Column experimental design requirements for estimating model parameters from temporal moments under nonequilibrium conditions

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Received 7 June 1999; accepted 6 November 1999

Abstract

Data truncation is a practical necessity of laboratory column experiments because of both time and detection-limit constraints. In this paper, we study the extent to which data truncation can affect estimates of transport modeling parameters, as derived from temporal moment calculations and in the context of solute transport experiments that are influenced by sorption and nonequilibrium partitioning among mobile and immobile phases. Our results show that, for a given amount of solute used, step changes in input conditions can give more accurate moment-derived parameters than Dirac or square-wave pulses, whereas Dirac and square-wave pulses are essentially identical in terms of accuracy of parameter estimates. By simulating data truncation for a wide range of column input and transport conditions, we provide guidance toward the experimental designs that are needed to keep parameter estimation error within specified bounds, assuming nonequilibrium conditions of transport that result from either first-order or diffusion-based rate processes. More specifically, we investigate the relationships between mass of solute added to the system, minimum solute quantification limits, experiment duration times, and accuracy of parameter estimation, all as a function of experimental conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Moments; Nonequilibrium; Column experiments; Modeling; Retardation factor; Mass transfer rate; Partitioning tracer

Nomenclature

- \( a \) spherical particle radius (length)
- \( c \) flux-averaged effluent concentration (mass/volume)
- \( c_{\text{im}} \) average immobile zone concentration (mass/volume)
- \( c_{\text{in}} \) local immobile zone concentration (mass/volume)
- \( c_{\text{in}} \) solute concentration of column input (mass/volume)
- \( c_{\text{initial}} \) initial column concentration (mass/volume)
- \( c_{m} \) volume-averaged mobile region concentration (mass/volume)
- \( D_{m} \) mobile region dispersion coefficient (length\(^2\)/time)
- \( D_{p} \) pore diffusion coefficient (length\(^2\)/time)
- \( f \) fraction of instantaneous sorption (–)
- \( g(T) \) residence time distribution function
- \( K_{d} \) linear partitioning coefficient (volume/mass)
- \( L \) length of column (length)
- \( M \) mass of solute used (mass)
- \( M_{c} \) calculated solute mass from truncated data (mass)
- \( P_{e} \) Peclet number, see Eq. (5) (–)
- \( r \) radial coordinate (length)
- \( R \) retardation factor, see Eq. (4) (–)
- \( R_{c} \) calculated retardation factor from truncated data (–)
- \( T \) pore volumes, see Eq. (2) (–)
- \( T_{p} \) duration of pulse in pore volumes
- \( T_{F} \) final point of data collection in pore volumes
- \( v_{m} \) mobile velocity (length/time)
- \( V \) total column volume (volume)
- \( x \) axial coordinate (length)
- \( Z \) dimensionless length, see Eq. (3) (–)
- \( \alpha \) first-order mass transfer coefficient (time\(^{-1}\))
- \( \beta \) see Eq. (6) (–)
- \( \gamma \) dimensionless diffusion parameter, see Eq. (9) (–)

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\( \delta \) Dirac delta function  
\( \mu'_n \) \( n \)th moment of residence time distribution  
\( \mu_n \) \( n \)th central moment of residence time distribution  
\( \theta_{im} \) immobile porosity (–)  
\( \theta_m \) mobile porosity (–)  
\( \theta \) total porosity (–)  
\( \rho_b \) bulk density (mass/volume)  
\( \omega \) dimensionless first-order parameter, see Eq. (12) (–)

1. Introduction

Temporal moments analysis is one means of estimating parameters from solute transport experiments, and the theoretical aspects behind its use have been previously discussed in the hydrogeologic literature \([2,35,36]\). Temporal moments have been used to estimate mean residence times and dispersion coefficients in the analysis of fixed-bed reactors \([7,9,18,20]\), to estimate sorption and related mass-transfer parameters from laboratory-scale \([4,12–14,19,22]\) and field-scale \([3,8,11,15,24,29]\) solute transport studies, and to compare retardation among non-partitioning and partitioning tracers \([10,16,17,40]\). Moment-derived parameters, however, do not always agree with parameters determined by other common parameter estimation methods, such as by least-squares fitting of column transport data or by independent batch sorption studies. Although the potential causes of such disagreement are numerous, one major potential source of error for the column-based estimates is data truncation – that is, exclusion of data from the longer-term, low-concentration portion of column effluent histories, owing to “premature” termination of the experiment. Such data-truncation effects are especially significant under nonequilibrium transport conditions in which breakthrough curves exhibit extended tailing.

Evidence suggesting that data truncation may significantly influence parameter estimates includes frequent reports that estimates of sorption distribution coefficients (i.e., retardation factors) determined from column experiments by the method of moments are less than the parameter values determined by batch experiments \([5,6,12,26,28]\). In this context, Heyse et al. \([12]\) proposed that solute-detection limitations necessitated data truncation which caused their moment-derived retardation factors to be less than their batch-derived retardation factors. Other evidence of truncation effects includes reports that moment-derived parameters often do not agree with parameters determined by least-squares fitting of models \([3,7,25]\). For example, Bianchi-Mosquera and Mackay \([3]\), in their analysis of a field study, postulated that data truncation could have caused retardation factors calculated by the method of moments to be lower than those determined by fitting routines. In other cases, lack of correspondence among parameters derived by different means may simply be indicative of fundamental inadequacies of simulation models to capture the physical or chemical properties of the system \([25]\).

Breakthrough data collection is usually terminated when responses are no longer quantifiable, or in some cases, at shorter times when a “sufficient” quantity of data is deemed to have been collected; however, precise mechanistic interpretation of the transport results requires a complete recovery of injected solute. Because parameter estimates can be quite sensitive to such data truncation, it is important to carefully evaluate the definition of “sufficient” in this context. In the present work, we quantify the effects that temporal data truncation has on moment-derived parameter estimates from column experiments run under nonequilibrium conditions. In an attempt to cover a broad range of potential nonequilibrium mechanisms, we use two common nonequilibrium models – one that characterizes mobile-immobile region transport by Fickian diffusion and one that characterizes such transport by a first-order process. Even though these specific model formulations may not always be directly applicable to any given experimental system, the analysis that follows provides a generally useful means of qualitatively considering the effect of rate-based limitations on moment results. Moreover, researchers who interpret their results in terms of the two specific models studied can quantitatively apply the results.

The parameters of interest in this paper are the retardation factor and the rate parameter that governs solute transport into and out of immobile regions. Perhaps most commonly, moment analysis is used to estimate the retardation factor, and the rate parameter is subsequently determined by a least-squares fit; however, moment analysis has also been used to determine rate parameters in some cases. In this work, we provide analyses of the degree to which rate limitations and data truncation will affect both the moment-derived retardation factor and the moment-derived rate parameter. This latter information also provides at least qualitative insight into the potential inaccuracies for exercises that involve direct “fitting” or calibration of mechanistically based models, where these are applied. In this regard, the situations that we find to give highly inaccurate estimates of rate coefficients by the method of moments are also likely to de-emphasize the importance of long-term “tailing” effects when data-fitting algorithms are used to calibrate models. Of course, our results have more direct applicability toward the estimation of retardation in solute transport studies that involve partitioning and/or adsorbing solutes.
The goal of this work is to provide a framework upon which column experiments can be designed. Skopp [32] performed related work, but considered only equilibrium conditions. However, when transfer to immobile zones is rate-limited, the asymmetric tailing of solute breakthrough or elution curves can lead to low concentrations over extended periods of time that can be difficult to detect and can deleteriously impact the accuracy of the moment calculation. Therefore, the need for low detection limits and extended experimental run times is increased for increasing extents of nonequilibrium and/or asymmetry. In this paper, we systematically explore this issue.

2. Transport models

In this work, commonly applied two-region (mobile-immobile) transport models will be considered, with mass transfer to and from the immobile region modeled both as a first-order mass transfer process and as Fickian diffusion in spheres. These two conceptualizations represent the two most common approaches for simulating nonequilibrium sorption processes at the laboratory-column scale. The following equation [38] describes one-dimensional solute transport for either of these conceptualizations in terms of some commonly used dimensionless parameters:

$$\beta R \frac{\partial c_m}{\partial T} + (1 - \beta)R \frac{\partial \sigma_m}{\partial T} = \frac{1}{Pe} \frac{\partial^2 c_m}{\partial Z^2} - \frac{\partial c_m}{\partial Z}.$$  
(1)

Note that we maintain dimensional units for concentration in order to facilitate subsequent discussion of injected solute mass (see Section 5.3). Terms are defined in the Nomenclature, and dimensionless parameters are defined as follows:

$$T = \frac{v_m \theta_m}{\theta^L},$$  
(2)

$$Z = \frac{x}{L},$$  
(3)

$$R = 1 + \frac{\rho K_d}{\theta},$$  
(4)

$$Pe = \frac{v_m L}{D_m},$$  
(5)

$$\beta = \frac{\theta_m + f \rho_s K_d}{\theta + \rho_s K_d}.$$  
(6)

For the spherical retarded-diffusion model, the average immobile concentration is

$$\tau_m = 3 \int_0^1 c_m \eta^2 d\eta,$$  
(7)

where the local aqueous concentration ($c_m$) is governed by Fickian diffusion

$$\frac{\partial c_m}{\partial T} = \frac{\gamma}{(1 - \beta)R} \frac{\partial^2 c_m}{\partial \eta^2}.$$  
(8)

The dimensionless rate parameter is defined as

$$\gamma = \frac{D_p L \theta_m}{\eta^2 v_m \theta_m}$$  
(9)

and the dimensionless radial distance as

$$\eta = \frac{r}{a}.$$  
(10)

For the first-order model,

$$(1 - \beta)R \frac{\partial \sigma_m}{\partial T} = \omega (c_m - \bar{c}_m).$$  
(11)

where the dimensionless rate parameter is defined as

$$\omega = \frac{\gamma L}{v_m \theta_m}.$$  
(12)

The boundary conditions that are most appropriate for modeling laboratory column experiments and which were used in this work are those of solute flux injection and solute flux detection [18,39]. The lower boundary condition is

$$\frac{\partial c_m}{\partial Z} (\infty, T) = 0.$$  
(13)

The upper boundary condition for a step decrease input is

$$c_m(0, T) - \frac{1}{Pe} \frac{\partial c_m}{\partial Z} (0, T) = 0.$$  
(14)

For a square-wave input, the upper boundary condition is

$$c_m(0, T) - \frac{1}{Pe} \frac{\partial c_m}{\partial Z} (0, T) = c_m,$$  
(15)

where $c_m$ is the solute concentration of the input square wave for $0 > T < T_p$, and $c_m = 0$ at all other times. For a Dirac input, the upper boundary condition is

$$c_m(0, T) - \frac{1}{Pe} \frac{\partial c_m}{\partial Z} (0, T) = \delta(T) \frac{M}{V0}.$$  
(16)

where $\delta$ is the Dirac delta function. Flux-averaged effluent concentrations at the end of the column ($Z = 1$) are determined from

$$c(1, T) = c_m(1, T) - \frac{1}{Pe} \frac{\partial c_m}{\partial Z} (1, T).$$  
(17)

Initial conditions are

$$c_m(Z, 0) = c_{\text{initial}},$$  
(18)

where $c_{\text{initial}}$ is 0 for square-wave and Dirac pulse experiments and is the aqueous concentration of solute for the fully equilibrated column for step-decrease experiments.
3. Temporal moments

3.1. Moments of the residence time distribution

The temporal moments of interest for determination of model parameters are those of the residence time distribution (RTD) and are defined as [20]

\[ \mu'_n = \int_0^\infty g(T)T^n \, dT, \]

where \( \mu'_n \) is the \( n \)th moment and \( g(T) \) is the RTD as a function of pore volumes. Central moments \( (\mu_n) \) are defined as

\[ \mu_n = \int_0^\infty g(T)(T - \mu'_0)^n \, dT. \]

For the transport parameters of interest here, only the first moment and the second central moment of the RTD are required.

3.2. Moments of RTDS from breakthrough curves

Moments of the RTD can be determined from any of the previously discussed column inlet conditions, provided that a sufficient amount of breakthrough data is collected. In theory, data must be collected for an infinite time in order to obtain exact moments; however, data collection from real column experiments must cease at a finite time because of solute detection limitations and experimental time constraints. It is this concentration detection limit and the associated termination time (denoted below by \( T_F \)) that the present work concerns. The equations given below represent the means to calculate moments of RTDs from truncated breakthrough curves. As such, the upper limits on the integrals are denoted by \( T_F \) rather than by infinity.

For the Dirac input, the first moment of the RTD can be determined from [35]

\[ \mu'_1 = \frac{\int_0^{T_F} Tc \, dT}{\int_0^{T_F} c \, dT} \]  \hspace{1cm} (21)

and the second central moment of the RTD can be determined from [1]

\[ \mu_2 = \mu'_2 - (\mu'_1)^2 \]  \hspace{1cm} (22)

or

\[ \mu_2 = \frac{\int_0^{T_F} T^2 c \, dT}{\int_0^{T_F} c \, dT} - \left[ \frac{\int_0^{T_F} Tc \, dT}{\int_0^{T_F} c \, dT} \right]^2. \]  \hspace{1cm} (23)

For a square wave pulse, the first moment of the RTD can be determined from [35]

\[ \mu'_1 = \frac{\int_0^{T_F} Tc \, dT}{\int_0^{T_F} c \, dT} - \frac{T_F}{2}, \]  \hspace{1cm} (24)

where \( T_p \) is the duration of the input pulse in pore volumes, and the second central moment of the RTD can be calculated by

\[ \mu_2 = \frac{\int_0^{T_F} T^2 c \, dT}{\int_0^{T_F} c \, dT} - \left[ \frac{\int_0^{T_F} Tc \, dT}{\int_0^{T_F} c \, dT} \right]^2 - \frac{T_F^2}{12}. \]  \hspace{1cm} (25)

Note that in Eqs. (24) and (25), it is assumed that \( T_F \) can be accurately measured from influent conditions. This is the only parameter used to calculate the moments that is not determined from the breakthrough curve.

For step decreases, the moments of the RTD can be calculated from [7,21]

\[ \mu'_1 = \frac{n \int_0^{T_F} \left( \frac{c}{c_{\text{initial}}} \right) T^{n-1} \, dT}{c_{\text{initial}}} \]  \hspace{1cm} (26)

and thus the first moment of the RTD is

\[ \mu'_1 = \frac{\int_0^{T_F} Tc \, dT}{c_{\text{initial}}}, \]

and the second central moment of the RTD can be calculated from

\[ \mu_2 = \frac{2 \int_0^{T_F} T^2 c \, dT}{c_{\text{initial}}} - \left[ \frac{\int_0^{T_F} Tc \, dT}{c_{\text{initial}}} \right]^2. \]  \hspace{1cm} (28)

For the step decrease experiment, it is assumed that \( c_{\text{initial}} \) is known and that the column is initially at equilibrium.

An apparent advantage of using a step input over a Dirac input or a finite pulse is that the exponent on the time weighting of the concentrations is reduced by one with respect to Dirac or square-wave input methods (compare Eq. (26) with Eqs. (21)–(25)). With this reduction in weight, errors due to random fluctuations of concentration measurements as well as errors due to truncation of the tail should be reduced [7].

Moments may be determined for either a step increase or a step decrease. The situations are mathematically equivalent for perfectly precise and accurate data, in which case the “truncation” issue relates only to an absolute “detectable difference” at the time of truncation, defined either as an absolute concentration level above zero (step decrease) or as an absolute level below the asymptotic long-term concentration (step increase). However, additional practical problems associated with step increases arise from the difficulty in distinguishing small differences between the effluent concentration and the influent concentration at the later stages of breakthrough, owing both to difficulties of maintaining sufficiently precise influent concentrations and to issues of absolute accuracy in measuring high concentrations. For example, consider a scintillation counter that is set up to count until a set accuracy is achieved (say ±1%), and consider an influent concentration of 100,000 dpm/ml; then it would be difficult to distinguish an
effluent concentration of say 99,500 dpm/ml from the 100,000 dpm/ml influent. In contrast, for an equivalent step decrease experiment, the column would be initially saturated with 100,000 dpm/ml solute and eluted at time zero with a solute-free solution. In this case, it would be easy to distinguish 500 dpm/ml from background (as long as background noise is well below 500 dpm/ml). We consider only the step decrease in this work; however, with regard to the step increase situation, our estimates of minimum quantification limits should apply to determining both the necessary (absolute) “detectable difference” in concentrations and the precision needed for the constant influent concentration.

3.3. Relationship of moments of RTD to parameters

For both the first-order model and the spherical diffusion model, the first moment of the RTD equals the retardation factor [35], that is,

\[ \mu_1 = R. \] (29)

For the first-order model, the second central moment is [35]

\[ \mu_2 = \frac{2R^2}{Pe} + \frac{2(1 - \beta)^2 R^2}{\omega} \] (30)

and for the spherical diffusion model, the second central moment is [35]

\[ \mu_2 = \frac{2R^2}{Pe} + \frac{2 (1 - \beta)^2 R^2}{\gamma} \] (31)

4. Methods

Analytical solutions were used for simulations of each of the two models. The first-order model simulations were performed with CXTFIT [34]. For the spherical diffusion model, the analytical solution given by van Genuchten [37] was solved using the convergence-acceleration methodology described by Rasmuson and Neretnieks [30].

Breakthrough curves for the models were generated for Dirac, square-wave and step-decrease inputs. The breakthrough curves consisted of a specific number of concentration points per pore volume. The density of points per pore volume was selected to provide good continuous simulation (no observable discontinuities at scales presented in the results). The point density thus varied depending upon the model being simulated, the input type, and the degree of nonequilibrium of the simulation. In no case did the point density have an effect on the results, as verified by selected trials. Moments were determined as a function of data truncation \((T_f)\) by using the trapezoid rule to numerically integrate Eqs. (21)-(28). These moments represent moments that would result if an experiment were terminated at any finite time, assuming perfect precision of concentration and time measurements. Note that the zeroth moments used for purposes of normalizing moments were similarly based on truncated data (see Eqs. (21)-(25)). In preliminary work using numerous simulations, we confirmed that a zeroth moment determined from input mass should not be used for moment-based parameter estimates, as this will cause more error in moment-derived parameter estimates than for the case when the zeroth moment is determined from the truncated breakthrough curve data as we have done here. (As an aside, we note that this recommendation is in contrast to that for parameter estimates made on the basis of data-fitting methods, such as least-squares. In these approaches, the input of a “true” value for any parameter, including solute mass added, should only be expected to improve the accuracy of all other parameter estimates.)

5. Results and discussion

5.1. Degree of nonequilibrium

In this section, we describe the effects of data truncation under modeling scenarios that reflect different extents of deviation from the transport that would occur under conditions of “local equilibrium” between mobile and immobile phases [35], and we use the term “degree of nonequilibrium” as a succinct means of qualitatively expressing the extent of such deviations. In this context, a “high degree of nonequilibrium” will occur in systems for which transfer between the mobile and immobile regions is very slow relative to the rate of advective transport (i.e., in systems for which \(\gamma \) or \(\omega \) are comparatively low). Conversely, scenarios that are at very high values of \(\gamma \) or \(\omega \) represent transport under conditions for which modeling under a local equilibrium assumption would be quite reasonable.

Example simulations of the spherical diffusion model for two different nonequilibrium scenarios are shown in Fig. 1 for a relatively moderate degree of nonequilibrium \((\gamma = 0.1)\) and in Fig. 2 for a relatively high degree of nonequilibrium \((\gamma = 0.01)\). Both examples were generated with a one-throughput square-wave input – that is, the input pulse was terminated at a time corresponding to \(T_f/R = 1\). The graphs are presented in terms of throughputs so that they are generally applicable to all retardation factors. Also shown in the figures are the relative parameters of \(R_e/R\) (where \(R_e\) is the retardation factor calculated using truncated data, and \(R\) is the actual retardation factor) and \(\gamma_c/\gamma\) (where \(\gamma_c\) is the rate parameter calculated using truncated data, and \(\gamma\) is the actual rate parameter) that would be calculated if the experiments were terminated at a finite time (given in throughputs – i.e., \(T_f/R\)). A mass balance with respect
to the influent mass \((M_c/M)\) is also shown, where \(M_c\) is the mass calculated by integrating the breakthrough curve, and \(M\) is the influent mass applied. In both figures, the calculated parameters approach their true values as time (i.e., data collection) approaches infinity. At high degrees of nonequilibrium (Fig. 2), considerably more data are required to obtain equivalent accuracy in parameters. Severe error in parameter estimates may occur if the experiment must be terminated early, as may occur, for example, if the concentration of solute in the effluent drops below the solute-measuring device’s quantification limits. Thus, very low quantification limits and high mass recoveries are required at high degrees of nonequilibrium. For example, Fig. 1 illustrates that a solute quantification limit of 0.024 \(c/c_{in}\), 4.2 throughputs, and a mass recovery of 97% are required to estimate the retardation factor to 90% of its actual value. For the higher nonequilibrium conditions in Fig. 2, a solute quantification limit of \(6 \times 10^{-5} c/c_{in}\), 41 throughputs, and a mass recovery of more than 99.99% are required to estimate the \(\gamma\) value to within 10% of its true value. It is thus clearly a difficult endeavor to accurately calculate rate parameters from laboratory experiments by the method of moments.

Fig. 3 shows a step decrease simulation for the same set of system conditions as in Fig. 1. Note that the mass balance curve is coincident with the \(R_c/R\) curve for step decreases. In comparison to the 1-throughput square-wave input, truncation effects are much less severe for the step decrease. The step-decrease method of first-moment analysis is analogous to frontal analysis in which the area above the breakthrough curve following a step increase is integrated to determine the retardation factor (first moment of the RTD), as applied by column experimentalists to estimate sorption parameters in column experiments \([23,27,28,33]\). One important difference is that an experimentalist may be likely to truncate a greater proportion of the data (in comparison to step-decrease analysis) because of the previously noted difficulty in distinguishing high effluent concentrations from the influent concentration (see Section 3.2).
5.2. Effect of $Pe$ and $\beta$

As Peclet number decreases, the relative importance of hydrodynamic dispersion on transport increases; thus, with all other things being equal, one should expect that truncation effects will become more severe at low Peclet number. However, for experiments in which nonequilibrium effects are the dominant cause of breakthrough data spreading [31], the role of dispersion on truncation effects will be comparatively less. For the range of $\omega$ and $\gamma$ tested in this work, separate testing of Peclet numbers of 30 and 200 revealed little difference (much less than 0.1%) in the quantification limits required to achieve a given parameter accuracy (presented later). Because this range of Peclet numbers represents typical values for sand-sized material in laboratory columns, the results presented here should generally apply to most laboratory column designs. Actual values of moments were calculated from breakthrough curves with a Peclet number of 200.

The parameter, $\beta$, is an indicator of the relative amount of mobile region solute capacity with respect to total solute capacity. As $\beta$ increases, more solute is at equilibrium, and therefore nonequilibrium-induced truncation effects will be less severe. In column experiments, $\beta$ is not normally known a priori, so a full investigation of the effects of $\beta$ would be of limited use to a column experimentalist. Instead, we selected a $\beta$ value of 0.2 for this work, which represents a lower limit for $\beta$ from a review of column-based literature. Therefore this work represents a reasonably conservative approach toward estimating constraints on the design of transport experiments.

5.3. Solute quantification limits and input mode effects

In order to fairly compare the quantification limits for the various modes of solute injection it is necessary to normalize effluent concentrations of the three different types of column experiments (Dirac, square wave, step) by a common reference concentration. As an example of why this is necessary, consider two square-wave input pulses of the same concentration but with different durations. Clearly, effluent from the longer pulse experiment can be detected for a longer time; however, from the perspective of moment estimation, it is not apparent if it would be better to concentrate the solute into a smaller pulse of short duration or dilute it into a longer pulse. In this regard, and barring density effects or other repercussions of high concentration, either experiment would be “improved” (with regard to issues of detection limit and data truncation) by the use of higher influent concentrations. An additional constraint, especially relevant to radio-labeled tracers, is how much solute can be afforded to a given experiment. In this work, concentrations for all experiments are normalized on the basis of mass of solute added. As a result of this approach, the normalized graphical results (subsequently presented) provide both (1) a means of comparing the injection mode for a given mass of solute and (2) a means of comparing accuracy among experiments that apply different total masses of solute.

In order to properly incorporate added solute mass as a model parameter, solute quantification limits were normalized by a concentration that represents the mass of influent solute used divided by an “effective” column volume. The latter is defined in a manner that accounts for total column “capacity” – that is, in a manner that includes both sorbed- and aqueous-phase solute (pore volume times retardation factor). For a square wave pulse, the normalizing concentration is thus

$$M = \frac{V_0 T \rho c_{in}}{V_0 R} = \frac{T \rho c_{in}}{R},$$

where $M$ is the mass of solute required for the experiment. For the step decrease experiment, this same normalizing concentration is

$$M = \frac{V_0 R}{V_0 R} = c_{\text{initial}}$$

and for the Dirac input, the normalizing concentration is simply $M/(V_0 R)$. With this normalization, the quantification limits can be compared in terms of solute required for all three types of inlet conditions – Dirac, square wave, and step decreases – as well as for various retardation factors.

The point at which data collection from a column experiment is terminated will depend upon the quantification limit of the solute detection device. Figs. 4 and 5 show the normalized quantification limits required in order to obtain values for retardation factor (Eq. (29)) and $\gamma$ (Eq. (31)), respectively, that are accurate to within 20%, 10%, and 5% of the actual values for the spherical...
Fig. 5. Normalized quantification limits required for determination of $\gamma$ that is accurate to within 20%, 10%, and 5% of its actual value when a spherical diffusion model applies.

Fig. 7. Normalized quantification limits required for determination of $\omega$ that is accurate to within 20%, 10%, and 5% of its actual value when a first-order model applies.

5.4. Practical applications

Figs. 4–7 can be used to assist in the design of column experiments by providing a means of specifying the required quantification limit and thus the necessary influent solute mass. The procedure requires initial

Fig. 6. Normalized quantification limits required for determination of retardation factor that is accurate to within 20%, 10%, and 5% of its actual value when a first-order model applies.

Fig. 8. Experiment duration time (given in throughputs) that is required for the determination of a retardation factor that is accurate to within 20%, 10%, and 5% of its actual value when a spherical diffusion model applies and for the cases of (a) pulse inputs, and (b) step inputs.
assumptions for the minimum value of the mass transfer parameter (either \( D_p/\alpha^2 \) or \( \alpha \), see Eqs. (9) and (12)), a maximum value for the retardation factor, and the column flow rate. Then, the figures can be used to choose an influent solute mass to match the quantification limit of the solute measuring device. For example, if a first-order model is assumed to apply, and if preliminary expectations of \( \alpha \) and a selected column flow rate give an \( x \) value of 0.1, then Fig. 6 shows that the normalized quantification limit for the solute should be around 0.0003 in order to determine the retardation factor to within 90% of its true value, using a square-wave pulse experiment. Given the preliminary estimate for retardation factor, the solute detection device’s quantification limit (the term \( c \) on the y axis), and the pore volume of the column (\( V_d \)), the required solute mass (\( M \)) can then be determined. An appropriate pulse width can be then be chosen based on concentration issues (e.g., the avoidance of high concentrations that could lead to oversaturation of solute, changes in solution density, or deviations from the assumed sorption behavior). A similar process can be applied using Fig. 7 if the rate parameter is to be determined by moments. Likewise if a spherical diffusion model is assumed to apply, Figs. 4 and 5 can be used in a similar manner.

Figs. 4–7 show that the duration of the pulse makes little difference as long as the solute input mass is kept constant. Small pulses may be preferable for identifying whether or not the proper model formulation has been used, since signals from these inputs are more direct measurements of the RTD [41]. On the other hand, parameter estimation results from very small pulses may be more sensitive to experimental errors such as flow variations and solute input concentration variations [9]. Because “error-free” data were used in the present work, such phenomena are not represented here; however, they clearly need to be considered in an actual experimental design.

Figs. 4–7 also illustrate that at relatively lower degrees of nonequilibrium, even rather high quantification limits result in little error in the estimated parameters. Thus, retardation factor estimates can be improved by using conditions closer to equilibrium (i.e., slower column flow rates). However, for rate estimation, there is a limit on the effectiveness of lowering the extent of non-equilibrium (e.g., by reducing the flow rate). This is
because the nonequilibrium-induced solute spreading at low flow rate may no longer be sufficiently large as to have a sensitive effect on the second moment, relative to the effects of hydrodynamic dispersion. This is evident from Eqs. (30) and (31), which show that at lower velocities (higher $\omega$ or $\gamma$, but constant $Pe$ if $D_m$ is proportional to $v_m$), Peclet number has a more pronounced effect on the value of the second moment. For example, for the column conditions explored here ($Pe = 200$), with an $\omega$ value of 100 (considering the first-order model), 78% of the value of the second moment is contributed by the hydrodynamic dispersion term. Thus, estimates of the immobile region mass transfer rate parameter become less reliable at very low nonequilibrium conditions.

One other important aspect of column experiment design is the required time of the experiment. The required time can be estimated from Figs. 8 and 11. The $y$ axes of these graphs represent the number of throughputs required to estimate the retardation factor (Figs. 8 and 10, for the spherical diffusion and first-order models, respectively) and the rate parameters (Figs. 9 and 11) for a given degree of nonequilibrium ($\gamma$ or $\omega$). In the case of pulse inputs (Figs. 8–11), for purposes of presentation clarity, we show only the case for the 1-throughput input pulse. For pulses shorter than one throughput, the graphs will overestimate the required time by less than one throughput. For pulses greater than one throughput, the graphs will underestimate the required time by somewhat less than the actual pulse size used minus one throughput. In light of the proposed use of these graphs and the need to make initial estimations of the parameters to be measured (which makes the method inherently approximate), these graphs should be sufficient to provide a means of roughly estimating the minimum required duration times for column experiments.

To use Figs. 8–11, initial estimates of the retardation factor and the rate parameter are required. Estimations of required experimental duration time can then be made in a manner similar to the method discussed previously for input mass determination. For example, consider a case where a first-order model is assumed to apply and a pulse input is to be used in a column experiment. If preliminary estimates of the rate parameter ($\omega$) and a selected column flow rate give an $\omega$ value of 0.1, then Fig. 10(a) shows that approximately 30 throughputs are required in order to estimate the retardation factor to within 10% of its actual value. If a step decrease were used, then Fig. 10(b) shows that approximately 18 throughputs would be required to estimate the retardation factor to within 10% of its actual value.

It is interesting to note that at higher nonequilibrium conditions, there is little benefit in using higher flow rates to speed up an experiment; however, at lower nonequilibrium conditions, there is a slight benefit of using a higher flow rate to hasten an experiment. For example, the required time (in hours) to estimate retardation factor from a column experiment conducted at a flow rate such that $\omega$ is 0.3 is the nearly the same as that required for a column experiment conducted at a flow rate 10 times higher such that $\omega$ is 0.03. In this case, even though the flow rate is increased by a factor of 10, the required number of throughputs to be fed is also increased by nearly a factor of 10, as is apparent from Fig. 10(a). At conditions closer to equilibrium, an experiment’s duration time may be shortened by using higher flow rates, as is apparent from the flattening out of the plots in Figs. 8–11 as $\omega$ or $\gamma$ increases. Selection of the actual flow rates would, of course, have to be made in conjunction with considerations for detection limits as described previously.

6. Conclusion

Temporal moment calculations are a practical and commonly applied means of interpreting solute transport experiments in laboratory columns and field experiments. For example, estimates of mean residence
time are a primary means of making estimates of solute partitioning or sorption characteristics and, when data are well represented by transport models, second central moments can be applied to the estimation of rates of exchange between mobile and immobile domains. However, truncation effects of data may severely distort the parameter estimates, and severe errors can occur even when good mass recovery is demonstrated. Although errors are especially great for second moments (i.e., rate parameters), truncation effects on the first moment are also very important and may be one reason that column-determined retardation factors are frequently reported to be lower than batch-estimated values.

By simulating data truncation for a wide range of column input and transport conditions, we provide guidance toward the experimental designs that are needed to keep parameter estimation error within specified bounds, assuming nonequilibrium conditions of transport that result from either first-order or diffusion-based rate processes. Our results show that, for a given amount of solute used, moment-derived parameters from step-decrease inputs should exhibit less truncation effects than moment-derived parameters from square-wave and Dirac pulses. Dirac and square-wave input experiments exhibit nearly the same truncation effects on moment-derived parameters, although longer pulse experiments tend to exhibit more truncation effects as equilibrium conditions are approached.

Regardless of the input type, Figs. 4–11 provide a means of estimating the minimum solute quantification limits and experiment duration times that are required for achieving a given accuracy of parameter estimation, and for a wide range of experimental conditions. For a given quantification limit or experimental duration, these figures also provide a means of determining the necessary amount of solute to use in order to estimate parameters to within a given level of accuracy. Overall, we hope that these results will be useful for designing solute transport experiments that provide more accurate estimation of solute partitioning and transport parameters.

References


