On the Late-Time Behavior of Tracer Test

Breakthrough Curves

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Abstract

We investigated the late-time (asymptotic) behavior of tracer test breakthrough curves (BTCs) with rate-limited mass transfer (e.g., in dual or multi-porosity systems) and found that the late-time concentration, $c$, is given by the simple expression:

$$ c = t_{ad} \left( c_0 g - m_0 \frac{\partial g}{\partial t} \right), \quad \text{for } t \gg t_{ad} \text{ and } t_a \gg t_{ad} $$

where $t_{ad}$ is the advection time, $c_0$ is the initial concentration in the medium, $m_0$ is the 0th moment of the injection pulse; and $t_a$ is the mean residence time in the immobile domain (i.e., the characteristic mass transfer time). The function $g$ is proportional to the residence time distribution in the immobile domain; we tabulate $g$ for many geometries, including several distributed (multirate) models of mass transfer. Using this expression we examine the behavior of late-time concentration for a number of mass transfer models. One key result is that if rate-limited mass transfer causes the BTC to behave as a power-law at late-time (i.e., $c \sim t^{-k}$), then the underlying density function of rate coefficients must also be a power-law with the form $\alpha^{k-3}$ as $\alpha \to 0$. This is true for both density functions of first-order and diffusion rate coefficients. BTCs with $k < 3$ persisting to the end of the experiment indicate a mean residence time longer than the experiment and possibly infinite, and also suggest an effective rate coefficient that is either undefined or changes as a function of observation time. We apply our analysis to breakthrough curves from Single-Well Injection-Withdrawal tests at the Waste Isolation Pilot Plant, New Mexico.
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1. Introduction

Mass transfer continues to be cited as a critical transport process in groundwater, soils, and streams. Estimation of rate coefficients (for both diffusion and sorption) is highly sensitive to the late-time behavior of breakthrough curves (BTCs). Indeed, recent studies have shown that the late-time data (i.e., after the advective peak has passed) may be the most important data for estimation of both the capacity coefficient and the rate coefficient or density function of rate coefficients [e.g., Farrell and Reinhard, 1994; Wagner and Harvey, 1997; Werth et al., 1997; Haggerty and Gorelick, 1998; Haggerty et al., in review]. With improvements in experimental and analytical techniques, concentration observations are now frequently available from laboratory and field experiments over several orders of magnitude of both time and concentration. Therefore, the examination of late-time behavior of BTCs is both feasible and critically important to the evaluation of rate-limited mass transfer, particularly if discrimination between different models of mass transfer is desired.

A rapidly growing body of recent work on mass transfer and transport has extended the basic model of single-rate mass transfer [e.g., Coats and Smith, 1964; van Genuchten and Wierenga, 1976; Cameron and Klute, 1977; Rao et al., 1980] or two-rate mass transfer [e.g., Brusseau et al., 1989] to models with distributed, or multiple rates of mass-transfer described by a density function of rate coefficients and primarily applied to laboratory data [Connaughton et al., 1993; Lafolie and Hayot, 1993; Pedit and Miller, 1994, 1995; Backes et al., 1995; Chen and Wagenet, 1995; Haggerty and Gorelick, 1995; Ahn et al., 1996; Chen and Wagenet, 1997; Culver et al., 1997; Cunningham et al., 1997;
Sahoo and Smith, 1997; Werth et al., 1997; Cunningham and Roberts, 1998; Deitsch et al., 1998; Haggerty and Gorelick, 1998; Kauffman et al., 1998; Lorden et al., 1998; McLaren et al., 1998; Hollenbeck et al., 1999; Stager and Perram, 1999]. It should be noted, however, that the concept of multiple time-scales of mass transfer has been employed for at least three orders of magnitude, primarily in chemical engineering and soil physics [Ruthven and Loughlin, 1971; Villermaux, 1981; Rao et al., 1982; Neretnieks and Rasmuson, 1984; Rasmuson, 1985; Fong and Mulkey, 1990; Valocchi, 1990], as have multiple time-scales of reaction in chemistry [e.g., Albery et al., 1985 and many others].

The work of Haggerty and Gorelick [1995, 1998] is particularly important to this current work. These papers develop and apply the “multirate” model, which is a transport model with a spatially-uniform density function of first-order mass transfer rate coefficients. These papers show that any density function of diffusion rate coefficients may be represented in a transport model by a different, but exactly equivalent, density function of first-order rate coefficients.

The multirate model has been applied to field data collected in a set of single-well and two-well convergent flow tracer tests conducted in a fractured dolomite (Haggerty et al., in review). After pulse injections of solute, the BTC data in the Single-Well Injection-Withdrawal (SWIW) tests showed a power-law behavior at late-time (i.e., \( c \sim t^k \)). Within the SWIW tests, \( k \) ranged from 2.1 to 2.8. The diffusion rate coefficients in this application were described by an assumed lognormal density function of diffusion rate coefficients, and interpretation of the BTC data focused on defining the mean and standard deviation of this lognormal density function to match data observed in
the tail of the BTC. While the lognormal density function provided excellent matches to
the data, the details of the power-law behavior of the tail of the BTC were left for a
future investigation. In particular, two issues were left: (1) an understanding of the
density functions of rate coefficients that could lead to late-time power-law behavior; and
(2) the range of late-time slopes that can be provided by a lognormal density function.

A power-law plots as a straight line on a double-logarithmic graph.

Consequently, in this paper we will frequently refer to the value of the power $k$ as the
"slope". Although the slope is always negative, for the sake of brevity, we will refer only
to its absolute value.

Power-law behavior at late time in BTCs has been noted in a number of other
laboratory and field experiments. Farrell and Reinhard [1994] and Werth et al. [1997]
observed power-law BTC and mass recovery curves with sorbing organic solutes in
unsaturated media. Cunningham et al. [1997] were able to represent the Werth et al.
[1997] data with a gamma density function of diffusion rate coefficients, while Haggerty
and Gorelick [1998] were able to approximate the power-law behavior with a lognormal
density function of diffusion rate coefficients. Both Cunningham et al. [1997] and
Haggerty and Gorelick [1998] noted the inability of conventional models of mass
transfer to yield the appropriate power-law behavior. Power-law behavior with a slope
of 3/2 has been observed in field data from the Grimsel test site and has been adequately
explained with conventional (single-rate) matrix diffusion [Eikenberg et al., 1994;
Hadermann and Heer, 1996]. However, single-rate diffusion is only able to yield a
power-law of exactly $t^{3/2}$, and can only maintain this behavior slightly longer than the
mean immobile-domain residence time \( t_a = \frac{a^2}{15D_a} \) for spheres and \( \frac{a^2}{3D_a} \) for layers), where \( D_a \) is the apparent diffusivity and \( a \) is the half-thickness of the immobile domain.

Power-law behavior such as that observed in Farrell and Reinhard [1994]; Werth et al. [1997]; or Meigs and Beauheim [in review] cannot be explained with conventional single-rate diffusion. Jaekel et al. [1996] showed that power-law BTCs result from a pulse injection of solute and equilibrium Freundlich sorption. Unfortunately, none of the data sets mentioned above are explained by this (the Meigs and Beauheim tracers were non-sorbing, and equilibrium Freundlich sorption is insufficient to explain the power-laws in the other data sets [Werth et al., 1997]).

The late-time (asymptotic) behavior of BTCs undergoing first-order linear nonequilibrium sorption has been examined by Vereecken et al. [1999]. Vereecken et al. [1999] develop late-time expressions for the BTC that are valid for time-varying velocity, but only after a pulse injection and in media with one- or two-site nonequilibrium sorption.

The purpose of this paper is to explore the nature of tailing in mobile-immobile (dual porosity) tracer test BTCs for a wide variety of linear mass transfer models. Specifically, we have the following objectives: (1) develop an analytic expression for the late-time BTCs for transport experiencing a distribution of either first-order sorption or diffusion time-scales and for both pulse injections and media with non-zero initial concentrations; (2) examine the information that can be provided by the late-time behavior of the BTC; (3) examine BTCs that exhibit power-law behavior at late time and the implications for mass transfer. Particular expressions describing the late-time BTCs
1 for single-rate models with both infinite and finite immobile domains, as well as
2 multirate models with first-order, and diffusion rate coefficients defined by lognormal,
3 gamma and power-law density functions are provided. Implications of the late-time
4 slopes defined by these equations are discussed with respect to mass transfer processes,
5 including implications for estimates of the mean residence time in the immobile zone (or,
6 equivalently, a characteristic mass transfer time). The power-law late-time behavior of
7 BTCs in two SWIW tests from the WIPP site are examined.

8 2. Mathematical Development

9 2.1. General case

10 2.1.1. Late-Time Solution for Concentration:

11 The mass balance equation for a solute advecting and dispersing in 1-D (i.e.,
12 along a single stream tube), and interacting with rock via diffusion, linear equilibrium
13 sorption, and/or linear nonequilibrium sorption is:

14 \[
\frac{\partial}{\partial x}\left(\frac{\alpha_L v}{R_a} \frac{\partial c}{\partial x} - \frac{v}{R_a} c\right) = \frac{\partial c}{\partial t} + \Gamma(x, t) \tag{1}
\]

15 where \(\alpha_L\) [L] is longitudinal dispersivity; \(v\) [LT\(^{-1}\)] is pore-fluid velocity; \(R_a\) [-] is the
16 retardation factor in the mobile (advective, effective or kinematic) porosity; \(c\) [ML\(^{-3}\)] is
17 solute concentration within the advective porosity; and \(\Gamma(x, t)\) [ML\(^{-3}\)T\(^{-1}\)] is the source-
18 sink term for mass exchange with the immobile (matrix or diffusive) porosity and
19 nonequilibrium sorption sites. From this point forward, we will adopt the terminology of
"mobile" and "immobile" domains and concentrations, which refer to either sorption or diffusion. We will employ the uniform initial conditions

\[ c(x, t = 0) = c_{\text{im}}(x, z, t = 0) = c_0 \]  

(2a)

where \( c_{\text{im}} [\text{ML}^{-3}] \) is solute concentration within the immobile domain, which may, in the case of diffusion, be a function of a second spatial coordinate \( z \) oriented normal to the mobile-immobile domain interface. We will also employ the boundary conditions

\[ c(x=0, t) = m_0 \delta(t) \]  

(2b)

\[ c(x \rightarrow \infty, t) = c_0 \]  

(2c)

where \( m_0 [\text{MTL}^{-3}] \) is the zeroth moment of the BTC; \( c_0 [\text{ML}^{-3}] \) is the initial concentration in the system; and \( \delta(t) [\text{T}^{-1}] \) is the Dirac delta. The Dirac injection is never met in practice. However, as long as the duration of the pulse is much shorter than the mean residence time in the immobile zone, (2b) will be a sufficiently good approximation. For a finite pulse injection with constant velocity, the zeroth moment \( m_0 \) is the injected concentration multiplied by injection time.

For initial and boundary conditions (2a-c), then at late time:

\[ \alpha_x \frac{\partial c}{\partial x} \ll c, \quad \text{for } t \gg t_{\text{ad}} \]  

(3)

where \( t_{\text{ad}} [\text{T}] \) is the average advective residence time (equal to \( LR_{\alpha}/v \) if velocity is constant in space). In other words, once the input pulse has advected far past the point of
observation $L$, then dispersion has a negligible effect on concentration. Similarly, if the immobile domain has a long mean residence time relative to advection, then at late time:

$$\frac{\partial c}{\partial t} \ll \Gamma(x, t), \quad \text{for } t >> t_{ad} \text{ and } t_a >> t_{ad}$$

(4)

where $t_a$ [T] is the mean residence time in the immobile domain. In other words, concentration change at late time is dominated by exchange between the mobile and immobile domains if the average immobile domain residence time is longer than the advective time. Note that from this point forward, it will be assumed that $t_a >> t_{ad}$ and $t >> t_{ad}$ unless otherwise stated. Therefore, the equation (1) may be re-written:

$$-\frac{\partial}{\partial x}\left(\frac{v}{R_a} c\right) = \Gamma(x, t)$$

(5)

By integration we can obtain a solution for concentration at late time:

$$c(x=L, t) = -\int_0^L \frac{R_a(x)}{v(x)} \Gamma(x, t) dx$$

(6)

where $L$ [L] is the distance from point of injection to point of observation along the flow path. If velocity, retardation, and the parameters and functions that comprise $\Gamma(x, t)$ are spatially uniform, then this leaves us with a very simple expression for concentration at late time:

$$c(x=L, t) = -t_{ad} \Gamma(t)$$

(7)
The spatially-variable case is left for a future paper. From this point on the dependency of $c$ on $x=L$ and $t$ is implicitly assumed.

2.1.2. Source-Sink Term $\Gamma(t)$:

The source-sink term $\Gamma(t)$ is the rate of loss or gain of concentration to or from the immobile domain (loss at early time and gain at late time). For any linear mass transfer problem with uniform initial conditions it is possible to express the source-sink term as the following, which is valid at all times:

$$\Gamma(t) = \int_{0}^{t} \frac{\partial c(t-\tau)}{\partial \tau} g(\tau) d\tau = \frac{\partial c}{\partial t} * g = c \frac{\partial g}{\partial t} + c g_{0} - c_{0} g$$  \hspace{1cm} (8)$$

where $g(t)$ is a "memory function" to be defined; * represents the convolution product; $g_{0}$ is the memory function at $t = 0$; and $c_{0}$ [ML$^{-3}$] is the initial concentration. Note that the Laplace transform of (8) is commonly used in analytical solutions [e.g., Villermaux, 1974 and many others since], and that the last transformation in (8) is most easily derived in the Laplace domain. Equation (8) has been expressed explicitly in the time domain by e.g., Peszynska [1996] and Carrera et al. [1998], and results in an integro-partial differential equation when substituted back into (1). The memory function $g(t)$ may be physically interpreted as the capacity coefficient ($\beta_{tot}$, see Section 2.3) multiplied by the residence time distribution in the immobile domain, given a Dirac pulse at the surface.

The derivative of $g(t)$ is proportional to what is commonly called in statistical physics the probability of first return or distribution of first passage times [e.g., Bouchaud and Georges, 1990, p. 271-272].
We desire to find a closed-form expression for the source-sink term in (8), accurate at late time, that may be substituted into (7). We recognize the following characteristics of $\Gamma(t)$: (1) at early time the function represents rapid loss from a high-concentration pulse in the mobile domain to the immobile domain; and (2) at late time the function represents slow gain to the mobile domain (which has very low concentration) from the immobile domain. To obtain a solution that is accurate at late time, we therefore require an approximate function for mobile-domain concentration that has the correct pulse size at early time, and that is approximately zero at late time. Such an approximation is available in $c \equiv m_0 \delta(t)$, where $m_0$ is the zero\textsuperscript{th} moment of the injection. Note that this approximation is used only for calculating the source-sink term, and not as an approximation for late-time concentration itself. That this approximation is sufficient will become apparent when the results are compared to a full numerical solution. Employing the properties of convolution, (8) can now be expressed:

$$\Gamma(t) \equiv m_0 \frac{\partial g}{\partial t} - c_0 g \text{, for } t >> t_{ad} \text{ and } t_a >> t_{ad}$$

The general form of the memory function is [modified from Carrera et al., 1998]

$$g(t) = \int_0^\infty \alpha b(\alpha) e^{-\alpha t} d\alpha$$

where $\alpha$ is a rate coefficient and $b(\alpha)$ is a density function of first-order rate coefficients. Note two differences between our definition of the memory function and that of Carrera et al. [1998, Eqn. (15), p. 182]. First, our memory function $g(t)$ includes the constants that are placed before the source-sink term in Carrera et al.'s mass balance equation.
Secondly, although Carrera et al. [1998] express (10) as a discrete function, the more general expression is as a continuous function, allowing for density functions of diffusion rate coefficients, etc. Various density functions $b(\alpha)$ are given in Table 1, along with the corresponding memory function $g(t)$.

We note that (10) is the Laplace transform of $\alpha b(\alpha)$, where $t$ substitutes for the Laplace variable. We also use the property of the Laplace transform [e.g., Roberts and Kaufman, 1966, p. 4]

\begin{equation}
\text{Lap}\{\alpha^2 b(\alpha)\} = -\frac{\partial g}{\partial t} \tag{11}
\end{equation}

where Lap\{\} indicates the Laplace transform.

Employing (7), (9), (10), and (11), we can now write an approximation for concentration at late time:

\begin{equation}
c = t_{ad}\left[\alpha \frac{\partial g}{\partial t} - m_o \frac{\partial g}{\partial t}\right] = t_{ad}\int_0^\infty (c_0 + \alpha m_o) \alpha b(\alpha) e^{-\alpha t} d\alpha \tag{12}
\end{equation}

All forms of (12) are equivalent and are useful in different ways for understanding the late-time behavior of BTCs. We expect that in most applications only one of $c_0$ or $m_o$ will be non-zero; however, (12) holds true regardless of the values of $c_0$ and $m_o$. Note that the late-time concentration can be calculated for various density functions $b(\alpha)$ using $g(t)$ supplied in Table 1.
At this point, we re-emphasize the restrictions on Equation (12). These are (1) time is much greater than the advection time; (2) the mean residence time in the immobile domain is much greater than the advection time; and (3) time is much greater than the duration of the injection pulse, meaning that an impulse (Dirac) function is a valid approximation to the injection. In a heterogeneous velocity field, restrictions (1) and (2) mean that both time and mean residence time in the immobile domain must be much greater than the sum of advection time across a control plane and the standard deviation of that advection time. In particular, a power-law distribution of advection times (such as invoked by e.g., Berkowitz and Scher [1997]) would invalidate the use of (12).

2.2. Notes on Application of Equation (12)

Equation (12) presents an interesting theoretical development for two reasons. First, the late-time behavior of the BTC is easily obtained for a wide variety of density functions $b(\alpha)$ using any comprehensive table of Laplace transforms. Equation (12) is simpler for first-order mass transfer than the equations developed by Vereecken et al. [1999]. The equation also provides an asymptotic expression for any mass transfer process with a known memory function $g(t)$, which is easily calculated for a wide range of sorption and diffusion processes. Conversely, it must be pointed out, the equations developed by Vereecken et al. [1999] allow for time-varying velocity.

Second, (12) suggests that the density function of mass transfer rate coefficients (whether from diffusion, nonequilibrium sorption, or a general density function of mass transfer processes) is available directly and analytically from breakthrough data. In fact,
if (12) is treated as an integral equation where $b(\alpha)$ is an unknown, the density function $b(\alpha)$ may be directly calculated using the inverse Laplace transform. If the medium is initially free of tracer, then $c_0 = 0$ and the density function $b(\alpha)$ is given analytically by the Bromwich integral:

$$b(\alpha) = \frac{1}{\gamma m_0 \alpha^2 (2\pi i)} \int_{Br} c(x = L, t) e^{-\alpha x} dt = \frac{1}{\gamma m_0 \alpha^2} \text{Lap}^{-1} \left\{ c(x = L, t) \right\}$$  \hspace{1cm} (13)

where $i$ is the unit imaginary number; and $Br$ represents the Bromwich contour [see, e.g., LePage, 1961, p. 319-320]. A similar equation may be easily constructed for the case of non-zero initial conditions and continuous flushing of tracer-free fluid, such as in a purge experiment. Unfortunately, the practical use of (13) is limited by the conditions that we can only use the late-time breakthrough data, and that any errors in the data introduce numerical instabilities in the inverse Laplace transform. Nonetheless, (13) will allow us to determine certain important properties of the density function $b(\alpha)$.

For relatively simple cases (i.e., single rate mass transfer), the properties of (12) allow estimation of the rate coefficient and capacity coefficient directly from the BTC [also see Vereecken et al., 1999]. For some more complex cases (e.g., gamma and power-law density functions), the properties of (12) will allow certain properties of the density function of rate coefficients to be determined. This will be discussed in the following sections.
Notes on the Density Function $b(\alpha)$

We add two notes regarding the density function $b(\alpha)$ before continuing. First, a useful definition is that of the $0^{th}$ moment of the density function of rate coefficients:

$$\int_0^\alpha b(\alpha) d\alpha = \beta_{tot} \quad (14)$$

where $\beta_{tot}$ is commonly known as the capacity coefficient. The capacity coefficient is the ratio of mass in the immobile domain to mass in the mobile domain at equilibrium; in the absence of sorption it is the ratio of the two volumes.

Second, we note without derivation that the Laplace transform of the density function of rate coefficients is a particularly useful function by itself. This function is proportional to the mass fraction remaining in an immobile domain, where the initial conditions are uniform concentration in the immobile domain and the boundary condition on the immobile domain is zero concentration. The mass fraction remaining in the entire system ($M/M_0$) is therefore:

$$\frac{M(t)}{M_0} = \frac{\text{Lap}\{b(\alpha)\}}{1 + \beta_{tot}} = \frac{\int_0^\alpha b(\alpha)e^{-\omega t} dt}{1 + \beta_{tot}} \quad (15)$$

In other words, the mass fraction remaining is calculated simply by finding the Laplace transform of the density function $b(\alpha)$. 
2.4. Mean Residence Time in Immobile Domain

One of the criteria for use of equation (12) is that the mean residence time in the immobile domain be much greater than the advection time. This sub-section outlines the calculation of this mean residence time, as well as providing an effective rate coefficient that may be used in an "equivalent" first-order model of mass transfer.

The residence time distribution in the immobile domain given a Dirac impulse at the surface is \( g(t)/\beta_{\text{tot}} \). The mean residence time (or characteristic mass transfer time) is therefore

\[
t_a = \frac{1}{\beta_{\text{tot}} \int_0^\infty tg(t) dt}
\]

\[
= \frac{1}{\beta_{\text{tot}}} \int_0^\infty \alpha b(\alpha) e^{-\alpha t} d\alpha dt
\]

\[
= \frac{1}{\beta_{\text{tot}}} \int_0^\infty \frac{b(\alpha)}{\alpha} d\alpha
\]  

(16)

It can be shown [e.g., Cunningham and Roberts, 1998] that the zeroth, first, and second temporal moments of the BTC are the same for any density function of rate coefficients provided that the mean residence time in the immobile domain is the same. Therefore, the best effective rate coefficient (i.e., the one that yields the same zeroth, first, and second moments of the BTC) is the harmonic mean of the density function, since:

\[
\alpha_H = \frac{1}{t_a} = \beta_{\text{tot}} \left( \int_0^\infty \frac{b(\alpha)}{\alpha} d\alpha \right)^{-1}
\]  

(17)
Notably, the harmonic mean may be zero for some density functions, meaning that the
mean residence time in the immobile domain is infinite. Note that an infinite mean
residence time does not require infinite size or infinite capacity in the immobile domain.
The harmonic means for a number of density functions $b(\alpha)$ are shown in Table 1.

3. Late-Time Behavior of BTCs

In this section we will consider a number of examples of BTCs after a pulse
injection into a medium with zero initial concentration. Many of the functions developed
in this section are summarized in Table 1, as are several others not discussed here.

3.1. Simple Example 1: First-Order Mass Transfer

Consider the simplest case of mass transfer described by a single first-order rate
coefficient. The density function of rate coefficients is

$$b(\alpha) = \beta_{\text{foo}} \delta(\alpha - \alpha_f)$$

(18)

The memory function $g(t)$, given by applying (10) to (18), is

$$g(t) = \alpha_f \beta_{\text{foo}} e^{-\alpha_f t}$$

(19)

The resulting late-time approximation for concentration in the mobile domain (with
initial concentration of zero) is given by substituting (19) into (12):

$$c = m_{\text{sol}} \beta_{\text{foo}} \alpha_f^2 e^{-\alpha_f t}$$

(20)
This solution displays the well-known behavior that late-time concentration is exponential with a semi-log slope \( \frac{d(\ln c)}{dt} \) of \(-\alpha t\).

### 3.2. Simple Example 2: Finite Spherical Blocks

Consider the case of diffusion into finite spherical matrix blocks. Haggerty and Gorelick [1995] showed that a particular discrete density function of first-order rate coefficients results in a model that is mathematically identical, from the perspective of the mobile domain concentrations, to that of diffusion into and out of various matrix geometries. Using mathematics that is more similar to that presented in this paper, Carrera et al. [1998] make the same assertion. In the case of spherical blocks, the density function is

\[
b(\alpha) = \sum_{j=1}^{\infty} \frac{6\beta_{\text{tot}}}{j^2 \pi^2} \delta \left( \alpha - j^2 \pi^2 \frac{D_\alpha}{a^2} \right)
\]

where \(\beta_{\text{tot}}\) is the capacity coefficient of the spherical blocks; \(D_\alpha [\text{T}]\) is the apparent diffusivity; and \(a [\text{L}]\) is the radius of the spherical blocks. This density function is a series of Dirac deltas with monotonically decreasing weight. The harmonic mean of (21) is the well-known linear driving force approximation \(\frac{D_\alpha a^2}{15} [\text{e.g., Glueckauf, 1955}]\), and the mean residence time in the spheres is therefore \(t_\alpha = \frac{a^2}{15D_\alpha}\). The memory function is

\[
g(t) = \sum_{j=1}^{\infty} 6\beta_{\text{tot}} \frac{D_\alpha}{a^2} \exp \left( -j^2 \pi^2 \frac{D_\alpha}{a^2} t \right)
\]
Readers familiar with diffusion in spherical geometry will recognize (22) as
proportional to the mass flux out of spheres initially saturated with a uniform solute
ccentration and with a boundary concentration of zero. [e.g., Crank, 1975, p. 91;
Grathwohl et al., 1994].

The resulting late-time approximation for concentration in the mobile domain
(with initial concentration of zero) is given by substituting (22) into (12):

\[ c = m_{tot} \beta \left( \frac{D_z}{a^2} \right)^2 \sum_{j=1}^{\infty} 6j^2 \pi^2 \exp \left( -j^2 \pi^2 \frac{D_z t}{a^2} \right) \]  

(23)

From this expression, we can see that the late-time concentration is exponential;
therefore, on a double-log plot, the late-time slope will approach \( \infty \) shortly after the mean
residence time in the immobile domain \( (t_a = \frac{a^2}{15D_a}) \) is reached.

Figure 1 shows the full solution to the advection-dispersion-mass transfer
(ADMT) equations and the late-time approximation. The ADMT equations were solved
using STAMMT-L [Haggerty and Reeves, 1999] for \( m_b = 1 \times 10^4 \) s kg m\(^{-3}\);
\( t_{ad} = 1 \times 10^4 \) s; \( D_a/\alpha^2 = 1 \times 10^{-8} \) s\(^{-1}\); \( \beta_{tot} = 1 \); and a Peclet number of 1000. All
concentrations have been nondimensionalized by the terms in front of the infinite series
in (23).

From Figure 1 we make four points. First, the approximation very accurately
represents the late-time behavior of the ADMT solution, but obviously does not contain
the advective-dispersive peak. We can see in the figure that the late-time approximation
is valid when \( t >> t_{ad} \) provided that \( t_a >> t_{ad} \).
Second, the late-time behavior demonstrates the well-known 3/2 slope for matrix diffusion [e.g., Hadermann and Heer, 1996], which ends when \( tD_\alpha a^2 > 1 \). As long as the block size \( a \) is large enough (or \( D_\alpha \) small enough) that \( tD_\alpha a^2 << 1 \) over the entire time of a tracer test, then the slope remains 3/2. In such a case it would not be possible to estimate the value of \( D_\alpha a^2 \) from the BTC. The limiting case of "infinite" matrix blocks is given in Table 1, for \( c \sim \frac{dg}{dt} \sim -t^{3/2} \). Note that the harmonic mean rate coefficient for this case is zero, meaning that the mean residence time for very large blocks approaches infinity.

Third, the location of the BTC peak in the ADMT solution may lie anywhere on the late-time approximation curve, dependent on the relative values of \( t_{ad} \) and \( D_\alpha a^2 \).

Last, we note that it is possible to estimate both \( \beta_{tot} \) and \( D_\alpha a^2 \) by using the late-time approximation as a type-curve, if the break in slope is present. The capacity coefficient \( \beta_{tot} \) would be estimated from the vertical shift, while \( D_\alpha a^2 \) would be estimated from the horizontal shift.

3.3. Gamma Density Function of First-Order Rate Coefficients

Gamma density functions of rate coefficients have been used to represent multirate mass transfer in several papers. Cunningham et al. [1997] developed the mathematics of a gamma density function of diffusion rate coefficients, while Werth et al. [1997] applied this model successfully to several mass-fraction-remaining data sets. Connaughton et al. [1993] used a gamma density function of first-order rate coefficients to model release of naphthalene from soil, while Pedit and Miller [1994] employed a gamma density function of first-order rate coefficients to examine diuron sorption. Other
examples include *Ahn et al.* [1996]; *Chen and Wagenet* [1997]; *Culver et al.* [1997]; *Sahoo and Smith* [1997]; *Deitsch et al.* [1998]; *Kauffman et al.* [1998]; *Lorden et al.* [1998], and *Stager and Perram* [1999]. The method we are using is applicable to both types of density functions, and the key relationships for both are given in Table 1. Although the early time behavior will differ between gamma density functions of first-order and diffusion rate coefficients, the late-time slope will be identical for the same value of \( \eta \).

The gamma density function of first-order rate coefficients is

\[
b(\alpha) = \frac{\beta_{\text{tot}}}{\gamma^\eta T(\eta)} \alpha^{\eta-1} e^{-\alpha/\gamma}
\]

(24)

where \( \gamma \) \([T^{-1}]\) is the scale parameter and \( \eta \) \([-]\) is the shape parameter. The harmonic mean of (24) is 0 if \( \eta \) is less than 1, a fact that is of particular importance for applications. As a consequence, the mean residence time in the immobile domain would be infinite. (These facts are also true for gamma density functions of diffusion rate coefficients.) If \( \eta \) is greater than 1, the harmonic mean of (24) is \((\eta-1)\gamma\).

The memory function is

\[
g(t) = \beta_{\text{tot}} \frac{\partial}{\partial t} (\gamma t + 1)^{-\eta}
\]

(25)

Therefore, the late-time concentration in the fracture is given by

\[
c = m_{\text{ad}} \beta_{\text{tot}} \frac{\eta(\eta + 1)}{(\gamma t + 1)^{\eta+2}}
\]

(26)

Note that when \( \gamma t \gg 1 \) the BTC follows a power-law:
The same late-time power-law behavior is also exhibited with a density function of diffusion rate coefficients. Note that a power-law behavior \( c \sim t^{-q} \) with \( k < 3 \) would indicate an infinite second (and higher) temporal moment and an infinite mean residence time in the immobile domain.

Figure 2 shows the late-time approximation in (26) nondimensionalized by the transport terms. We have normalized time by the mass transfer rate \( \gamma \). Figure 2 also shows a solution to the ADMT equations with STAMMT-L \((\text{Haggerty and Reeves, 1999})\) for \( m_0 = 1 \times 10^4 \text{ s kg m}^{-3} \), \( t_{ad} = 1 \times 10^4 \text{ s} \), \( \gamma = 1 \times 10^{-4} \text{ s}^{-1} \), \( \eta = 0.5 \); \( \beta_{tot} = 1 \); and a Peclet number of 1000.

We see from (27) and Figure 2 that the late-time double-log slope of concentration will be \(-\eta \pm 2\). For comparison to published values, \textit{Connaughton et al.} [1993] estimated values of \( \eta \) in the range of 0.17 to 0.37 for a gamma density function of first-order rate coefficients, while \textit{Pedit and Miller} [1994] estimated \( \eta = 0.11 \) from their experiments; \textit{Culver et al.} [1997] estimated \( \eta = 0.023 \) to 0.054 for their column experiments; \textit{Deitsch et al.} [1998] estimated \( \eta \) from 0.092 to 350 in 15 experiments with different materials, with the majority having \( \eta \) below 1. \textit{Kauffman et al.} [1998] estimated \( \eta = 0.60 \) and 0.84 in two column experiments. \textit{Werth et al.} [1997] found values of \( \eta \) equal to approximately 0.5 for a gamma density function of diffusion rate coefficients. Note that almost all of these estimated \( \eta \) (i.e., those below 1) will lead to an infinite mean residence time within the immobile domain. Consequently, the variance of

\[ c \sim t^{-q} \]
the breakthrough times will be infinite with these models. Late-time behavior associated with gamma density functions is discussed further in Section 4.2.

3.4. Lognormal Density Function of Diffusion Rate Coefficients

Lognormal density functions of rate coefficients have also been used to represent mass transfer in natural systems. *Pedit and Miller* [1994]; *Backes et al.* [1995]; *Hagger* [1995]; *Culver et al.* [1997]; *McLaren et al.* [1998] all used a lognormal density function of first-order rate coefficients to model uptake and release of sorbing solutes in soils. *Pedit and Miller* [1995] and *Hagger and Gorelick* [1998] used a lognormal density function of diffusion rate coefficients to model diffusion of sorbing solutes in soils. As is true for the gamma density functions of rate coefficients, the behavior of both lognormal models is very similar, especially at late time and large variances. In our analysis here we will employ only a density function of diffusion rate coefficients:

\[
\beta^*\left(\frac{\bar{D}_a}{\bar{a}^2}\right) = \frac{\beta_{tot}}{\sqrt{2\pi} \sigma} \frac{D_a}{\bar{a}^2} \exp\left\{-\frac{\left[\ln\left(\frac{\bar{D}_a}{\bar{a}^2}\right) - \mu\right]^2}{2\sigma^2}\right\}
\]

(28)

The equivalent density function of first-order rate coefficients is given by *Hagger and Gorelick* [1998]:
The harmonic mean of \(29\) is \(3 \exp(\mu - \sigma^2/2)\). Consequently, the effective rate coefficient is approximately 0.22\(\sigma^2\) orders of magnitude smaller than the geometric mean. For large \(\sigma\), the effective rate coefficient is approximately zero and the mean residence time in the immobile domain approaches infinity. In the limit of very large \(\sigma\), the density function is log-uniform and is equivalent to a power-law density function with \(\sim \alpha^{-1}\). As we shall see in the following sections, this corresponds to a late-time BTC of \(\sim \ell^2\).

The Laplace transform of \(29\) must be done numerically. The result may then be inserted into \(12\). After taking the second derivative in time (numerically), the late-time approximation for a concentration BTC is shown in Figure 3 for various values of \(\sigma\).

The time axis of Figure 3 is normalized by the geometric mean of \(24\), and concentration is normalized the same as previously. Figure 3 also shows the solution to the ADMT equations in the presence of a lognormal density function of diffusion rate coefficients.

The ADMT equations were solved using STAMMT-L [Haggerty and Reeves, 1999] for \(m_\theta = 1 \times 10^4\) s kg m\(^{-3}\); \(t_{ad} = 1 \times 10^4\) s; \(e^{-\mu} = 1 \times 10^4\) s\(^{-1}\); \(\sigma = 5\); \(\beta_{tot} = 1\); and a Peclet number of 1000. The discrepancy at late time is due to numerical error in the series of numerical steps for the late-time approximation; however, the late-time slopes are correct. Note that the late-time slopes for the lognormal distribution lie between 2 and 3 for a large range of time, provided that \(\sigma\) is greater than approximately 3.
Published values of $\sigma$ for lognormal distributions of rate coefficients are typically larger than 3 [e.g., *Pedit and Miller*, 1994, 1995; *Culver et al.*, 1997; *Haggerty and Gorelick*, 1998; *Haggerty et al.*, in review], suggesting that mass transfer rate coefficients have large variability in natural media. With such large values of $\sigma$, we would expect to see late-time slopes on double-log BTCs after a pulse-injection between 2 and 3.

### 3.5. Power Law Density function of First-Order Rate Coefficients

An alternative density function that has been less commonly used to describe mass transfer in groundwater and soils is a power-law density function. *Hatano and Hatano* [1998] used a power-law density function of waiting times in the context of a continuous-time random walk to model the sorption of radionuclides in a column experiment. Power-law density functions of waiting times have been used in statistical physics to describe anomalous transport behavior [e.g., *Bouchard and Georges*, 1990; *Scher et al.*, 1991]. Frequently such density functions arise from diffusion or rate-limited sorption on a fractal geometry. A particular advantage of a power-law distribution, within the context of this work, is that it allows us to investigate power-law BTC behavior for a larger range of late-time slopes.

As with a gamma density function it is possible to define both a density function of first-order rate coefficients and an equivalent density function of diffusion rate coefficients. Again, although the early time behavior will differ for power-law density functions of first-order and diffusion rate coefficients, the late-time slope will be identical for the same value of $k$. For the sake of brevity, we show only the power-law density function of first-order rate coefficients.
A truncated power-law density function may be written as follows:

\[
b(\alpha) = \frac{\beta \alpha^{k-2}}{\alpha_{\text{max}}^{k-2} - \alpha_{\text{min}}^{k-2}} \alpha^{k-3}, \quad k > 0 \text{ and } k \neq 2, \quad \alpha_{\text{min}} \leq \alpha \leq \alpha_{\text{max}} \tag{30a}
\]

where \( \alpha_{\text{max}} \) [T\(^{-1}\)] is the maximum rate coefficient; \( \alpha_{\text{min}} \) [T\(^{-1}\)] is the minimum rate coefficient; and \( k \) is the exponent. The value of \( \alpha_{\text{min}} \) may be zero if \( k > 2 \). The reason for choosing to write the power-law as \( k-3 \) will become apparent shortly. If \( k = 2 \), the density function may be written

\[
b(\alpha) = \frac{\beta \alpha^{k-2}}{\ln\left(\frac{\alpha_{\text{max}}}{\alpha_{\text{min}}}\right)} \tag{30b}
\]

The late-time concentration in the mobile domain is

\[
c = \frac{m_{\text{tot}} \beta \alpha^{k-2}}{(\alpha_{\text{max}}^{k-2} - \alpha_{\text{min}}^{k-2})} \int_{\alpha_{\text{min}}}^{\alpha_{\text{max}}} \alpha^{k-1} e^{-\sigma} d\alpha, \quad k > 0 \text{ and } k \neq 2 \tag{31}
\]

For arbitrary (non-integer) values of \( k \), (31) must in general be evaluated numerically. However, the most important point about (31) is that

\[
c \sim t^{-k}, \quad \alpha_{\text{max}}^{-1} << t << \alpha_{\text{min}}^{-1} \tag{32}
\]

Expressed in words, the slope of the BTC is \( k \) for times much greater than \( \alpha_{\text{max}}^{-1} \) and much less than \( \alpha_{\text{min}}^{-1} \) for all values of \( k \). At times greater than \( \alpha_{\text{min}}^{-1} \) the slope goes to \( \infty \).
It is possible to present closed form solutions for many specific cases of (31); we will provide the solutions for the cases $k = 1$, $k = 2$, and $k = 3$. First, let us define three other variables in terms of $\alpha_{\text{max}}$ and $\alpha_{\text{min}}$:

\[ \tau = \alpha_{\text{max}} \]  
\[ \lambda_i = \frac{\alpha_{\text{max}}}{\alpha_{\text{min}}} \]  
\[ \alpha_p^2 = \begin{cases} \frac{\alpha_{\text{max}}^2}{1 - \lambda_i^{-k}} & k \neq 2 \\ \frac{\alpha_{\text{max}}^2}{\ln \left( \lambda_i \right)} & k = 2 \end{cases} \]

Note that $\alpha_p$ is a function of $\alpha_{\text{max}}$, $\alpha_{\text{min}}$, and $k$, and is used for the purpose of simplifying the following equations only.

Using these variables, the late-time concentration for $k = 1$ is therefore:

\[ c = m_{\phi} \beta_{\text{tot}} \alpha_p \tau \left[ e^{-\tau / \lambda_i} - e^{-\tau} \right] \tau^{-1} \]  
\[ c = m_{\phi} \beta_{\text{tot}} \alpha_p \left[ e^{-\tau / \lambda_i} \left( \frac{\tau}{\lambda_i} + 1 \right) - e^{-\tau} (\tau + 1) \right] \tau^{-2} \]

If $k = 3$, then the density function is uniform, and the late-time concentration is:

\[ c = m_{\phi} \beta_{\text{tot}} \alpha_p \left[ e^{-\tau / \lambda_i} \left( \frac{\tau^2}{\lambda_i^2} + 2\frac{\tau}{\lambda_i} + 2 \right) - e^{-\tau} (\tau^2 + 2\tau + 2) \right] \tau^{-3} \]
From the above equations we see that a family of curves is required for each value of \( k \) since both \( \alpha_{\text{min}} \) and \( \alpha_{\text{max}} \) appear in all equations. However, inspection of the equations indicates that the curves for each value of \( k \) will be identical until \( t \) approaches \( \alpha_{\text{min}}^{-1} \).

The harmonic mean of the density function (30a) and (30b) is

\[
\ln \left( \lambda_i \right) \frac{\alpha_{\text{min}}}{\lambda_i - 1}, \quad k = 2
\]

\[
\alpha_H = \frac{\alpha_{\text{max}}}{\ln \left( \lambda_i \right)}, \quad k = 3
\]

\[
\alpha_{\text{min}} \frac{(k - 3) \lambda_i^{k-2} - 1}{(k - 2) \lambda_i^{k-3} - 1}, \quad \text{otherwise}
\]

Approximations may be made to (37) that are useful in understanding what controls the harmonic mean of the distribution. These approximations are given in Table 2. Note again that the mean residence time in the immobile domain is simply the inverse of \( \alpha_H \).

We make two points in regard to (37) and Table 2, and leave further discussion of late-time behavior associated with power-law density functions to Section 4.2. First, if the late-time slope of the BTC is less than 3 (i.e., \( k < 3 \)), then the harmonic mean is controlled by \( \alpha_{\text{min}} \). However, if the late-time behavior of the BTC remains power-law until the end of the experiment, the parameter \( \alpha_{\text{min}} \) cannot be estimated from a BTC.

Consequently, the harmonic mean (and therefore the mean residence time in the immobile domain) cannot be estimated if the BTC remains power-law until the end of the experiment with a slope less than 3.

Second, if \( k < 3 \) and \( \alpha_{\text{min}} = 0 \), then the harmonic mean is 0. Therefore, if a BTC has a late-time slope of \( k < 3 \), and the behavior is due to mass transfer, this may
indicate an infinite mean residence time in the immobile domain. It also causes the second and higher temporal moments of the BTC to be infinite.

Note that there is nothing that physically precludes a late-time slope between 2 and 3 being maintained to infinite time (i.e., $2 < k < 3$ as $t \rightarrow \infty$). A slope of $k \leq 2$ to infinite time, however, would require an infinitely large immobile domain (i.e., infinite capacity). Therefore, a slope of $k \leq 2$ cannot be maintained for infinite time (for this reason, $k = 3/2$ is possible with diffusion, but only until a time of $\sim \alpha^2/D_a$).

The late-time behavior of concentration, as given by (34) - (36) is shown in Figure 4 for $\alpha_{min} = 10^{-3} \alpha_{max}$. Figure 4 also shows the solution to the ADMT equations in the presence of a power-law density function of rate coefficients. The ADMT equations were solved using STAMMT-L [Haggerty and Reeves, 1999] for $m_o = 1$ s kg$^{-1}$, $t_{ad} = 1$ s; $\beta_{max} = 1$ s$^{-1}$; $\alpha_{min} = 1 \times 10^{-5}$ s$^{-1}$; $k = 1$; $\beta_{tot} = 1$; and a Peclet number of 1000.

3.6. Summary of Late-Time Slopes

Figure 5 provides a summary of late-time slopes for several of the models presented. Late-time slopes are given versus nondimensional time. Note that a BTC with advection and dispersion will mask some portion of the slopes shown in this figure at earlier times. The slopes given in Figure 5 will only be present when $t >> t_{ad}$. A power-law slope is a constant at late-time, such as provided by the gamma and power-law density functions. Note that the conventional diffusion model is equivalent to the lognormal density function with $\sigma = 0$. The slope in the conventional model is 3/2 until
approximately the mean residence time in the immobile domain ($\sigma^2/3D_\alpha$ for 1-D diffusion). Note that the lognormal density function with larger $\sigma$ cannot provide a true power-law BTC, but can hold the slope relatively constant over a long time. All lognormal density functions will approach an infinite slope as time goes to infinity.

4. Applications to Tracer Tests and Discussion

4.1. WIPP Tracer Tests

Figure 6a shows data and confidence intervals from two single-well injection-withdrawal (SWIW) tracer tests conducted in the Culebra Dolomite Member of the Rustler Formation at the Waste Isolation Pilot Plant (WIPP) Site in southeastern New Mexico. The Culebra is a 7-m-thick, variably fractured dolomite, and is a potential pathway to the accessible environment in the event of a radionuclide release from the WIPP. These two tests were performed in the central well at two multi-well sites, designated H-11 and H-19. The SWIW tests consisted of the consecutive injection of one or more slugs of conservative tracers into the Culebra Dolomite, followed by the injection of a Culebra brine chaser (containing no tracer), and then by a resting period of approximately $6.5 \times 10^4$ s (18 h). The tracers were then removed from the formation by pumping on the same well until concentration was close to or below detection levels. The total residence time (i.e., $t_{ad}$) of the slug in the formation was approximately $9.0 \times 10^4$ s (25 h). Details of the tracer tests are given in Meigs and Beauheim [in review] and in Meigs et al. [in press]. Interpretation of the SWIW tests by Haggerty et al. [in review] suggest that the late-time behavior of the BTC is due to multiple rates of mass transfer.
It is clear that neither heterogeneity nor tracer drift alone can be responsible for the observed behavior, though a combination of the two may explain some fraction of it [Meigs et al., in press; Lesoff and Konikow, 1997].

The SWIW data in Figure 6a display late-time slopes that are approximately constant over several hundred hours. The slopes at all times for both BTCs are given in Figure 6b, which was calculated using a 5-point, moving-window average. As can be seen from both figures, the late-time behavior of both BTCs is essentially power-law. The H11-1 BTC has a slope of about 2.1 after $3 \times 10^5$ s (83 h). The slope of the H11-1 BTC appears to become more negative after about $3 \times 10^6$ s (830 h), but this may be due to a 70% increase in the pumping rate at that time. In addition, the accuracy of the data is relatively low after $3 \times 10^6$ s, making slope calculations uncertain. The H19S1-1 BTC has a constant slope of about 2.3 from $6 \times 10^5$ s (170 h) to the end of the test. Note that conventional (single-rate) diffusion can only provide a constant late-time slope of $3/2$, which is shown for comparison in Figure 6a.

The late-time behavior of the SWIW tests was interpreted by Haggerty et al. [in review] using a lognormal density function of diffusion rate coefficients ($D_\alpha/\alpha^2$). As shown in that paper, a lognormal density function does an excellent job of representing the entire BTC (with $\sigma = 3.55$ for H11-1 and $\sigma = 6.87$ for H19S1-1). However, based on the BTC data alone it is not possible to rule out other density functions of rate coefficients, including a gamma density function or a power-law density function.
4.2. Implications of Power-Law BTC Behavior

We note again that both the gamma and power-law density functions result in power-law BTCs at late time. The conventional diffusion model also causes power-law BTCs with a slope of 3/2 prior to $t \sim x^2/D_a$. There are four important scenarios for such power-law behavior.

CASE 1 – Power-law behavior to infinite time and $k \leq 3$: The first scenario is that the BTC behaves as a power law over all time (i.e., the slope of the BTC would be power-law to infinite time) and the slope is less than 3. It is important to note that (1) this is physically possible provided that the slope $k$ is also greater than 2; and (2) several papers effectively invoke Case 1 by assuming a gamma density function and finding estimates of $\eta$ less than 1 [e.g., Connaughton et al., 1993; Pedit and Miller, 1994; Culver et al., 1997; Werth et al., 1997; Deitsch et al., 1998; Kauffman et al., 1998; Lorden et al., 1998]. In Case 1, the mean residence time in the immobile domain must be infinite.

Consequently, there can be no effective single-rate model that is equivalent to the multirate model in the way that a single-rate first-order model is approximately equivalent to a conventional single-rate diffusion model. No single-rate (either first-order or diffusion) model can yield the same second or higher temporal moments as the multirate model. In fact, any single-rate model (either first-order or diffusion) fit to data will have parameters that are a function of the experimental observation time (i.e., the experiment length).

CASE 2 – Power-law behavior longer than experimental time-scale and $k \leq 3$: The second scenario is that the power-law behavior ends at a particular time that is
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1 beyond the experimental observation time, and the slope is less than 3. In this case, the
2 mean residence time in the immobile domain cannot be ascertained from the
3 experimental data alone. In other words, it is impossible, based solely on the BTC data,
4 to estimate an effective rate coefficient: the effective rate coefficient could be either
5 undefined (as in Case 1) or simply longer than the inverse of the experimental time.
6
7 If the slope $k$ is less than 2, then the power-law behavior either must end at some
8 time or the slope must steepen to greater than 2. Such is the case with conventional
9 diffusion and a slope of 3/2. Because the immobile domain cannot be infinitely thick, the
10 power-law behavior with $k$ less than 2 must end at some time. However, without
11 information external to the tracer test data, the time at which the power-law behavior
12 ends (and therefore the mean residence time in the immobile domain) cannot be known.
13
14 **CASE 3 – Power-law behavior ends within experimental time-scale:** The third
15 scenario is that the power-law behavior ends within the experimental observation time.
16 An example of this is the conventional diffusion model with a slope of 3/2 at
17 intermediate time. In this case, an effective rate coefficient or mean residence time in the
18 immobile domain can be estimated. The mean residence time will be larger for smaller
19 slopes, and for very small slopes will approach the inverse of the time at which the
20 power-law behavior ends. Note that Case 3 cannot be modeled by a gamma density
21 function because a gamma density function does not allow for an end to the power-law
22 behavior.
23
24 **CASE 4 – Power-law behavior with $k > 3$:** The fourth scenario is that the BTC
25 has a slope greater than 3. In this case the mean residence time can be estimated even if
26 the power-law behavior extends to infinite time. This is because the harmonic mean of a
power-law density function is non-zero and dominated by the value of \( \alpha_{\text{max}} \), provided that 
\( k > 3 \).

Which scenario do the WIPP SWIH tracer tests fall into? Based on the BTC data alone, H19S1-1 must be either Case 1 or Case 2. Since the power-law behavior extends to the end of the data set, it is not possible to estimate the mean residence time of the immobile domain. We know only that the mean residence time must be at least the inverse of the experimental time (i.e., \( \sim 1.9 \times 10^6 \) s). H11-1, on the other hand, may be Case 3. If the marked change in slope at approximately \( 3 \times 10^6 \) s is not primarily due to the increase in pumping rate, then H11-1 is Case 3. However, if this is an artifact of the increase in pumping rate, then H11-1 may be Case 1 or 2. Given the data uncertainty after approximately \( 2 \times 10^6 \) s (560 h) and the fact that we have not investigated the case of time-varying pumping rate, we remain uncertain as to which case H11-1 falls under.

5. Conclusions

With improvements in experimental and analytical techniques, breakthrough curves (BTCs) are now available from many laboratory and field experiments with several orders of magnitude of data in both time and concentration. The late-time behavior of BTCs is critically important for the evaluation of rate-limited mass transfer, especially if discrimination between different models of mass transfer is desired. Double-log plots of BTCs are particularly helpful and commonly yield valuable information about mass transfer.

We have six primary conclusions.
First, we derived a simple analytical expression for late-time BTC behavior in the presence of mass transfer. Equation (12) gives the late-time concentration for any linear rate-limited mass transfer model for either zero-concentration or equilibrium initial conditions. The expression requires the advection time-scale, the zeroth moment of the injection pulse, the initial concentration in the system, and the memory function $g(t)$ be known. Note that caution is advised in using (12) if the variance of $t_{ad}$ may be large (such as in a strongly heterogeneous velocity field).

Second, the memory function $g(t)$ is proportional to the residence time distribution in the immobile domain given a unit impulse at the surface of the immobile domain. This memory function is simply the derivative of the Laplace transform of the density function of rate coefficients describing the immobile domain. Consequently, the late-time concentration is proportional to the first or second derivative of the Laplace transform of the density function of rate coefficients.

Third, the effective rate coefficient that yields the same zeroth, first, and second BTC temporal moments as does the full density function is the harmonic mean of the density function of rate coefficients. However, for any density function of rate coefficients with power-law $\alpha^{k-3}$ as $\alpha \to 0$ and where $k \leq 3$, the harmonic mean is zero. Consequently the mean residence time in the immobile domain is infinite and there is no single effective rate coefficient. This applies both to density functions of diffusion rate coefficients and density functions of first-order rate coefficients. Many such distributions have been invoked in the literature.
Fourth, if the BTC (after a pulse injection) goes as \(- t^k\) as \(t \to \infty\), then the underlying density function of rate coefficients must be \(- \alpha^{k-3}\) as \(\alpha \to 0\). This holds for density functions of both first-order and diffusion rate coefficients. For a BTC from a medium with initially non-zero but equilibrium concentrations, the equivalent BTC goes as \(t^{-k}\).

Fifth, if the slope of a BTC (after a pulse injection) goes to \(k\) as \(t \to \infty\), and \(k \leq 3\), then the mean residence time in the immobile domain is infinite. (This is a corollary to the third and fourth conclusions.) Consequently there is no single effective rate coefficient in this medium. A second consequence is that any single-rate (either diffusion or first-order) rate coefficient estimated from the BTC will be a function of experimental observation time. Again, for a BTC from a medium with initially non-zero but equilibrium concentrations, then the equivalent BTC goes as \(t^{k+1}\).

Sixth, if a BTC exhibits power-law behavior \((c \sim t^k)\) to the end of the experiment, then one of two cases must exist. If \(k \leq 3\) then the mean residence time (and effective rate coefficient) cannot be estimated from the BTC. The mean residence time must be at least the experimental observation time and could be infinite. If \(k > 3\) then the mean residence time (and its inverse, the effective rate coefficient) can be estimated.

References


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Figure 1: Late-time solution and full ADMT solution for spherical diffusion.

\[
\frac{c}{f_{ad}m^0\beta_{tot}\left(\frac{D_{ad}}{a^2}\right)^2} \quad [-]
\]

Figure 2: Late-time solution and full ADMT solution for gamma distribution of first-order rate coefficients.

\[
\frac{c}{f_{ad}m^0\beta_{tot}\left(\frac{D_{ad}}{a^2}\right)^2} \quad [-]
\]
Figure 3: Late-time solution and full ADMT solution for lognormal distribution of diffusion rate coefficients. The value $e^m$ is the geometric mean of the distribution.

Figure 4: Late-time solution and full ADMT solution for power-law distribution of first-order rate coefficients.
Figure 5: Slopes of late-time double-log breakthrough curves. Note that during the time that the BTC is dominated by advection and dispersion (i.e., at early time), the slopes will be different from those shown here. Nondimensional time is given as in Figures 2, 3, and 4 for each of the models.
Figure 6: Plots of SWIW data from the WIPP site (a) and the slopes of the data (b). For comparison of slopes to conventional diffusion, the extra lines in 6(a) have slopes of 3/2 and 5/2. Confidence intervals (95%) are shown as thin solid lines above and below the data.