What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental results

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Received 13 September 2002; revised 26 June 2003; accepted 7 August 2003; published 14 January 2004.

[1] Estimates of mass transfer timescales from 316 solute transport experiments reported in 35 publications are compared to the pore-water velocities and residence times, as well as the experimental durations. New tracer experiments were also conducted in columns of different lengths so that the velocity and the advective residence time could be varied independently. In both the experiments reported in the literature and the new experiments, the estimated mass transfer timescale (inverse of the mass-transfer rate coefficient) is better correlated to residence time and the experimental duration than to velocity. Of the measures considered, the experimental duration multiplied by $1 + \beta$ (where β is the capacity coefficient, defined as the ratio of masses in the immobile and mobile domains at equilibrium) best predicted the estimated mass transfer timescale. This relation is consistent with other work showing that aquifer and soil material commonly produce multiple timescales of mass transfer. *INDEX TERMS:* 1829 Hydrology: Groundwater hydrology; 1831 Hydrology: Groundwater quality; 1832 Hydrology: Groundwater transport; 3210 Mathematical Geophysics: Modeling; *KEYWORDS:* multirate, scale-dependence, rate limitations, heavy tails, diffusion, sorption

Citation: Haggerty, R., C. F. Harvey, C. Freiherr von Schwerin, and L. C. Meigs (2004), What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental results, *Water Resour. Res.*, *40*, W01510, doi:10.1029/2002WR001716.

1. Introduction

[2] Understanding rate-limited mass transfer in natural permeable media is critical for predicting contaminant and natural geochemical behavior in groundwater. However, developing accurate physically based model of transport and mass transfer over multiple spatial and temporal scales is difficult because effective parameters at larger scales, particularly at the field scale, may not be simple averages of these small-scale parameters, even though these parameters may have a well-defined and physically based meaning at the small scale. For rate-limited mass transfer, the effective parameters may depend on the temporal as well as spatial scale. Developing an understanding of how mass transfer parameters depend on temporal scale is important if mass-transfer models are to be usefully applied to long-term solute transport problems at the field or regional scale.

[3] Mass transfer is the movement of solute between mobile and immobile zones or states by either physical or chemical processes. Physically immobile zones have low hydraulic conductivity (K [L T^{-1}]) and may be of any size including individual mineral grains. Movement between these low-K and high-K zones is by advection and diffusion, and occurs over multiple timescales within a typical medium. Sorption and desorption transfer solute between mobile and immobile states in both the low- and high-K zones, increase the capacity for the low-K zones to take up mass, and decrease the rate of exchange between zones. Variability in sorption strength and kinetics also add to the variability in mass-transfer timescales. Mass transfer is considered rate-limited when an exchange timescale is of the same magnitude or longer than the characteristic timescale of advection through the medium. This exchange may be controlled by either advection or diffusion within low-K immobile regions (depending on which process is faster) or rate-limited sorption (slow kinetics). Key consequences of mass transfer on solute transport include (1) increased sequestration time within geologic formations; (2) reduction in average solute velocity relative to a conservative solute by up to several orders of magnitude; (3) long "tails" in concentration histories during solute from a permeable medium; (4) poor predictions of solute behavior over long timescales; and (5) increased solute mixing and access to rock surface for reactions.

[4] Several papers have found that field- and lab-scale values of mass transfer parameters obtained from groundwater tracer tests are dependent upon velocity, but the reason for the velocity dependence remains unclear. *Brusseau* [1992] reports that the first-order rate coefficient α [T^{-1}] for sorbing compounds changes in proportion to average pore-water velocity (v [LT^{-1}]), and suggests that this may be due to averaging of a time-dependent process or averaging of multiple rates. *Bajracharya and Barry* [1997] report that α changes approximately linearly with v when

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0043-1397/04/2002WR001716

the dispersion coefficient is also varied with v. *Griffioen et al.* [1998] review literature values of α for sorbing and nonsorbing compounds in saturated and unsaturated media and report a linear relationship between α and v. They also report a correlation between α and advection rate (v/L) [T^{-1}] (where L [L] is the distance along a stream tube from injection to measurement) but attribute the correlation only to a correlation with velocity. *Pang and Close* [1999] report, based on field breakthrough curves (BTCs) over multiple distances in a single aquifer, that α is more highly correlated to v/L than to v alone. *Maraqa* [2001], in a review of a large number of experiments with sorbing and nonsorbing tracers, find that α and v are strongly correlated, but that the relationship is sublinear, $\alpha \sim v^{\eta}$, with η ranging from 0.71 to 0.85 for nonsorbing solutes and approximately 0.97 for sorbing solutes. However, Maraqa finds a stronger correlation between α and advection rate that is also sublinear.

[5] Previous theoretical work has suggested two primary mechanisms for the correlation between α and v. The first is advection through low-K zones. *Li et al.* [1994] show that advection through low-K lenses in a binary medium causes α to scale with v if the inclusion Peclet number, Pe_i ($Pe_i \sim v_i a/D_p$, where v_i [LT^{-1}] is the average pore-water velocity in the inclusion, a [L] is the inclusion radius, and D_p [L^2T^{-1}] is the pore diffusivity), is larger than 1. *Bajracharya and Barry* [1997] confirm from a numerical study that in nonstructured media with random heterogeneities α increases in proportion to v^{η}, where η [] was typically well approximated as 1. *Guswa and Freyberg* [2000] demonstrate that advection through low-K inclusions can lead to BTCs with tailing very similar to the tailing caused by diffusive mass transfer when $Pe_i > 1$, and that the equivalent α would scale linearly with v. However, when $Pe_i < 1$, the behavior of the BTC is well described by a diffusive mass transfer model. *Zinn and Harvey* [2003] show that α varies linearly with v (1) if high-K regions are spatially connected, (2) if the variance and spatial scale of K heterogeneity fall in a range where tailing occurs, and (3) if transport into low-K regions is not controlled by diffusion. *Zinn and Harvey* conclude that advection into low-K areas may create tailing that cannot be explained by a Fickian macrodispersion model in fields with connected high-K paths, even though these fields have conventional univariate lognormal histograms and covariance functions.

[6] A second explanation for the correlation between α and v, stated in a very general way, is that the mass transfer model does not adequately characterize the underlying physics of mass transfer. This explanation has received less attention, but has been known in the literature for almost 50 years. *Glueckauf* [1955] and *Rao et al.* [1980a] show that when a simple linear mass-transfer model is used to approximate diffusion into spheres, the effective α changes with the duration of the experiment. Rao et al. also show that the estimated value of α decreases with increasing experimental duration until the mass transfer time ($a^2/15D_p$ for diffusion in spheres [*Glueckauf*, 1955]) is reached. Consequently, the estimated α may vary with v/L because increased v/L typically reduces the experimental duration. In a series of numerical experiments, *Young and Ball* [1995] estimate the parameters of a first-order mass transfer model by fitting BTCs generated by a diffusive mass transfer model and found results consistent with Rao et al.'s: Estimated values of α decreased as a power of v/L until the mass transfer time was reached.

[7] Many studies have found diffusion or sorption to be characterized by multirate mass transfer [*Haggerty and Gorelick*, 1995], typically described by a distribution of rate coefficients (either first-order or diffusion) [*Ball and Roberts*, 1991; *Connaughton et al.*, 1993; *Pedit and Miller*, 1994, 1995; *Backes et al.*, 1995; *Chen and Wagenet*, 1997; *Culver et al.*, 1997, 2000; *Werth et al.*, 1997; *Deitsch et al.*, 1998; *Haggerty and Gorelick*, 1998; *Kauffman et al.*, 1998; *Lorden et al.*, 1998; *McLaren et al.*, 1998; *Sahoo and Smith*, 1997; *Hollenbeck et al.*, 1999; *Rügner et al.*, 1999; *Stager and Perram*, 1999; *Haggerty et al.*, 2000, 2001; *Karapanagioti et al.*, 2000; *Werth and Hansen*, 2002]. Multirate mass transfer is conceptualized as being a result of sub-REV-scale heterogeneity and may be the result of variability in sorption, diffusion, or advective properties of the medium. For a discussion on sources of variability, see *Pedit and Miller* [1994], *Haggerty and Gorelick* [1995, 1998], *Pignatello and Xing* [1996], and *Karapanagioti et al.* [2000]. No natural geologic materials are truly homogeneous; thus, where mass transfer is important, we would always expect at some scale that there would be multiple rates of mass transfer.

[8] Since single-rate mass transfer models do not capture multirate behavior, we hypothesize that where multiple rates mass transfer are important, the timescale of mass transfer estimated from a single rate model will increase with the duration of the experiment t_{exp}. Correlation between α and v should also exist, but may to some extent be spurious because v is confounded with the experimental duration. Our objectives in this paper and accompanying auxiliary material[1] are to examine how mass-transfer parameters depend on pore-water velocity and experimental duration across a wide range of diverse experiments. We tabulate a large number of estimated groundwater mass transfer parameters reported in the literature within a unified mathematical framework for mass transfer and also provide a new experimental data set in which diffusion into multiple grain sizes produced mass transfer rate coefficients that scale with experimental duration.

2. Mass Transfer Parameters in the Literature

2.1. Transport ADE With Mass Transfer

[9] One challenge for comparing mass transfer data across different studies is finding consistent definitions of parameters, which originate in the numerous forms of the advection-dispersion-mass transfer (ADMT) equations. The main variations of the equations result from a choice between a first-order mass transfer equation and a diffusion equation. Other variations result from different parameter definitions, such as inclusion or exclusion of porosity from the mass transfer rate coefficient. Numerous authors have compared the various models [e.g., *Villermaux*, 1974, 1981; *Rao et al.*, 1980a, 1982; *Nkedi-Kizza et al.*, 1984; *van Genuchten*, 1985; *Parker and Valocchi*, 1986; *Goltz and Roberts*, 1987; *Harmon et al.*, 1989; *Sudicky*, 1990; *Sardin*

[1] Auxiliary materials are available at ftp://ftp.agu.org/apend/wr/2002WR001716.

et al., 1991; *Haggerty and Gorelick*, 1995; *Harvey and Gorelick*, 1995; *Young and Ball*, 1995; *Cunningham and Roberts*, 1998; *Haggerty et al.*, 2000]. Throughout this paper, we will refer to the following form of the ADMT equation [*Haggerty et al.*, 2000], which encompasses all linear mass transfer models, provided that initial concentrations are at equilibrium (could be zero):

$$\frac{\partial c}{\partial t} + \beta \int_0^t \frac{\partial c(t-\tau)}{\partial t} g^*(\tau) d\tau = \frac{\alpha_L v}{R_m} \frac{\partial^2 c}{\partial x^2} - \frac{v}{R_m} \frac{\partial c}{\partial x} \qquad (1)$$

where c [ML^{-3}] is mobile concentration; β [] is the capacity coefficient, equal to the ratio of tracer mass in the immobile zone divided by that in the mobile zone at equilibrium; g^* [T^{-1}] is a memory function and is formally the probability density that a molecule having entered the immobile zone at $t = 0$ remains in the immobile zone at time t; τ [T] is a variable of integration; α_L [L] is dispersivity; v [LT^{-1}] is the average pore-water velocity (equal to q/θ_m where q [$L^3\ L^{-2}\ T^{-1}$] is the specific discharge and θ_m [] is the effective porosity of the medium); R_m [] is the retardation factor in the mobile zone, which is equal to 1 in the absence of an instantaneously sorbing or immobile fraction; t [T] is time; and x [L] is the space coordinate. The derivative of the memory function g^* is linearly proportional to the residence time distribution in the immobile zone. For a mathematical discussion of the convolution approach given in equation (1), see *Hornung and Showalter* [1990], *Peszyńska* [1996], and *Hornung* [1997].

[10] Equation (1) is a general formulation of the ADMT equations and encompasses all forms of linear mass transfer (single or multiple zones for sorption and/or diffusion in series or parallel, and either advection- or diffusion-controlled) through specification of g^*, the memory function. *Haggerty et al.* [2000] provide the function βg^*, denoted as g in that paper, for a range of conventional and unconventional models, which from a functional perspective are either of form $g^*(t) \sim e^{-\alpha t}$ or $g^*(t) \sim t^{1-k}$. Recent work shows that equation (1) can be represented as a continuous-time random walk and that equation (1) can be extended to include non-Fickian dispersion [*Dentz and Berkowitz*, 2003]. When $g^*(t) \sim t^{1-k}$, *Schumer et al.* [2003] show that equation (1) can be represented with a fractional-in-time ADE.

[11] The characteristic residence time in the immobile zone or zones of slow advection (hereinafter called the "mass transfer time"), t_α [T], is

$$t_\alpha = \int_0^\infty t\, g^*(t) dt \qquad (2)$$

The characteristic residence time in the mobile zone (hereinafter called the "advection time"), t_{ad} [T] is

$$t_{ad} = \frac{LR_m}{v} \qquad (3)$$

The ratio of the advection time scaled by $(1 + \beta)$ and the mass transfer time is a Damkohler number [],

$$Da_1 = \frac{t_{ad}(1+\beta)}{t_\alpha} \qquad (4)$$

In the absence of dispersion, t_{ad} represents the pore water residence time in the mobile domain and t_{ad} $(1 + \beta)$ represents the mean solute residence time [*Harvey and Gorelick*, 1995] (hereinafter referred to as the "solute residence time").

[12] Equation (1) reduces to the Fickian case (ADE) when $t \gg t_\alpha$, so that $Da_1 \gg 1$. This occurs when $g^*(t) \sim e^{-\alpha t}$ or $g^*(t) \sim t^{1-k}$ and $k > 3$. Interestingly, equation (1) can never reduce to an ADE if $g^*(t) \sim t^{1-k}$ and $k < 3$ [*Margolin and Berkowitz*, 2000; D. Benson, personal communication, 2002].

2.2. Selection of Literature Data

[13] We compiled estimates of mass transfer parameters from 316 solute transport experiments described in 35 publications [*Angley et al.*, 1992; *Bajracharya and Barry*, 1997; *Brusseau et al.*, 1991; *Brusseau et al.*, 1994; *Cameron and Klute*, 1977; *Connaughton et al.*, 1993; *de Smedt and Wierenga*, 1984; *de Smedt et al.*, 1986; *Freiherr von Schwerin*, 2002; *Goltz and Roberts*, 1986; *Gvirtzman and Gorelick*, 1991; *Haggerty and Gorelick*, 1998; *Haggerty et al.*, 2001; *Jones et al.*, 1992; *Koch and Flühler*, 1993; *Kookana et al.*, 1993; *Krupp and Elrick*, 1968; *Lee et al.*, 1988; *Li et al.*, 1994; *Mallants et al.*, 1994; *Moench*, 1995; *Nkedi-Kizza et al.*, 1984, 1989; *Pang and Close*, 1999; *Pignatello et al.*, 1993; *Ptacek and Gillham*, 1992; *Quinodoz and Valocchi*, 1993; *Seyfried and Rao*, 1987; *Smettem*, 1984; *Thorbjarnarson and Mackay*, 1994a, 1994b; *van Genuchten and Wierenga*, 1977; *van Genuchten et al.*, 1977; *Harvey and Gorelick*, 2000; *Miller and Weber*, 1986]. While our search was not exhaustive, we attempted to include the majority of studies reported in the groundwater literature. We included studies employing both first-order and diffusive mass transfer as a modeling method, sorbing and nonsorbing solutes, and lab and field experiments of various flow configurations. Both fractured and porous media were included. The majority of experiments reported by *Griffioen et al.* [1998], *Maraqa et al.* [1999], *Pang and Close* [1999] and *Maraqa* [2001] were included, as well as many that were not reported in these papers. Studies that were intentionally excluded were those where (1) nonlinear sorption or sorption hysteresis was modeled; (2) no transport was involved in the experiments, such as where rates were determined from batch studies; or (3) two or more rate-limited processes were modeled. Studies that modeled nonlinear sorption were excluded because the parameters estimated in these studies cannot be directly compared to those estimated using a linear isotherm. Studies of systems with no transport (i.e., batch experiments) were excluded because solutes do not pass through heterogeneities, and hence these studies provide no insight into the relation of estimated mass-transfer parameters to velocity. In using the data, we have retained the originally published characterization of the material in terms of isotherm linearity, sorbing/nonsorbing, etc., and have not attempted to modify or correct authors' interpretations of their own data. Furthermore, where authors chose to model the data with a linear isotherm even though the isotherm was somewhat nonlinear (e.g., a Freundlich exponent near but not equal to 1.0), we have included their data. We recognize, however, if sorption isotherms or other parameters frequently have been improperly characterized or modeled, that this could affect our results.

[14] Most studies estimated parameters by minimizing the squared difference between arithmetic values of concentration and model. A number of recent studies, however, minimize the difference between the logarithms of concentration and model. These studies emphasize the late-time behavior of the breakthrough curve or mass balance. Parameters determined from logarithms of breakthrough concentration are hereinafter referred to as "estimates from log concentration."

2.3. Comparison of Literature Data

[15] For our investigation, we require v, L, t_α, t_{ad}, t_{exp}, R_m, Da_1, β, and combinations of these parameters from each of the studies in the literature. In this section we outline how these parameters were obtained (1) from studies that employed the same model but with different choices of parameters and (2) from studies that employed different models (the diffusion model versus the first-order model). The parameters v and L generally were provided in each paper, though in many cases v had to be determined from q and values of porosity. The experimental duration t_{exp} was read manually from graphs of BTCs and was assumed to be the time of the last data point. The value of Da_1 was calculated from other parameters. In two-region models (with a rate-limited and an instantaneous mass transfer fraction), equations were placed in a "canonical" form as presented by *Haggerty and Gorelick* [1995] and then needed parameters were calculated from other parameters (e.g., see equation (8) below).

2.3.1. First-Order Mass Transfer Models

[16] *Nkedi-Kizza et al.* [1984] and *Haggerty and Gorelick* [1995] showed that various first-order mass transfer models (e.g., one- and two-site models, chemical and physical nonequilibrium models) are mathematically identical. The majority of studies have employed one of these forms of the ADMT equations, which makes the task of obtaining t_α and other parameters a matter of algebraic manipulation and careful attention to parameter definitions in each of the papers. Typically this model defines the rate of change of immobile concentration as

$$\frac{\partial c_{im}}{\partial t} = \alpha(c - c_{im}) \tag{5}$$

where c_{im} [ML^{-3}] is the average immobile zone concentration and α is a first-order rate coefficient. The memory function for the first-order model in equation (1) is [*Haggerty et al.*, 2000]

$$g^*(t) = \alpha e^{-\alpha t} \tag{6}$$

and therefore (from equation (2)) its mass transfer time is

$$t_\alpha = \frac{1}{\alpha}. \tag{7}$$

[17] While there are other formulations of this model, they are mathematically equivalent. One of the most common sets of formulations is that of *van Genuchten and Wierenga* [1976], employed by the frequently used CXTFIT code [*Toride et al.*, 1995]. Comparing equations (15)–(16) of *van Genuchten and Wierenga* [1976, p. 475] to equations (1) and (5) results in

$$t_\alpha = \frac{\theta_{im} + (1-f)\rho K_d}{g} \tag{8}$$

where t_α is as previously defined; θ_{im} [] is immobile water content; f [] is the fraction of the total adsorption sites that are in the mobile zone; ρ [$M\ L^{-3}$] is the bulk density of the medium; K_d [$L^3\ M^{-1}$] is the linear distribution coefficient for a sorbing solute; and α_{vg} [T^{-1}] is the first-order rate coefficient used by *van Genuchten and Wierenga* [1976], which is equal to $\theta_{im}\alpha$. Our capacity coefficient is given by

$$\beta = \frac{\theta_{im} + (1-f)\rho K_d}{\theta_m + f\rho K_d}, \tag{9}$$

where θ_m [] is the mobile water content. Note that β is the same as we have previously defined it, but that this definition is not the same as that of *van Genuchten and Wierenga*'s [1976] β. The relationship between the two definitions is $\beta = (1 - \beta_{vg})/\beta_{vg}$, where β_{vg} is parameter defined by *van Genuchten and Wierenga* [1976, p. 476].

2.3.2. Diffusion Models

[18] While less common than first-order models, diffusion models of mass transfer are also frequently used. The mass transfer time, which can be derived from equation (2) or directly from the diffusion equation and appropriate boundary conditions, is

$$t_\alpha = \frac{a^2}{k_g D_a} \tag{10}$$

where k_g [] is a geometry-dependent coefficient (e.g., 3 for layers and 15 for spheres, and 15 was used in our analysis); a [L] is the radius of the sphere or half-thickness of the layer; and D_a is the apparent diffusivity, equal to the pore diffusivity divided by the retardation factor (R_{im}) within the immobile zone. For diffusion models, the capacity coefficient β is defined the same as for first-order models.

[19] Unfortunately, our data set includes only 22 experiments where diffusion models compatible with equation (10) were reported in the literature. A number of models employ a diffusion model in series with a first-order exchange (resistance) term, which is effectively a "two-rate" model. These were not included in our study since they are not directly comparable to the other models.

3. Analysis

3.1. Time-Averaging of Mass Transfer Rate Coefficients

[20] The mass transfer time given in equation (2) cannot be measured directly, since experiments cannot be run to infinite time. Instead, an effective mass transfer time t'_α is measured, which is approximately the average of the memory function over the experimental duration, t_{exp}:

$$t'_\alpha = \int_0^{t_{exp}} t g^*(t) dt \tag{11}$$

The simple single-rate (or single diffusion component) mass transfer models described above often cannot represent the distribution of mass-transfer rates encountered in nature. When this is the case, the estimated rate coefficient becomes a function of how the experiment was conducted, particularly the timescale of the experiment. For the case of the linear driving force approximation (first-order model)

to spherical diffusion, this has been shown previously [*Glueckauf*, 1955; *Rao et al.*, 1980a; *Young and Ball*, 1995]. In the more general case, if a first-order (or diffusion with a single diffusivity and length scale) model is used to model a system where the memory function is actually a different multirate function, the estimated rate coefficient will change with experimental conditions.

[21] Consider the case where the memory function is a power law. The resulting effective rate coefficient will scale with powers of experimental duration. The effective mass-transfer timescale (11) for such a memory function is

$$t'_\alpha \sim t_{\exp}^{3-k},\ k < 3 \tag{12}$$

Equation (12) will hold true over the time period where the memory function is power law, and scaling will stop once the memory function becomes exponential (e.g., once the longest timescale of mass transfer that is associated with significant capacity is reached). Scaling behavior will be important for $k < 3$ and will be particularly strong as k approaches 2 or smaller. Near $k = 2$, $t'_\alpha \sim t_{exp}$. For $k > 3$, other terms in the memory function dominate the average and t'_α does not change significantly with t_{exp}.

[22] A number of tracer tests have been reported with power law memory functions, with $g^*(t) \sim t^{1-k}$ [*Haggerty et al.*, 2000], which includes gamma distributions of rate coefficients (where the shape factor $\eta = k - 2$). *Connaughton et al.* [1993], *Pedit and Miller* [1994], *Culver et al.* [2000, 1997], *Werth et al.* [1997], *Deitsch et al.* [1998], *Kauffman et al.* [1998], and *Haggerty et al.* [2000] used gamma distribution or another power law distribution of rate coefficients and report most cases $2 < k < 3$. *Deitsch et al.* [2000] fit a gamma distribution of rate coefficients to five materials over five different times; 24 of the 25 experiments yielded $2 < k < 3$, with most being very close to $k = 2$. A number of studies have also used lognormally distributed rate coefficients. While not true power laws, lognormal distributions produce similar behavior if the variance is large, with the limit of large variance being equivalent to $k = 2$ [*Haggerty et al.*, 2000]. The number of results with k slightly larger than 2 suggests that we should find estimated mass transfer time correlated to experimental and advection time with powers slightly less than 1.

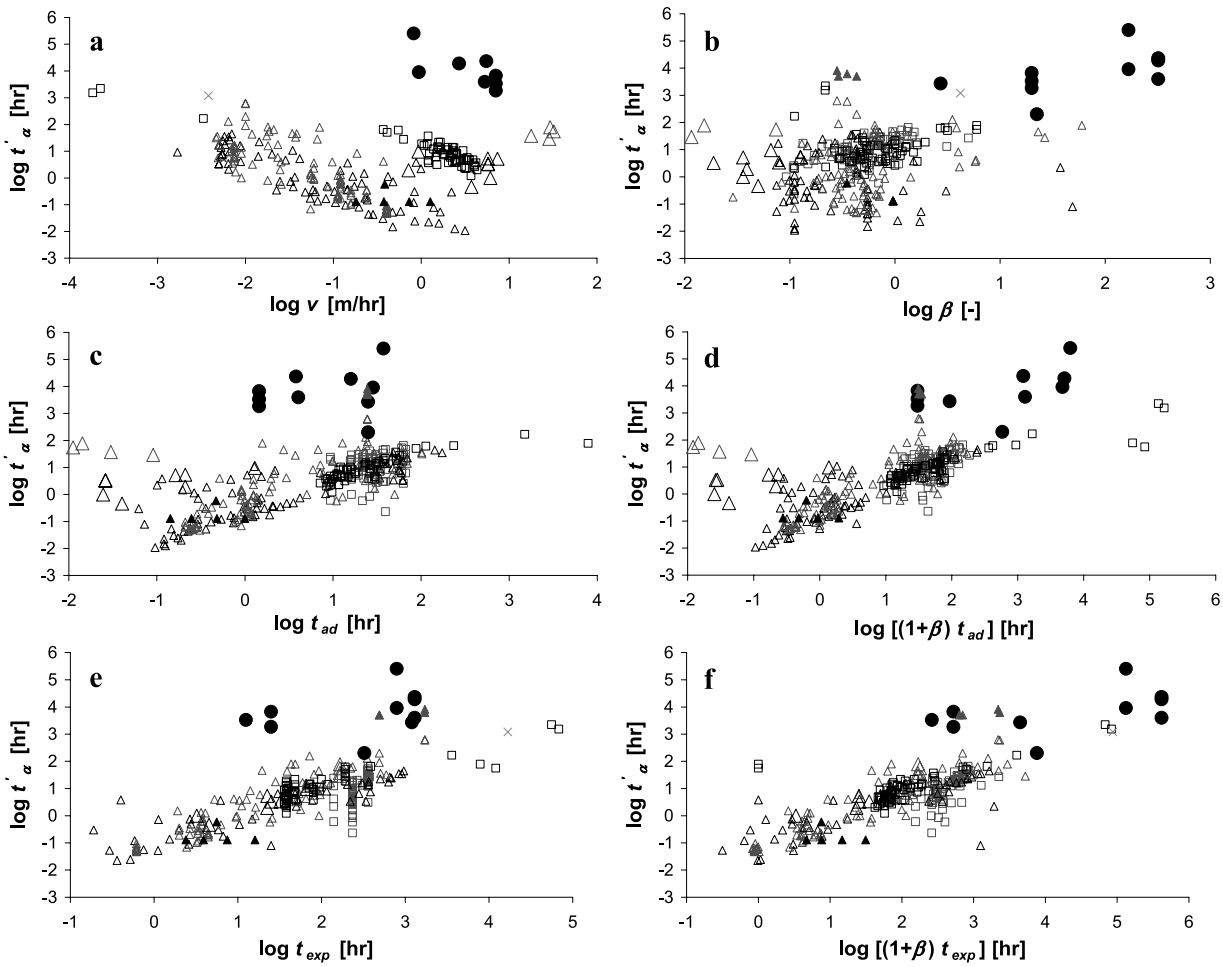
3.2. Analysis of Literature Data

[23] The experiments from the literature were grouped according to four criteria: sorption (yes, no), medium and scale (lab, porous medium field experiment, fractured medium field experiment), the type of model used (first-order model (abbreviated FO in Figure 1), diffusion model), and fitting method (arithmetic concentrations, logarithmic concentrations). This results in 24 possible categories, of which nine have members. One other category is also shown, which refers to cases where moment analysis was used to estimate t_α'. These categories are distinguished by a four-dimensional matrix of symbol properties (color, shape, filled or not filled, size) that can be seen by attribute in Figure 1. For example, all experiments where the tracer was reported to sorb are shown in red, and all experiments modeled by a first-order equation are shown with open symbols. See the legend in Figure 1. All logarithms are base-10. Graphs of t_α' versus various parameter groups are shown in Figure 1; since some papers did not measure or did not report all parameters (or reported zero), all graphs contain less than the maximum of 316 points.

[24] A set of linear regressions was performed on each graph in Figure 1 (i.e., $\log(t'_\alpha)$ versus the logs of v, β, t_{ad}, $(1 + \beta)t_{ad}$, t_{exp}, and $(1 + \beta)t_{exp}$). For each graph, a regression was performed for the following categories: (1) all experiments; (2) experiments with estimates derived by fitting log-concentrations removed); (3) experiments with only sorbing tracers; (4) experiments with only nonsorbing tracers; (5) experiments fit with diffusion models; and (6) experiments fit with first-order models. With the exception of experiments fit with diffusion models, all categories on all graphs have more than 95 points, with most having more than 150 points. We only have 22 points for diffusion models, with 17–19 of them plotted in each graph (some papers did not report all necessary information). For each regression, we calculated the slope, intercept, r^2, p-statistic, the standard errors of the slope and intercept, and the standard deviation of the residuals (the square root of the sum of square errors/degrees of freedom]). All of this is reported in the auxiliary material, and a subset of the information is reported in Table 1. It is important to note that none of these statistics tests the hypothesis that one fit is better than another fit. When the p-statistic and the standard errors of the estimated slope and intercept are reduced from one fit to another, this indicates that the fit is better; however it does not provide a measure of the significance of the improvement. It is possible that the improved fit is not a statistically significant improvement.

[25] The velocity-dependence of the mass transfer rate coefficient is frequently noted [*Brusseau*, 1992; *Griffioen et al.*, 1998; *Maraqa*, 2001; *Maraqa et al.*, 1999; *Pang and Close*, 1999; *Young and Ball*, 1995]. Figure 1a shows $\log t'_\alpha$ versus $\log v$ for 249 experiments. The correlation between $\log t'_\alpha$ and $\log v$ is very poor overall (see Table 1). While there is a slight correlation between $\log t'_\alpha$ and $\log v$ when parameters estimated from log concentration are neglected ($r^2 = 0.16$), the correlation disappears when all values are considered ($r^2 = 0.019$). The p-statistics ($p < 0.05$) do indicate the likely existence of a relation, but the small r^2 shows that velocity poorly predicts t'_α for specific cases. Sorbing solutes show a correlation ($r^2 = 0.19$) which does not exist for nonsorbing solutes ($r^2 = 6.6 \times 10^{-4}$). Several papers have reported high correlation for individual sets of experiments with a single medium and tracer, suggesting that the dominant mechanism for mass transfer may be advection through low-K material (as opposed to diffusion or rate-limited sorption). While in some experiments advection may be the dominant mechanism controlling mass transfer, it is clear that only a weak relationship exists from one study to another when different materials and designs are compared.

[26] While the capacity coefficient β does not appear in equation (11) or (12), some results suggest that the effective mass transfer time scales with β or $1 + \beta$. A plot of $\log t'_\alpha$ versus $\log \beta$ (Figure 1b) also shows a weak correlation ($r^2 = 0.17$ with the parameters estimated from log concentration, and 0.059 without). The stronger correlation with estimates from log concentration may be because late-time concentrations of BTCs are linearly proportional to β and are a simple but nonlinear function of t_α [*Haggerty et al.*, 2000]. Nonsorbing solutes show a stronger correlation ($r^2 = 0.31$)



Symbol	Sorbing	Non-sorbing	Field/ porous	Field/ fractured	Lab	Diffusion	FO	Log	Arithmetic
△	*				*		*	*	
△		*			*		*	*	
●		*		*		*		*	
▲	*				*	*			*
□	*		*				*		*
△		*			*		*		*
△	*				*		*		*
□		*	*				*		*
▲		*			*	*			*
×	*		*			Moment analysis			*

Figure 1. Effective mass transfer time, t'_α, plotted against other parameters from 316 experiments. Red indicates sorbing; black indicates nonsorbing. Symbols are as follows: triangles, lab experiments; circles, field experiments in fractured media; squares, field experiments in porous media; open symbols, parameters estimated from first-order model; closed symbols, parameters estimated from diffusion model; large symbols, parameters estimated from log concentration; small symbols, parameters estimated from arithmetic concentration. See color version of this figure at back of this issue.

than sorbing solutes (r^2 = 0.036). In a series of numerical experiments *Young and Ball* [1995] found, for α fit to models of spherical diffusion, that t'_α is a function of β (note that their definition of β corresponds to that of *van Genuchten and Wierenga* [1976]). In their study, t'_α was correlated with β due to the effect of β on residence time. In our analysis, log t'_α is more strongly correlated with log β for diffusion models (r^2 = 0.27) than for first-order models (r^2 = 0.044), but this m be significant due to the small number of diffusion models in our data set (see the end of this section for further discussion). Other studies [e.g., *Griffioen et al.*, 1998; *Pang and Close*, 1999] have reported that t'_α and β are not correlated.

[27] Figure 1c shows log t'_α versus log t_{ad} (recall $t_{ad} = LR_m/v$, the advective residence time). The correlation between log t'_α and log t_{ad} is stronger than between log t'_α and log v alone, a fact that has also been noted by *Maraqa* [2001] and *Pang and Close* [1999]. Without the parameters

Table 1. Parameters From Linear Fits to Mass Transfer Parameters

Linear fit to	With Log Estimates	r^2	Slope	Intercept	Number of Experiments
Figure 1a: log t'_α versus log v	yes	0.019	−0.19	0.40	249
Figure 1b: log t'_α versus log β	yes	0.17	0.78	0.87	312
Figure 1c: log t'_α versus log t_{ad}	yes	0.36	0.69	0.11	311
Figure 1d: log t'_α versus log $[(1 + \beta)\ t_{ad}]$	yes	0.50	0.76	−0.15	311
Figure 1e: log t'_α versus log t_{exp}	yes	0.61	0.94	−0.84	271
Figure 1f: log t'_α versus log $[(1 + \beta)\ t_{exp}]$	yes	0.69	0.88	−0.95	269
Figure 1a: log t'_α versus log v	no	0.16	−0.46	−0.01	229
Figure 1b: log t'_α versus log β	no	0.059	0.56	0.71	290
Figure 1c: log t'_α versus log t_{ad}	no	0.62	0.85	−0.21	289
Figure 1d: log t'_α versus log $[(1 + \beta)\ t_{ad}]$	no	0.65	0.86	−0.40	289
Figure 1e: log t'_α versus log t_{exp}	no	0.71	0.88	−0.84	249
Figure 1f: log t'_α versus log $[(1 + \beta)\ t_{exp}]$	no	0.65	0.82	−0.90	247

estimated from log concentration, $t'_\alpha \sim t_{ad}^{0.85}$ ($r^2 = 0.62$), and with the estimates from log concentration, $t'_\alpha \sim t_{ad}^{0.69}$ ($r^2 = 0.36$). Mass transfer parameters are better correlated to timescale of transport than to the advection rate alone, particularly if parameters are estimated from arithmetic concentrations. If advection through low-K zones (with a single timescale for advection) were the only mass transfer mechanism, we would expect scaling to be stronger with v than with t_{ad}. Models using log-concentration estimated parameters are more sensitive to small, late-time concentrations, and it is therefore not surprising that these make up a separate population in this figure. Both sorbing and nonsorbing solutes show weak correlation ($r^2 = 0.32$ and 0.39, respectively), probably because estimates from log concentration are included in the analysis of both data sets.

[28] Figure 1d shows log t'_α versus log $[(1 + \beta)t_{ad}]$. In this plot, data with the same value of Da_I lie along a diagonal line with slope 1 (increasing Da_I plot along diagonal lines lower in the graph). The correlation in this plot is stronger than between log t'_α and log v or log t_{ad} alone. Without the estimates from log concentration, $r^2 = 0.65$, and with the estimates from log concentration $r^2 = 0.50$. Nonsorbing solutes show a greater correlation in this plot ($r^2 = 0.62$) than sorbing solutes ($r^2 = 0.35$), but the standard deviation of the residuals is similar (0.81 and 0.86, respectively).

[29] Figure 1e shows log t'_α versus the experimental duration, log t_{exp}. For the first time, we see a relationship that shows similar correlations with and without estimates from log concentration. Without the estimates from log concentration, $t'_\alpha \sim t_{exp}^{0.88}$ ($r^2 = 0.71$), and with estimates from log concentration, $t'_\alpha \sim t_{exp}^{0.94}$ ($r^2 = 0.61$). On the basis of equation (12) we would expect a strong correlation between log t'_α and log t_{exp} if mass transfer is described by a power law distribution of timescales. The slope of the graph in Figure 1e corresponds to an average value of $3 - k$, suggesting k in the range of 2.0–2.2, which corresponds to many values reported in the literature (see section 3.1).

[30] It is possible that the correlation between log t'_α and log t_{exp} is partly due to an underlying correlation between log t_{exp} and log t_{ad}. For model parameters estimated from arithmetic concentrations, log t_{exp} and log t_{ad} are strongly correlated ($r^2 = 0.82$, $N = 248$), but the correlation is weak for log-concentration estimates ($r^2 = 0.38$, $N = 22$). Given a strong correlation between t_{exp} and t_{ad}, the correlation between t'_α and t_{exp} may in part be due to underreporting of parameters where Da_I is very large or very small, an explanation we explore discussion.

[31] We also investigated the relationship between log t'_α versus log $[(1 + \beta)t_{exp}]$, shown in Figure 1f. We find correlations that are similar to those in Figure 1e, with $r^2 = 0.65$ without the estimates from log concentration and with $r^2 = 0.69$ with the estimates from log concentration. Again, the slope is slightly less than 1, suggesting k is slightly larger than 2; however, the inclusion of $(1 + \beta)$ has some effect on the slope, and therefore these slopes may be less meaningful than the plots without $(1 + \beta)$.

[32] As mentioned above, we calculated regression statistics for first-order models and for diffusion models in each of the graphs in Figure 1, and we report these in the auxiliary material. The correlations between log t'_α and other parameters are generally similar to the overall trends for each graph, with the following caveat. Since there are only 22 data points for diffusion models (with only 17–19 of them appearing on any given graph), the statistical significance of the correlations is questionable. While the p-statistic for the regressions with large r^2 is very small (most are smaller than 10^{-10}), the values for the diffusion models are of the order of 10^{-5}. Furthermore, the diffusion model data are clustered, due to the influence of two to three experiments with similar scales. Consequently, any conclusions regarding how diffusion model timescales are correlated to other parameters are tentative and do not have the strength of conclusions for first-order model parameters. With that caveat, and the caveat that we do not test the significance of changes to the fit, the correlation between log t'_α and log t_{ad} is stronger for diffusion models ($r^2 = 0.63$) than for first-order models ($r^2 = 0.50$). Similarly, the correlation between log t'_α and log $(1 + \beta)t_{ad}$ is stronger for diffusion models ($r^2 = 0.71$) than for first-order models ($r^2 = 0.52$), following the trend of increasing correlation for the overall data between log t'_α to log t_{ad}, and log t'_α to log $[(1 + \beta)t_{ad}]$. The correlations between log t'_α and log t_{exp} are similar for diffusion ($r^2 = 0.65$) and first-order ($r^2 = 0.72$) models. The correlations between log t'_α and log $(1 + \beta)t_{exp}$ are also similar for diffusion ($r^2 = 0.68$) and first-order ($r^2 = 0.67$) models.

4. Experimental Evaluation of Mass Transfer Scaling

[33] While it is valuable to compare results across experiments, it is also instructive to consider the results of experiments designed to measure the rate coefficient of a particular material that vary the residence time while hold-

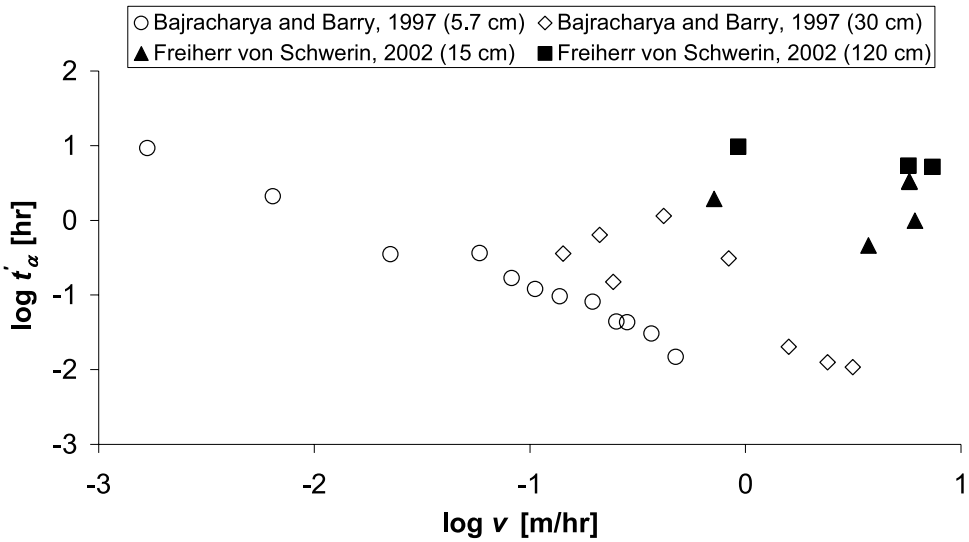


Figure 2. Effective mass transfer time, t'_α, plotted against velocity for experiments from *Bajracharya and Barry* [1997] and *Freiherr von Schwerin* [2002].

ing the velocity constant, or vary the velocity while holding the residence time constant. Experiments conducted at the same velocity, in both short and long columns packed with the same material, separate the effects of multiple timescales of mass transfer from the effects of velocity. Likewise, experiments that hold the advective residence time constant in short and long columns by using different velocities remove the confounding effect that velocity has on residence time for experiments of one length.

[34] *Bajracharya and Barry* [1997] compared estimated rate coefficients between two columns, one 5.7 cm and the other 30 cm, that were both packed with fine sand and polyethylene cylinders of slightly lower hydraulic conductivity, K [L T^{-1}]. The design of the experiments was such that mass transfer was expected to be dominated by advection. The results from Bajracharya and Barry's experiments show that the longer column leads to large estimated values of t_α at the same velocity. Replotting Bajracharya and Barry's data (Figure 2) shows that values of log t'_α plot consistently above and to the right of values for the short column on a plot of log t'_α versus log v. Figure 3 shows that log t'_α is better correlated to log t_{ad} ($r^2 = 0.86$) than log v ($r^2 = 0.65$), and the relation of t'_α to residence time is not related to column length (see Table 2 for regression parameters). This analysis suggests that it may not be the change in v, but the change in t_{ad} or t_{exp}, that affects t'_α (Bajracharya and Barry do not report t_{exp}). A consistent explanation is that there are multiple advective pathways through the low-K material with different residence times, resulting in multiple timescales of mass transfer. At different t_{ad} or t_{exp}, different mass transfer timescales dominate the estimate of t'_α.

[35] To investigate this issue further, we conducted tracer experiments in saturated columns (1-cm-diameter, low-pressure chromatography columns, Kimble/Kontes, Vineland, New Jersey) filled with an artificial sand composed of

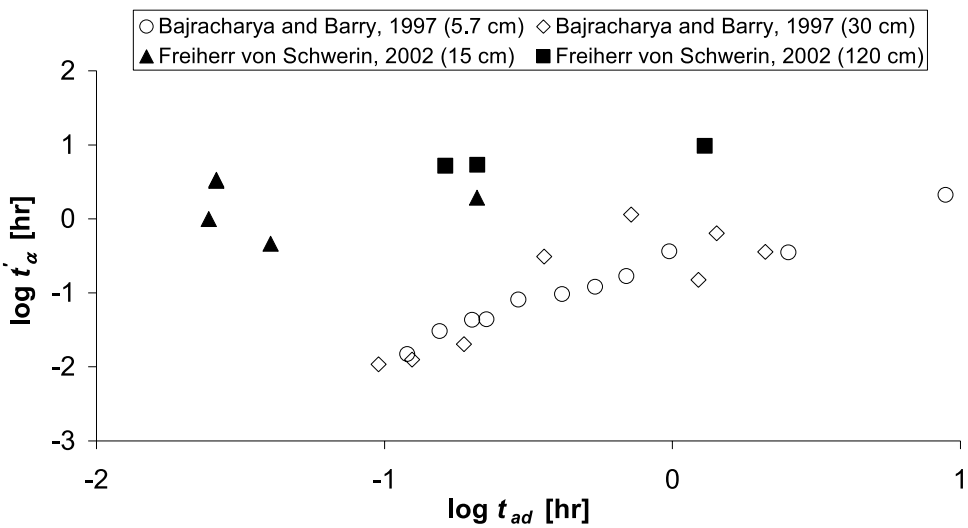


Figure 3. Effective mass transfer time, t'_α, plotted against advection time for experiments from *Bajracharya and* [1997] and *Freiherr von Schwerin* [2002].

Table 2. Parameters From Linear Fits to Mass Transfer Experiments Where Velocity Was Controlled

Linear fit to	r^2	Slope	Intercept	Number of Experiments
Bajracharya and Barry [1997] data: log t'_α versus log v	0.65	−0.79	−1.43	20
Bajracharya and Barry [2002] data: log t'_α versus log t_{ad}	0.86	1.10	−0.61	20
Freiherr von Schwerin [2002] data: log t'_α versus log v	0.016	−0.14	0.50	8
Freiherr von Schwerin [2002] data: log t'_α versus log t_{ad}	0.41	0.44	0.88	8
Freiherr von Schwerin [2002] data: log t'_α versus log [$(1 + \beta)\ t_{exp}$]	0.83	0.84	−0.67	8

a mesoporous silica glass (Vycor, Corning Glass, Inc., New York, New York), crushed and packed in small aliquots into 15- and 120-cm-long columns. The grain size distribution was approximately power law with the probability density function scaling approximately as $(\text{diameter})^{-1}$ over the diameter range 0.18–3.4 mm. A 1-pore-volume pulse of uranine (Fisher Scientific, Pittsburgh, Pennsylvania) was injected into the column followed by tracer-free deionized water. Uranine was selected as the tracer because it enabled us to make concentration measurements spanning several orders of magnitude using an inline Turner 10-AU fluorometer equipped with a small-volume (3-mm diameter) flow cell (Turner Designs, Sunnyvale, California). The tracer and flushing solutions were maintained at pH 8 so that uranine would be anionic and sorption would be negligible [*Kasnavia et al.*, 1999]. Diffusion into and out of the multiple grain sizes produced long tails in breakthrough curves, which were analyzed using a Laplace-domain solution of equation (1). Additional experimental and analytical details are provided by *Freiherr von Schwerin* [2002] and in a forthcoming paper by C. Freiherr von Schwerin et al. (manuscript in preparation, 2003).

[36] The values of log t'_α are graphed space versus log v, log t_{ad}, and log [$(1+\beta)\ t_{exp}$] in Figures 2, 3, and 4, respectively. Parameters for the corresponding linear regressions in log space are shown in Table 2. The relationship between log t'_α and log v is extremely weak, with $r^2 = 0.016$. The correlation is stronger between log t'_α and log t_{ad} ($r^2 = 0.40$), and is strongest for log t'_α versus log [$(1 + \beta)\ t_{exp}$] ($r^2 = 0.83$).

[37] In these experiments the porous medium has a power law grain-size distribution resulting in diffusion-limited mass transfer and $g^*(t) \sim t^{-1}$ (i.e., $k \approx 2$) over all timescales observed in the lab. Therefore equations (11)–(12) predict that $t'_\alpha \sim t_{exp}^{1.0}$. In fact, we see $t'_\alpha \sim t_{exp}^{0.84}$. In contrast to *Bajracharya and Barry*'s [1997] experiments, the range of mass-transfer rates is caused by diffusion rather than advection in the low-K inclusions.

5. Discussion

[38] Two general explanations exist in the literature for t'_α scaling with velocity. One general explanation, which we favor, is that mass transfer is primarily controlled by diffusion, but that single-rate models oversimplify the process of mass transfer and therefore model fits become dependent upon the experimental conditions. The most basic oversimplification, of course, is the assumption of a single timescale of diffusion when a large range of timescales are present. This explanation is first of all supported by the information presented above in Figure 1, showing the much stronger correlation of log t'_α to log t_{ad}, log t_{exp}, or log [$(1 + \beta)\ t_{exp}$] than of log t'_α to log v. Lab experiments that specifically control for velocity in a medium with multiple timescales of mass transfer also show a strong correlation of log t'_α to log t_{ad}, log t_{exp}, and log[$(1 + \beta)\ t_{exp}$]. Material that produces multiple timescales of mass transfer will produce tailing in experiments of different duration. The strongest tailing in an experiment is always due to the mass transfer process with approximately the same timescale as advection through the system. Consequently, a model assuming a single timescale of mass transfer fits the data best when $t'_\alpha \approx t_{ad}$. This scaling will persist over different experimental durations as long as significant capacity exists for a distribution of mass transfer rates.

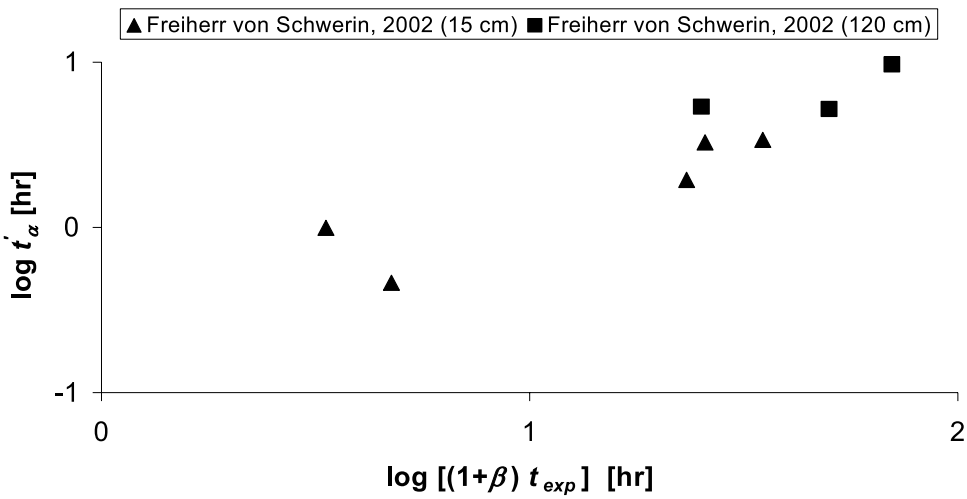


Figure 4. Effective mass transfer time, t'_α, plotted against experimental duration multiplied by $(1 + \beta)$ from *Freiherr hwerin* [2002].

[39] Another explanation is that mass transfer is due primarily to advection through low-K zones, resulting in t'_α directly proportional to v, in a specific material. Although the weak correlation between t'_α and v across many experiments conducted in different materials does not strongly support this mechanism, the process undoubtedly causes some of the variability in t'_α in media where the inclusion Peclet number is larger than 1 [e.g., *Bajracharya and Barry*, 1997; *Guswa and Freyberg*, 2000; *Zinn and Harvey*, 2003]. The inclusion Peclet number is expressed in terms of fundamental parameters as

$$Pe_i = \frac{iKa}{n_e D_p} \tag{13}$$

where i [] is hydraulic gradient and n_e is effective porosity (approximately $10^{-0.5}$ to $10^{-2.5}$). D_p ranges from approximately $10^{-9.5}$ to $10^{-11.5}$ m^2/s for liquid diffusion (minimum agrees with the approximate value found in a literature review of granitic rocks by *Ohlsson and Neretnieks* [1995]). K and a range much more widely. For Pe_i to be greater than 1, (iKa) must be greater than at 10^{-10} to 10^{-14} m^2/s. This criterion is unlikely to be met by individual grains within lab-scale experiments, or within field experiments in fractured rock with low-K matrix blocks (e.g., crystalline rock) for reasonable values of the gradient. Consequently, the trends in the majority of the data presented in Figure 1 cannot be explained by advection through low-K materials. However, this criterion may be met for large inclusions of loosely consolidated material in field experiments. For example, see *Harvey and Gorelick*'s [2000, section 4.3] discussion for the MacroDispersion Experiment (MADE) aquifer, a heterogeneous fluvial aquifer composed of partially consolidated sand, silt, and clay. Consequently, some scaling of mass transfer parameters with velocity would be expected in porous materials at the field scale.

[40] A third potential explanation for the correlations that has not, to our knowledge, been mentioned in the literature is that either nonlinear or hysteretic sorption could create spurious correlations between estimated parameters such as t'_α and velocity when a linear model is fit to the data. *Jaekel et al.* [1996] showed that power law tailing can result from a pulse injection of solute and equilibrium Freundlich sorption. From a single experiment, the tail can look identical to that resulting from multirate mass transfer with a power law memory function. Consequently, if such tailing were interpreted as linear sorption, the result would be a rate coefficient that scales with velocity and the other system parameters. However, purely physical mass transfer is linear and only 51% of the data we evaluated are from sorbing tracer tests. Furthermore, the solutes in each of the tracer tests used here are described in the original papers as linearly sorbing, so the issue of nonlinear sorption has already been rejected by the original authors. However, to the extent that authors have mistakenly characterized a solute with a linear isotherm when the isotherm is nonlinear, or authors have neglected sorption hysteresis, this will affect our results, since we have followed the authors' characterization.

[41] A fourth explanation for the correlations is that t'_α that are much less than or much greater than t_{exp} are not reported in the literature. Experiments with Damkohler numbers ($Da_I = (1 + \beta)t_{ad}/t_\alpha$) very different from 1 may be modeled reasonably well without considering mass transfer at all [e.g., *Bahr and Rubin*, 1987; *Jennings and Kirkner*, 1984], so mass-transfer coefficients are unlikely to be reported. When mass transfer is relatively fast ($t'_\alpha \ll t_{ad}$), chemical sorption may be modeled with a retardation factor and physical mass transfer will not be detected by most experiments [*Zinn and Harvey*, 2003]. When mass transfer is slow ($t'_\alpha \gg t_{ad}$) neither chemical nor physical mass transfer will have time to occur and for the physical case a small mobile porosity or domain volume will be estimated. Recall that a diagonal line on Figure 1d with slope of 1 would represent all mass transfer parameters with a single value of Da_I. An analysis of Da_I without the log-concentration estimates shows that this dimensionless parameter is lognormally distributed with a mean log(Da_I) of 0.56 and a standard deviation log(Da_I) of 0.63. The fifth percentile of the reported values of Da_I without log-concentration estimates is 0.29 and the 95th percentile is 24.7, and 50% of the reported values are between 2.2 and 7.4. The majority of reported parameters fall within the range needed to see a significant mass transfer effect, suggesting that experiments that would fall far off the diagonal in Figure 1d are not frequently reported with mass transfer parameters. Experimentalists may also choose the length of their experiments t_{exp} to be of the order of t'_α based on prior experience. This bias may be most prevalent for lab experiments where researchers may have experience with the timescales required to produce tailing. The degree to which these biases occur is unknown.

[42] To the extent that memory functions have fat tails (i.e., power law distributions of mass transfer rate coefficients), the strong correlation between log t'_α and log t_{exp} suggests that in many experiments information important to the mass transfer model is being lost due to truncation of data collection. Collection of more data, which in most cases likely requires examination of log values of small late-time concentrations, would modify the estimated mass transfer parameters. Inclusion of such late-time data will be more important for smaller values of k (shallow late-time slopes in the data) than for larger values of k. Small values of k result in solute behavior that can never adequately be modeled as Fickian using the ADE. Modeling errors caused by failure to characterize fat-tailed memory functions will be particularly serious when making predictions at timescales larger than the experimental duration. For example, transport models of nuclear waste escape are used to make predictions that are orders of magnitude in time beyond what can be experimentally examined, and are therefore most susceptible to errors in upscaled plume velocities and peak concentrations.

[43] Separate analysis of sorbing and nonsorbing (as reported in the original publications) solutes shows that both have similar trends and correlations. The correlations of t'_α to v and β are weak for both sorbing and nonsorbing solutes (although the p-statistics indicate a relation). The correlations of log t'_α to log t_{ad} and log $[(1 + \beta)t_{ad}]$ are greater for both solutes: r^2 is generally between 0.3 and 0.4, with the exception of log t'_α to log $[(1 + \beta)t_{ad}]$ for nonsorbing solutes, where $r^2 = 0.62$. The correlations of log t'_α to log t_{exp} and log $[(1 + \beta)t_{exp}]$ are generally strongest for both sorbing and nonsorbing solutes with r^2 ranging from

0.56 to 0.71, with the greatest correlation for both solutes between log t'_α and log $[(1 + \beta)t_{exp}]$ This suggests that t'_α scales with advection and experimental durations for both sorbing and nonsorbing solutes in a similar fashion. While the underlying mechanisms for the scaling may be different (i.e., possibly multiple timescales of diffusion for nonsorbing solutes versus multiple timescales of kinetic limitations for some sorbing solutes), both appear to cause t'_α to change with timescale.

[44] The literature contains far more examples of first-order than diffusion models, and our data set contains only 22 experiments that employed a diffusion model. While the correlations between log t'_α and other parameters follow the same trends for diffusion models as for the overall data set, the statistical significance of the correlations is questionable. In all cases where log t'_α for diffusion models was strongly correlated to other variables, the *p*-statistic was much larger than for first-order models, suggesting that the results for diffusion models are not as significant, and the clustering of data from particular sources also raises doubts. Both *Rao et al.* [1980a] and *Young and Ball* [1995] showed that given diffusion into a single grain size, a first-order model fit to data from a transport experiment in that material would show power law scaling (up to the mass transfer time for diffusion), whereas the diffusion model would not. It is therefore likely that some of the scaling observed with first-order models would not exist if diffusion models had been used. In media where multiple timescales of diffusion are present, the diffusion models will have the same type of scaling problem that the first-order models have. However, results are inconclusive as to whether such scaling behavior is present in data from the literature.

[45] The strong correlation of effective mass transfer times with both advection time and experimental duration raises the question of whether an estimated mass transfer time from data over one timescale can be adjusted to model a different temporal scale. While it is better, where feasible, to accurately represent the underlying phenomenon, in many practical situations where this is infeasible, the parameters in the linear fits to the data in Figure 1 may be helpful. The auxiliary material provides fits of the form

$$t'_\alpha = 10^{-intercept \pm 2 \text{ std err}}\, t_{\text{exp}}^{slope \pm 2 \text{ std err}} \qquad (14)$$

For example, models of data with estimates from log concentration removed, the following scaling relationship is strongest:

$$t'_\alpha = 10^{-0.84 \pm 0.14}\, t_{\text{exp}}^{0.88 \pm 0.07} \qquad \left(r^2 = 0.71\right) \qquad (15)$$

where times are in units of hours. This is approximated by the relationship $t'_\alpha = t_{exp}/10$ (i.e., $\alpha = 10/t_{exp}$), which we have commonly found as a good starting point for modeling our own data.

6. Conclusions

[46] We examine estimated mass transfer parameters from 316 experiments, including a set of experiments that we conducted to control for the effects of velocity and experimental duration. We converted the reported results of these diverse experiments into a unified mathematical framework for mass transfer (equat (1), (2), and (11)). The data include large numbers of experiments with both sorbing and nonsorbing tracers modeled predominantly with first-order mass transfer.

[47] Effective mass-transfer times are much better correlated to the experimental (observational) duration and solute residence time than to velocity. These strong correlations can be explained by the presence of multiple timescales of mass transfer, a characteristic of natural aquifer and soil material that has been documented by many studies of specific material. Fitting data from systems with multiple timescales of mass transfer with models that assume a single timescale of mass transfer typically results in estimated mass transfer timescales similar to the experimental duration or solute residence time. Mass-transfer coefficients are estimated to fit the tail of breakthrough curves, and solute tailing is predominantly controlled by mass transfer processes operating over the experimental duration. Specifically, when the mass transfer memory function is a power law of the form $g^*(t) \sim t^{1-k}$ and $k < 3$, then the effective mass transfer time can be expected to change with experimental time as $t'_\alpha \sim t_{exp}^{3-k}$.

[48] Several alternative explanations may also account for some of the correlation between effective mass-transfer times and experimental duration or residence times. First, if natural material were to produce only a single timescale of mass transfer, then tailing would only be evident from experiments conducted over a timescale similar to the mass-transfer timescale. Thus some of the correlation of estimated mass-transfer timescale to experimental duration could be explained by the fact that mass-transfer timescales would only be reported when they are similar to experimental timesscales in single-rate material, if such material exists in nature. Second, when tailing is caused by advection through low-conductivity zones, then the effective rate coefficient is linearly related to the velocity and hence is also related to the solute residence time. Although we find a poor correlation of mass-transfer time to velocity, such behavior probably occurs in field studies where low-*K* inclusions are large. Third, it is possible that nonlinear or hysteretic sorption could explain some of the correlation between mass-transfer time and solute residence time. We only use data from experiments modeled as nonsorbing or sorbing with a linear isotherm; however, if this has been widely misreported, then such processes could explain some of the correlation.

[49] Just as previous work [*Neuman*, 1990; *Gelhar et al.*, 1992] found that effective dispersivity may increase with the length scale of the experiment, we find that effective mass-transfer time generally increases with the duration of the experiment. Thus this work may be viewed as a temporal analogy to previous work comparing dispersivities across experiments of different length scales. The relation of mass-transfer time to experimental duration implies that one should be cautious about using a single-rate mass transfer model to predict behavior over longer or shorter timescales than the duration of the experiment used to develop the model. The finding also emphasizes the value of late-time, low-concentration, experimental data that may provide the most information about long timescale processes.

[50] **Acknowledgments.** Funding for this work was provided by the U.S. Department of Energy's Basic Energy Sciences Program (grants DE-FG03-00ER15030 and DE-FG02-OOER15029) and the National Science

Foundation (EAR-9875995). Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000. Financial support does not constitute an endorsement by DOE of the views expressed in the article. We thank the reviewers (Sean McKenna and three anonymous) for their careful attention to the paper and exceptionally helpful comments, and Peter Oates for assistance with the statistical analyses.

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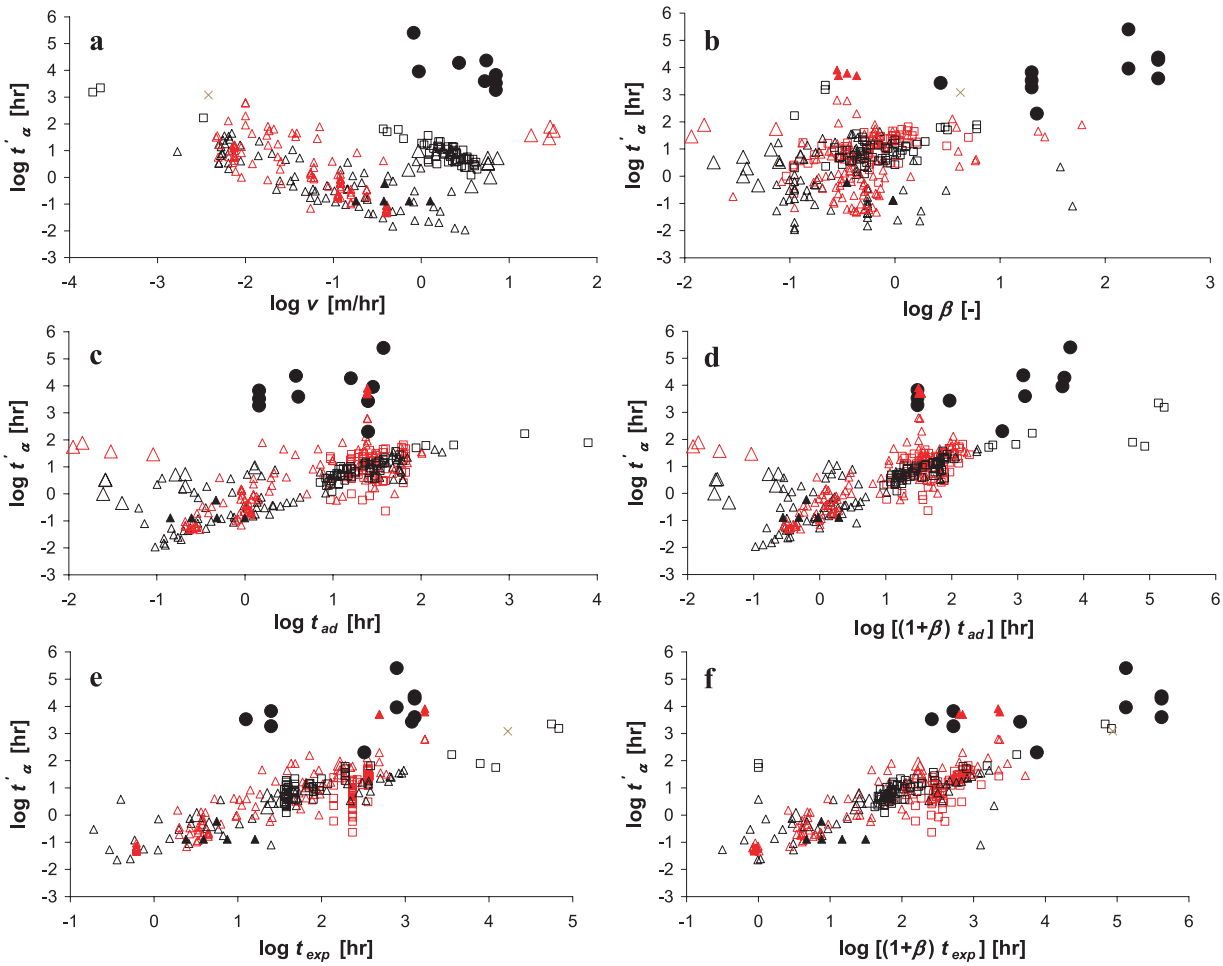

Symbol	Sorbing	Non-sorbing	Field/porous	Field/fractured	Lab	Diffusion	FO	Log	Arithmetic
△	*				*		*	*	
△		*			*		*	*	
●		*		*		*		*	
▲	*				*	*			*
□	*		*				*		*
△		*			*		*		*
△	*				*		*		*
□		*	*				*		*
▲		*			*	*			*
×	*		*			Moment analysis			*

Figure 1. Effective mass transfer time, t'_{α}, plotted against other parameters from 316 experiments. Red indicates sorbing; black indicates nonsorbing. Symbols are as follows: triangles, lab experiments; circles, field experiments in fractured media; squares, field experiments in porous media; open symbols, parameters estimated from first-order model; closed symbols, parameters estimated from diffusion model; large symbols, parameters estimated from log concentration; small symbols, parameters estimated from arithmetic concentration.