GEOPHYSICAL RESEARCH LETTERS, VOL. 33, L18407, doi:10.1029/2006GL027251, 2006

Relationship between flux and resident concentrations for anomalous dispersion

Yong Zhang,[1] Boris Baeumer,[2] and David A. Benson[1]

Received 15 June 2006; revised 12 August 2006; accepted 18 August 2006; published 28 September 2006.

[1] A concentration measurement in the field or laboratory will be most closely related to either the resident or the flux concentration. The former describes all solute particles present at some point while the latter describes solute particles that have moved irrevocably past some point. In addition, either measurement may preferentially sample a relatively mobile phase (say, by drawing a water sample) or both the mobile and immobile phases (say, by measuring in-situ electrical conductivity). The relationship between the resident and flux concentrations for anomalous, fractional-order, transport equations is developed analytically using an integral transform and explored further using a random walk model. The late-time resident and flux concentrations may differ by several orders-of-magnitude, so that the relationships developed here are critical for making predictions of flux based on resident concentration measurements and vice-versa. **Citation:** Zhang, Y., B. Baeumer, and D. A. Benson (2006), Relationship between flux and resident concentrations for anomalous dispersion, *Geophys. Res. Lett.*, *33*, L18407, doi:10.1029/2006GL027251.

1. Introduction

[2] The distinction and transformation between the resident and the flux concentrations of a dissolved solute are groundwater is well known for the case of Fickian diffusion and dispersion. The resident concentration is a measure of all of the mass present at some location. This may be measured by a variety of means, including discrete soil or groundwater samples, or electric conductivity or radioactivity sensors. Some of the solute mass may be totally immobile, while some may, according to classical Brownian motion diffusion, move upstream of that point. These possibilities led to the definition of the flux concentration, which describes all of the mass that has moved irrevocably downstream of some point [e.g., *Danckwerts*, 1952; *Kreft and Zuber*, 1978; *Parker and van Genuchten*, 1984; *Kim and Feyen*, 2000; *Kocabas and Islam*, 2000]. This measure is important, for example, when estimating the risk posed by a toxic solute: when rapid, preferential flow is present, the flux concentration for early arrivals may exceed the resident concentration; at later time, however, the flux concentrations may be far less than the resident concentrations reported from well samples. The discrepancy between the two depends on 1) the relative percentage of solute motion dictated by dispersion versus mean advection, and 2) the mechanisms of solute retention; thus it increases with the dispersivity and/or the existence of preferential pathways or diffusion-limited immobile zones [e.g., *Parker and van Genuchten*, 1984; *Kreft and Zuber*, 1978]. Confusion between the two concentrations may lead to gross misinterpretations of observations [*Parker and van Genuchten*, 1984] and serious mis-calibration of transport parameters [*Kim and Feyen*, 2000].

[3] Previous work was mainly limited to classical, Fickian, diffusion or dispersion. Several studies have emphasized the importance of distinguishing between the resident and flux concentrations and thus calculated the flux concentration for "anomalous" (non-Fickian) diffusion [see *Roth and Jury*, 1993; *Dentz and Berkowitz*, 2003; *Dentz et al.*, 2004]. However, the analytical transformation between the two concentrations for anomalous diffusion remains unknown, despite the fact that it has been observed frequently in laboratory [e.g., *Benson et al.*, 2000; *Levy and Berkowitz*, 2003] and field experiments [e.g., *Benson et al.*, 2001]. An additional requirement arises from the prejudicial sampling process: the solute in a mobile phase is preferentially collected in the field. Therefore, the relationship between concentrations in mobile and total phases also needs to be analyzed to fully understand a "measurement". This study examines the quantitative (functional) relationship between the resident and flux concentrations for anomalous diffusions governed by the fractional-order advection-dispersion equations (fADEs, described in the next section). Super- and sub-Fickian diffusion rates, and mixtures of the two, are considered. An integral transform is used to relate analytically the resident concentration to its flux counterpart. A random walk particle-tracking numerical method is also developed to explore the relationship between concentrations of solutes in mobile and immobile phases.

2. Transformation Between the Resident and the Flux Concentrations

[4] Conservation of mass requires that the cumulative solute mass that passes through a given control plane at location x through time t must be equal to the total mass downstream of x at time t:

$$v\theta_m \int_0^t C_F(x,t')dt' = \theta_{tot} \int_x^\infty C_{R,tot}(x',t)dx', \qquad (1)$$

where C_F is the flux concentration defined as the mass of solute per unit fluid discharge, $C_{R,tot}$ is the resident concentration defined as the mass of solute per unit total (mobile+immobile) fluid volume, v is the mean mobile

[1]Colorado School of Mines, Golden, Colorado, USA.
[2]University of Otago, Dunedin, New Zealand.

0094-8276/06/2006GL027251$05.00

water velocity, and θ_m and θ_{tot} are the mobile and the total porosities. Equation (1) leads to the following definition

$$C_F(x,t) = \frac{1}{\varphi v}\frac{\partial}{\partial t}\int_x^\infty C_{R,tot}(x',t)dx', \tag{2}$$

where $\varphi = \theta_m/\theta_{tot}$ is the volume fraction of mobile water.

[5] If there is no partitioning to immobile water ($\theta_m = \theta_{tot}$), then equations (1) and (2) reduce to the mass balance law and definition of flux concentration proposed by *Kreft and Zuber* [1978] (see their equations (1) and T_1), later verified for classical Fickian diffusion by *Parker and van Genuchten* [1984, equation (23b)].

[6] Taking the Fourier ($x \rightarrow k$) and Laplace ($t \rightarrow s$) transforms of (2), we get

$$\widetilde{\widehat{C}}_F(k,s) = \frac{\widetilde{C}_{R,tot}(k,t=0)}{\varphi v i k} - \frac{s}{\varphi v i k}\widetilde{\widehat{C}}_{R,tot}(k,s), \tag{3}$$

where the tilde and the hat represent the Fourier and the Laplace transform, respectively. We can solve $\widetilde{\widehat{C}}_{R,tot}(k,s)$ using the governing differential equation of $C_{R,tot}(x, t)$, and then get $C_F(x, t)$ based on the reverse transform of (3).

[7] Here we restrict our attention to constant transport parameters and the single injection mode of a Dirac pulse placed entirely in the mobile phase so that $C_{R,tot}(x, t = 0) = \varphi\delta(x)$. The detection mode can be either the resident or the flux concentration. For simplicity, the porosities are assumed to be constants and the governing equation is 1-D. Finally, the boundary condition for an infinite domain is $C_{R,tot}(x, t) = 0$ for $|x| \rightarrow \infty$.

2.1. Space-Fractional Advection-Dispersion Equation

[8] If the random distance that solute "particles" move during small amounts of time are heavy tailed (i.e., the probability density decays like a power law), then the overall transport equation has a fractional-order dispersion term [e.g., *Benson et al.*, 2001]. Here the total concentration is equivalent to the mobile concentration, since all particles are mobile, and no distinction is made. The solution to the space-fractional advection-dispersion equation with a scale index $1 < \alpha \leq 2$ [e.g., *Benson et al.*, 2001; *Deng et al.*, 2004]

$$\frac{\partial}{\partial t}C_{R,tot}(x,t) = -v\frac{\partial}{\partial x}C_{R,tot}(x,t) + D\frac{\partial^\alpha}{\partial x^\alpha}C_{R,tot}(x,t) \tag{4}$$

has Fourier-Laplace transform (FLT)

$$\widetilde{\widehat{C}}_{R,tot}(k,s) = \frac{1}{s + vik - D(ik)^\alpha}. \tag{5}$$

Using equation (3) with $\varphi = 1$, the flux concentration has FLT

$$\widetilde{\widehat{C}}_F(k,s) = \frac{1}{v}\frac{v - D(ik)^{\alpha-1}}{s + vik - D(ik)^\alpha}. \tag{6}$$

In order to invert, we relate the flux concentration back to the resident concentration, noting that

$$\frac{x}{t}\widetilde{\widehat{C}}_{R,tot}(k,s) = -i\frac{\partial}{\partial k}\int_\infty^s \widetilde{\widehat{C}}_{R,tot}(k,s)ds = \frac{v - \alpha D(ik)^{\alpha-1}}{s + vik - D(ik)^\alpha}. \tag{7}$$

Hence $\frac{x}{t}C_{R,tot}(x, t) = v\alpha C_F(x, t) + v(1 - \alpha)C_{R,tot}(x, t)$, or simply:

$$C_F(x,t) = C_{R,tot}(x,t) + \frac{x - vt}{v\alpha t}C_{R,tot}(x,t). \tag{8}$$

Therefore, $C_F > C_{R,tot}$ ahead of the mean plume position (vt) and $C_F < C_{R,tot}$ behind the mean position.

2.2. Fractional-in-Time Transport

[9] Certain time-fractional transport equations have been shown to correspond to mobile/immobile (MIM) models with a fractal distribution of transfer rates. Here we look at a fractional-in-time model where the dispersion and apparent plume velocity is governed by the delay of particles in an immobile phase. We must distinguish between the total versus mobile resident concentrations with the subscripts $C_{R,tot}$ and $C_{R,m}$. A model of $C_{R,tot}$, where all jumps have the same constant size that is independent of the waiting time, is given by

$$\beta\frac{\partial^\gamma}{\partial t^\gamma}C_{R,tot}(x,t) + \frac{\partial}{\partial t}C_{R,tot}(x,t) = -v\frac{\partial}{\partial x}C_{R,tot}(x,t), \tag{9}$$

with initial condition $C_{R,tot}(x, t = 0) = \varphi\delta(x)$ and FLT

$$\widetilde{\widehat{C}}_{R,tot}(k,s) = \frac{\varphi(1 + \beta s^{\gamma-1})}{s + \beta s^\gamma + vik}, \tag{10}$$

where β is the capacity coefficient. The FLT of C_F is then

$$\widetilde{\widehat{C}}_F(k,s) = \frac{1}{s + \beta s^\gamma + vik}, \tag{11}$$

with inverse transform:

$$\beta\frac{\partial^\gamma}{\partial t^\gamma}C_F(x,t) + \frac{\partial}{\partial t}C_F(x,t) = -v\frac{\partial}{\partial x}C_F(x,t) - \frac{\beta t^{-\gamma}\delta(x)}{\Gamma(1-\gamma)}. \tag{12}$$

It is easy to show [*Schumer et al.*, 2003] that this is also the governing equation for the mobile portion of the resident concentration ($C_{R,m}$), so that for piston flow in the mobile zone and arbitrary partitioning to the immobile zone, $C_{R,m} = C_F$.

[10] To relate C_F to $C_{R,tot}$, note that

$$\frac{t}{x}\widetilde{\widehat{C}}_F(x,t) = \frac{1}{v}\frac{1 + \beta\gamma s^{\gamma-1}}{s + \beta s^\gamma + vik}, \tag{13}$$

and hence

$$C_F(x,t) = \frac{x\gamma}{\varphi[vt - x(1-\gamma)]}C_{R,tot}(x,t). \tag{14}$$

Note that $C_{R,tot}(x, t) = 0$ if $vt \leq x(1 - \gamma)$. Here we restrict the scale index to $0 < \gamma \leq 1$, although the governing equation

and the transformation can be extended with slight modifications to the case $1 < \gamma \leq 2$ [*Baeumer et al.*, 2005].

[11] In the case of coupled waiting time in the immobile phase and subsequent jump sizes [*Meerschaert et al.*, 2002], the governing equation of $C_{R,tot}$ is given by

$$\left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial x}\right)^{\gamma} C_{R,tot} = \frac{\varphi t^{-\gamma}}{\Gamma(1-\gamma)}\delta(x) \tag{15}$$

with FLT

$$\widetilde{\widehat{C}}_{R,tot}(k,s) = \frac{\varphi s^{\gamma-1}}{(s+vik)^{\gamma}}. \tag{16}$$

In this case, the FLT of C_F is

$$\widetilde{\widehat{C}}_F(k,s) = \frac{1}{vik} - \frac{s^{\gamma}}{vik(s+vik)^{\gamma}}, \tag{17}$$

and therefore differentiation shows that $\varphi vt\widetilde{\widehat{C}}_F(k, s) = \widetilde{\widehat{xC}}_{R,tot}(k, s)$ and hence

$$C_F(x,t) = \frac{x}{\varphi vt} C_{R,tot}(x,t). \tag{18}$$

Now $C_F > C_{R,tot}/\varphi$ ahead of the point of mean groundwater travel (vt) and $C_F < C_{R,tot}/\varphi$ behind this point.

2.3. Mixed Models

[12] Many models developed to better predict anomalous transport consist of a mixture of the models. They are the stochastic scaling limit of random jumps with random waiting times and the concentration can be computed by subordinating the jump process limit against the waiting time limit. That is, if $p_R(x, t)$ is a solution to equation (4) and $q_R(x, t)$ is a solution to equation (9), then

$$C_{R,tot}(x,t) = \int_0^{\infty} p_R(x,s) q_R(s,t)\, ds \tag{19}$$

is the solution to [*Baeumer et al.*, 2005]:

$$\left(\beta\frac{\partial^{\gamma}}{\partial t^{\gamma}} + \frac{\partial}{\partial t}\right) C_{R,tot}(x,t) = \left(-v\frac{\partial}{\partial x} + D\frac{\partial^{\alpha}}{\partial x^{\alpha}}\right) C_{R,tot}(x,t), \tag{20}$$

the full MIM equation considered by *Schumer et al.* [2003]. Similarly, if $q_R(x, t)$ is a solution to equation (15), then equation (19) is the solution to

$$\left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial x} - D\frac{\partial^{\alpha}}{\partial x^{\alpha}}\right)^{\gamma} C_{R,tot}(x,t) = \frac{\varphi t^{-\gamma}}{\Gamma(1-\gamma)}\delta(x). \tag{21}$$

[13] In the case that $C_{R,tot}$ is of the form (19), we can obtain C_F via integration by parts so that

$$C_F(x,t) = \frac{v}{\varphi}\int_0^{\infty} p_F(x,s) q_F(s,t)\, ds, \tag{22}$$

where p_F and q_F are the respective flux concentrations. For example, the flux concentration for the full MIM model is given by

$$\begin{aligned} C_F(x,t) &= \frac{1}{\varphi}\int_0^{\infty}\left(1 + \frac{x - vs}{v\alpha s}\right) p_R(x,s)\frac{s\gamma}{t - s(1-\gamma)/v} \times q_R(s,t)\, ds \\ &= \frac{\gamma}{\varphi\alpha}\int_0^{\infty}\frac{x - vs(1-\alpha)}{vt - s(1-\gamma)} p_R(x,s) q_R(s,t)\, ds, \end{aligned} \tag{23}$$

where p_R solves equation (4) and q_R solves equation (9). We can also use the MIM decomposition, $C_{R,tot} = (\theta_m C_{R,m} + \theta_{im} C_{R,im})/\theta_{tot}$ where θ_{im} is the porosity of the immobile zone and $C_{R,im}$ is the resident concentration in the immobile zone, to show that the flux concentration

$$C_F(x,t) = \left(\frac{x - vt}{v\alpha t} + 1\right) C_{R,m}(x,t) + \frac{\gamma x}{v\alpha t}\beta C_{R,im}(x,t). \tag{24}$$

3. Illustrative Examples and Properties of Solutions of the Full MIM Model

[14] To test the analytic expressions relating resident concentration for solutes in the mobile and total phases and the flux concentration—denoted here $C_{R,m}$, $C_{R,tot}$ and C_F—we developed a random walk particle tracking method to approximate equation (20) by combining the random walk approximation of superdiffusion proposed by *Zhang et al.* [2006] and the stable particle waiting times (in an immobile phase) developed by *Baeumer et al.* [2005]. This algorithm is similar to that proposed by *Dentz et al.* [2004] to allow variable transport parameters. Here we ignore the immobile concentration, since it is merely the difference between the concentrations in the total and mobile phases. We compare the evolution of different concentrations, by looking at both C_F and C_R as functions of time at a fixed observation point. Although the same direct comparison of the two quantities was shown for Fickian dispersion by *Kreft and Zuber* [1978] and *Parker and van Genuchten* [1984], to our knowledge it has not been done for anomalous, fractional-order dispersion. Also note here we plot C_F and C_R as functions of time at a fixed point in space to explore the quantitative distinction and potential relationship between these two quantities, but not to suggest that they should have the same physical meaning. In fact, the flux concentration denotes a distribution density in time, while the resident concentration denotes a distribution density in space.

[15] Several of the different concentrations measured at a single point over time should be equivalent for very early and very late time. The concentration measured at earliest time is due to particles that are not partitioning to an immobile phase, so the mobile concentration $C_{R,m}$ should be equal to $C_{R,tot}/\varphi$. At later time, 1) $C_{R,m}$ should be approximately equal to C_F since any mobile particles are driven mainly by advection and are the only ones that cross the point within a unit time; and 2) since most particles are immobile at later time, the highest concentrations should be in $C_{R,tot}$. These predictions are validated by the random walk simulations (Figure 1a). Furthermore, the slopes of the late-time tails of concentration versus time in a double-log plot depend on γ (Figure 1). The slope of the flux concentration is steeper by unity than the total resident concentra-

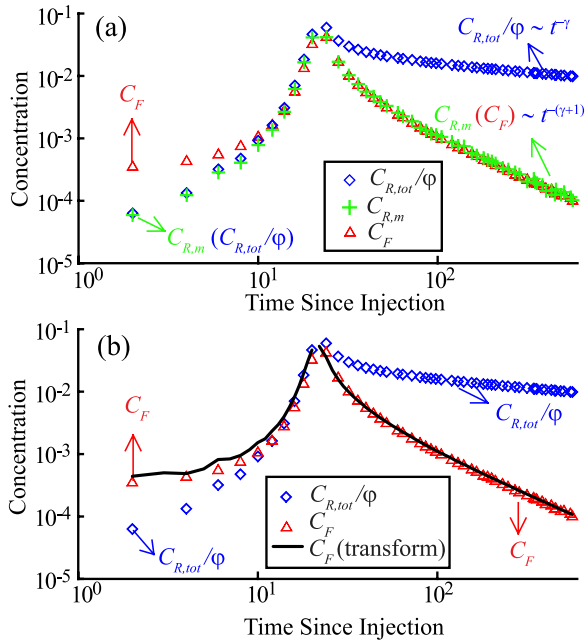

Figure 1. The random walk solution (symbols) of (20) and transformation results (lines) of (25), with $v = 1$, $D = 0.1$, $\alpha = 1.5$, $\gamma = 0.3$, $\beta = 0.1$, $x = 20$, and a Dirac pulse at $x_0 = 0$. (a) The random walk approximation of $C_{R,tot}/\varphi$, $C_{R,m}$ and C_F. The subscripts "tot" and "m" denote the total (mobile+immobile) and mobile only phases, respectively. (b) Comparison of simulated C_F and the transformation from $C_{R,tot}$ to C_F using (25).

tion. This -1 difference of slopes can be derived directly from equation (24). At later time when $t \gg x/v$, the slopes for $C_{R,tot}$ and $C_{R,m}$ (or C_F) are $-\gamma$ and $-(\gamma + 1)$, respectively. These slopes can be derived from the analytical transformations discussed above. When $\alpha = 2$, the same difference between $C_{R,m}$ and $C_{R,tot}$ was also found by *Schumer et al.* [2003].

[16] To the best of our knowledge, the equivalence of $C_{R,m}$ and C_F at later time for advection-dominated systems has not been discussed previously in the literature. The solutes entrained temporarily in the mobile domain (i.e., $C_{R,m}$) provide the main potential source for flux concentration. If 1) there are no apparent preferential jumps from distant upstream zones, and 2) the back diffusion is overwhelmed by the fast forward advection, then $C_{R,m}$ is very close to C_F (Figure 1a). For the case of $\alpha = 2$, the $C_{R,m}$ approximates C_F even at the early time for advection-dominated systems (Figure 2), since there are no large jumps from distant upstream zones at any time.

3.1. A Simple Formula

[17] For advection-dominated systems, the transformation between $C_{R,tot}$ and C_F can be approximated directly without the burden of solving the integration (23), using the empirical formula taken from equations (8) and (14):

$$C_F(x,t) \approx \left[\frac{x+(\alpha-1)vt}{v\alpha t}H(x/v-t) + \frac{x\gamma}{vt-x(1-\gamma)}H(t-x/v)\right]\frac{C_{R,tot}(x,t)}{\varphi}, \quad (25)$$

where $H()$ is the Heaviside step function. This approximate transform typically preforms very well (Figure 1b). Numerous numerical tests show that (25) holds as long as the fractional dispersivity, defined by D/v is less than about $0.5\ L^{\alpha-1}$ (where the length units L must be the same as in D and v). Since most groundwater systems are advection-dominated, the approximation (25) should be applicable to many real problems.

3.2. Fickian Versus Anomalous Dispersion

[18] The discrepancy between the resident and the flux concentrations for anomalous diffusion depends on the orders of both space and time derivatives of the fADEs. For the case of pure advection and heavy tailed waiting time in an immobile phase, $C_F = (\gamma x/\varphi v t)C_{R,tot}$ for subdiffusion governed by $\partial^\gamma C_{R,tot}/\partial t^\gamma = -v\partial C_{R,tot}/\partial x$, while $C_F = C_R$ for pure piston (wave equation) flow $\partial C_R/\partial t = -v\partial C_R/\partial x$. Here the operator $\partial^\gamma/\partial t^\gamma$ disperse the solutes in time (similar to classical spatial dispersion), resulting in the difference between $C_{R,tot}$ and C_F.

[19] The previous transformation for Fickian dispersion from a point source in an infinite domain is a specific case of this study. When $\alpha = 2$, (8) reduces to the transform formula proposed by *Kreft and Zuber* [1978]. For this Fickian case, the resident and the flux concentrations satisfy the same PDE with different boundary conditions. Although the same conclusion can be found for the space-fractional ADE (4), it is not true when an immobile phase present as can be seen by comparing equation (10) to (11). Similar to the results of *Roth and Jury* [1993], who demonstrated that the flux concentration and the mobile resident concentration satisfy the same PDE with Fickian dispersion and a multi-adsorption model (see their equations (13) and (14)), the fractional-in-time solutions for C_F and $C_{R,m}$ agree when there is little or no mobile phase dispersion. This occurs with piston flow, Fickian dispersion (Figure 2), or at very late time (Figure 1a).

4. Summary

[20] Preferential flowpaths and/or relatively stagnant (immobile) domains, which are believed to cause anomalous dispersion, cause a discrepancy between the resident and the flux concentrations. For the super- (or sub-) Fickian dispersion governed by the fADE, the relationship between these two concentrations depends on the order of space (or time) fractional derivatives, but not the dispersivity as in the case of Fickian diffusion.

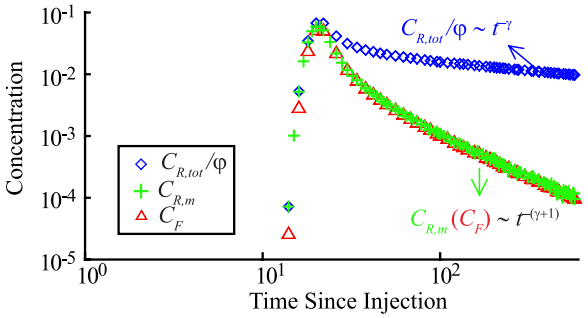

Figure 2. The random walk approximation of (20), with the same parameters used in Figure 1 except $\alpha = 2$.

[21] For anomalous dispersion governed by the full fractal MIM model, the flux concentration can be transformed from the total resident concentration using either the integral transform (23) or an empirical approximation (25) for advection-dominated systems. Additionally, for advection-dominated systems, the mobile phase resident concentration $C_{R,m}$ approximates the flux concentration C_F at later time. In this case, the concentrations for any of the phases can be transformed from one to another. The discrepancy of late-time slopes shown here is critical to predicting long-term remediation or repository suitability studies, since the log concentrations diverge and may differ by several orders of magnitude. Furthermore, the late-time slope of a log-log plot of measured concentration versus time must be used to estimate the parameter γ, so the correct concentration type must be identified.

[22] The memory function (i.e., particle waiting times) considered in this study is a power law form, so that the late-time concentration tail decays as a power law of time. Future work may extend the memory function to other forms, such as the truncated power law used by *Dentz et al.* [2004], or a finite sum of exponentials [*Haggerty et al.*, 2000] where the late-time tail can decay faster than a power law.

[23] In the real world, the transport parameters may vary locally, and the injection mode may also be in flux fluid or continuous resident fluid. The spatial variability of parameters, finite domain size, and other injection modes may be explored in a future study.

[24] **Acknowledgments.** D. A. B. and Y. Z. were supported by the National Science Foundation under DMS−0417972 and DMS−0139943. Y. Z was also partially supported by Desert Research Institute. Any opinions, findings, conclusions or recommendations do not necessary reflect the views of the NSF. We thank the editor James Saiers and the reviewer Marco Dentz for their insightful suggestions.

References

Baeumer, B., D. A. Benson, and M. M. Meerschaert (2005), Advection and dispersion in time and space, *Physica A*, *350*(2–4), 245–262.

Benson, D. A., S. W. Wheatcraft, and M. M. Meerschaert (2000), Application of a fractional advection–dispersion equation, *Water Resour. Res.*, *36*(6), 1403–1412.

Benson, D. A., R. Schumer, M. M. Meerschaert, and S. W. Wheatcraft (2001), Fractional dispersion, Lévy motion, and the MADE tracer tests, *Transp. Porous Media*, *42*(1/2), 211–240.

Danckwerts, P. N. (1952), Continuous flow systems distribution of residence times, *Chem. Eng. Sci.*, *2*(1), 1–13.

Deng, Z. Q., V. P. Singh, and L. B. Bengtsson (2004), Numerical solution of fractional advection-dispersion equation, *J. Hydraul. Eng.*, *130*(5), 422–431.

Dentz, M., and B. Berkowitz (2003), Transport behavior of a passive solute in continuous time random walks and multirate mass transfer, *Water Resour. Res.*, *39*(5), 1111, doi:10.1029/2001WR001163.

Dentz, M., A. Cortis, H. Scher, and B. Berkowitz (2004), Time behavior of solute transport in heterogeneous media: Transition from anomalous to normal transport, *Adv. Water Resour.*, *27*, 155–173.

Haggerty, R., S. A. McKenna, and L. C. Meigs (2000), On the late-time behavior of tracer test breakthrough curves, *Water Resour. Res.*, *36*(12), 3467–3479.

Kim, D. J., and J. Feyen (2000), Comparison of flux and resident concentrations in macroporous field soils, *Soil Sci.*, *165*(8), 616–623.

Kocabas, I., and M. R. Islam (2000), Concentration and temperature transients in heterogeneous porous media: I. Linear transport, *J. Petrol. Sci. Eng.*, *26*, 211–220.

Kreft, A., and A. Zuber (1978), On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions, *Chem. Eng.*, *33*, 1471–1480.

Levy, M., and B. Berkowitz (2003), Measurement and analysis of non-Fickian dispersion in heterogeneous porous media, *J. Contam. Hydrol.*, *64*, 203–226.

Meerschaert, M. M., D. A. Benson, H.-P. Scheffler, and P. Becker-Kern (2002), Governing equations and solutions of anomalous random walk limits, *Phys. Rev. E*, *66*(6), 060102(R).

Parker, J. C., and M. T. van Genuchten (1984), Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport, *Water Resour. Res.*, *20*(7), 866–872.

Roth, K., and W. A. Jury (1993), Linear transport models for adsorbing solutes, *Water Resour. Res.*, *29*(4), 1195–1203.

Schumer, R., D. A. Benson, M. M. Meerschaert, and B. Baeumer (2003), Fractal mobile/immobile solute transport, *Water Resour. Res.*, *39*(10), 1296, doi:10.1029/2003WR002141.

Zhang, Y., D. A. Benson, M. M. Meerschaert, and H. P. Scheffler (2006), On using random walks to solve the space-fractional advection-dispersion equations, *J. Stat. Phys.*, *123*(1), 89–110.

D. A. Benson and Y. Zhang, Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA. (dbenson@mines.edu; yzhang@mines.edu)

B. Baeumer, Department of Mathematics and Statistics, University of Otago, P.O. Box 56, Dunedin, Postcode 9010, New Zealand. (bbaeumer@maths.otago.ac.nz)