (t + it_0)^{k-1} c_{\text{out}}(t) dt \right)
\]
\[
= T^k \sum_{i=0}^{n} c_{\text{out}}(T - it_0) - k \sum_{i=0}^{n} \left( (T + it_0)^{k-1} c_{\text{out}}(t) dt \right)
\]
\[
= T^k \sum_{i=0}^{n} c_{\text{out}}(T - it_0)
\]
\[
- k \sum_{i=0}^{n} \sum_{j=0}^{k-1} \left( \binom{k-1}{j} (it_0)^{k-j-1} \hat{m}_{k-j}^{out}(T - it_0) \right)
\]  
(21)

Explicitly, the zeroth to second truncated moments of the transfer function are

\[
\hat{m}_0^t(T) = \sum_{i=0}^{n} c_{\text{out}}(T - it_0)
\]  
(22)
\[
\hat{m}_1^t(T) = T \hat{m}_0^t(T) - \sum_{i=0}^{n} \hat{m}_{\text{out}}^t(T - it_0)
\]  
(23)
\[
\hat{m}_2^t(T) = T^2 \hat{m}_0^t(T) - 2 \sum_{i=0}^{n} (\hat{m}_1^t)^{\text{out}}(T - it_0)
\]
\[
+ it_0 \hat{m}_{\text{out}}^t(T - it_0)
\]  
(24)
Thus, the truncated moments of the transfer function can be computed using the BTC of step-pulse inputs. Eq. (14) can be derived by assuming \( T = t_0 \) in Eq. (21). Thus, the solution to the case of step inputs is included in Eq. (21).

3.3. Parameter estimation

Next, we fit a parametric distribution to the transfer function by matching the truncated temporal moments. As an example we consider a log-normal distribution, which is often used to parameterize the distribution of travel time \( \tau \) in advective-dispersive transport. In this case, the truncated temporal moments are given by (e.g., [4]):

\[
\begin{align*}
\hat{m}_0^l(T) &= \frac{1}{2} \left[ \text{erf} \left( \frac{\ln T - \mu_{\ln \tau}}{\frac{\sigma_{\ln \tau}}{\sqrt{2}}} \right) + 1 \right] \\
\hat{m}_1^l(T) &= \frac{1}{2} \text{exp} \left( \mu_{\ln \tau} + \frac{\sigma_{\ln \tau}^2}{2} \right) \\
&\times \left[ \text{erf} \left( \frac{\ln T - \mu_{\ln \tau}}{\frac{\sigma_{\ln \tau}}{\sqrt{2}}} - \frac{\sigma_{\ln \tau}}{\sqrt{2}} \right) + 1 \right] \\
\hat{m}_2^l(T) &= \frac{1}{2} \text{exp}(2\mu_{\ln \tau} + 2\sigma_{\ln \tau}^2) \\
&\times \left[ \text{erf} \left( \frac{\ln T - \mu_{\ln \tau}}{\frac{\sigma_{\ln \tau}}{\sqrt{2}}} - \frac{2\sigma_{\ln \tau}}{\sqrt{2}} \right) + 1 \right]
\end{align*}
\]  
(25–27)
in which \( \mu_{\ln \tau} \) and \( \sigma_{\ln \tau} \) are the mean and standard deviation of the complete log travel-time distribution. From these values, we can compute the mean \( \mu_\tau \) and variance \( \sigma_\tau^2 \) of the non-logarithmic travel time \( \tau \):

\[
\mu_\tau = \text{exp} \left( \mu_{\ln \tau} + \frac{1}{2} \sigma_{\ln \tau}^2 \right)
\]  
(28)
\[
\sigma_\tau^2 = \text{exp}(2\mu_{\ln \tau} + 2\sigma_{\ln \tau}^2) - \exp(2\mu_{\ln \tau} + \sigma_{\ln \tau}^2)
\]  
(29)
Thus, we have identified the transfer function, parameterized as a lognormal distribution.

Sometimes, however, one is interested in identifying a few effective transport parameters. One practical approach is to utilize the moments found from the fitted transfer function and the relation of these moments to the velocity \( v \) and dispersion coefficient \( D \) in a one-dimensional ADE with constant coefficients (e.g., [5]):

\[
v = \frac{x}{\mu_\tau}
\]  
(30)
\[
D = \frac{\sigma_\tau^2 v^3}{2x}
\]  
(31)
where \( x \) is the distance from the point of injection, and the moments are related to flux concentrations [5].

The estimation of transport parameters thus consists of the following steps: (1) Evaluating the truncated moments of the BTC by numerical integration, e.g., the trapezoidal rule; (2) Computing the corresponding truncated moments of the transfer function, considering the type of injection; (3) Fitting a parametric distribution by matching the truncated moments to the expressions developed in [4]; and, if needed, (4) Interpreting the parameters of the fitted distribution in a physical way.
For the conceptual model of advective–dispersive transport with uniform coefficients, a two-parameter model of travel-time distribution is appropriate. Including kinetic mass transfer between the mobile and an immobile phase, or other processes, requires a model with more parameters. Typically, the physical parameters, such as the velocity and the dispersion coefficients, are apparent quantities. They interpret the moments of the BTC in the context of a certain macroscopic model with uniform coefficients.

4. Applications

4.1. Numerical case

We illustrate the approach with a simulated semi-infinite column study in which transport can be described by the one-dimensional advection–dispersion equation (ADE) with constant parameters:

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \quad (32)$$

in which $x$ is distance, $t$ is time, $v$ is the seepage velocity, and $D$ is the dispersion coefficient. Assume $v = 1$ m/day and $D = 0.05$ m$^2$/day. The length from the injection boundary to the observation point is 0.2 m. In the initial state, the concentration is zero throughout the domain:

$$c(x, 0) = 0 \quad (33)$$

We consider three injection modes: Dirac inputs, step inputs, and step-pulse inputs with an injection duration $t_0$ of 6 h. The concentration is injected into and measured in the flux [5].

Fig. 1 shows the analytical solutions of the flux concentrations at the observation point corresponding to the different input modes [8]. It takes about 24 h (5 pore volumes) to complete the BTCs.

Fig. 2 compares the first three truncated temporal moments of the transfer function as a function of the truncation time using the trapezoidal rule of integration. The solid lines are the analytical results directly integrated from the BTC of Dirac inputs in Fig. 1, the circles are calculated using Eqs. (13) and (14) and the BTC corresponding to step input, and the crosses are calculated using Eqs. (22)–(24) and the BTC of step-pulse inputs. The analytical results for step and step-pulse inputs, derived in this paper, match perfectly with the results of direct integration of the BTC of Dirac inputs.

Fig. 3 compares the derived mean velocity and dispersion coefficient for step-pulse inputs either using the method of truncated moments or assuming that the BTC is complete at the truncation time, respectively. The truncation time is normalized by the injection duration, $t_0$. The results show that assuming a complete BTC at the truncation time may result in significant errors. Actually, in this case, if $T/t_0$ is less than 1.3, the estimated dispersion coefficient is negative. This is so because the mean travel time is under-estimated and the velocity is over-estimated, resulting in a negative variance evaluated by Eq. (3). When $T/t_0$ is larger than 4, i.e., 5 pore volumes, the BTC is essentially complete. The two methods give similar results.

In practice, experimentalists use short-duration step-pulse inputs to approximate Dirac inputs. Here, we use the numerical case to address the issue of how short the input duration must be to estimate accurately the tem-
poral moments and moment-derived transport parameters. The input duration, \( t_0 \), is assumed variable, and for each input duration, the BTC is completely computed. Fig. 4 shows that the accuracy of estimated moment-derived parameters decreases with the increase of input duration, indicating a shorter input duration approximates a Dirac input better. In addition, the estimation of \( v \) is less sensitive to the input duration than \( D \) because only the first order moment is required for \( v \), whereas \( D \) also requires the second moment. For the example considered here, in order to accomplish an accuracy of 5% in the estimation of \( v \) and \( D \), the input

Fig. 2. Comparison of truncated temporal moments. The curves of Dirac inputs are evaluated by integrating the BTC of Dirac inputs. The moments for step inputs are calculated from the BTC of step inputs using Eqs. (13) and (14). The moments for step-pulse inputs are calculated from the BTC of step-pulse inputs using Eqs. (22)–(24).

Fig. 3. Moment-derived parameters as a function of truncation time for step-pulse inputs. The solid lines are evaluated by matching truncated moments, and the dashed lines assume truncated moments as complete moments. The truncation time is normalized by the injection duration.
duration must be shorter than 0.11 and 0.02 pore volumes (about half an hour and 6 min), respectively.

4.2. Field case

We applied the method of truncated moments to analyze a field-scale nitrate elution experiment implemented by a multiple-well system at Oak Ridge, TN [7]. Fig. 5 shows the measurements at a monitoring well about 1m away from the injection point. The elution experiment is the reverse process of an injection experiment with step inputs and zero initial condition. By plotting $1 - c/c_0$ versus time, one can obtain the BTC corresponding to step inputs. Assume the transport from the injection point to the monitoring point can be described by a one-dimensional ADE, i.e., Eq. (32). The BTC shows that the experimental period, 6 days, is not sufficiently long to complete the elution BTC although the dimensionless concentration has dropped to only 0.03, which indicates that the BTC of step inputs can only reach 0.97 at the end. Three approaches are employed to estimate the effective transport parameters $v$ (seepage velocity) and $D$ (dispersion coefficient). The first approach is to fit the BTC of step inputs using Eq. (32), the second assumes the BTC is complete and uses the approach presented by Yu et al. [17] to estimate the moment-derived parameters, and finally we apply the method of truncated moments proposed above to estimate the moment-derived parameters.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Fitting ADE</th>
<th>Complete moments</th>
<th>Truncated moments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ (m/day)</td>
<td>0.64</td>
<td>0.77</td>
<td>0.63</td>
</tr>
<tr>
<td>$D$ (m²/day)</td>
<td>0.41</td>
<td>0.33</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Table 1 lists the fitted parameters. The approaches of fitting the ADE and using truncated moments give similar results, which reproduce the BTC well (Fig. 5). By contrast, the approach relying on complete moments over-estimates the seepage velocity and under-estimates the dispersion coefficient, similarly to the numerical case discussed above, because it under-estimates the mean and variance of travel times due to truncation of the BTC.

5. Summary

Truncation of BTCs is very common in column studies and field tests. When transport parameters are estimated by matching of moments, neglecting the effects of truncation may result in significant errors. Estimating transport parameters by fitting the truncated temporal moments of BTCs instead of using the complete-moment solutions leads to more accurate estimates. In this study, analytical relations of truncated moments between step, step-pulse inputs and Dirac inputs are derived so that the truncated moments of the transfer function can be calculated directly from the measured BTCs, thereby avoiding deconvolution. By matching the truncated moments to the moment expressions of truncated parametric distributions, one can evaluate the transfer function and transport parameters. This method minimizes the error introduced by truncation, and improves the estimation of moment-derived transport parameters, compared to the method using analytical solutions for complete moments.

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