

## Reply

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## Introduction

We thank *Griffioen et al.* [this issue] for their interest in and comments on our recent paper. Their comments are primarily concerned with the mass transfer processes occurring in the aggregated media used by *Hu and Brusseau* [1995] and with the applicability of a particular equation relating the mass transfer coefficient ( $\alpha$ ) to the aqueous diffusion coefficient ( $D_0$ ).

First of all, we wish to point out that the main objective of *Hu and Brusseau* [1995] was to investigate the effect of solute size on transport in structured porous media with a series of experiments using well-defined systems. The results clearly showed that the extent of nonideality, reflected in the measured breakthrough curves, was related to solute size. A specific equation relating  $\alpha$  to  $D_0$  was used to help evaluate the results. However, this specific equation, which is the focus of the comments by *Griffioen et al.* [this issue], is a minor part of *Hu and Brusseau's* work. Furthermore, contrary to *Griffioen et al.'s* mistaken assumption, its use was in no way meant to be a test of its general validity. In fact, *Hu and Brusseau* conclude their paper with the following statements: "However, it must be remembered that the dual-porosity approach is a simplification of reality. The binary demarcation of a structured system into advective and nonadvective regions may not be sufficient or appropriate for many systems" (p. 1645).

In this context, respective concerns related to the comments will be discussed in the following paragraphs. Incidentally, *Griffioen et al.* [this issue] are correct about the error in Table 5; the headings of  $D_0^S/D_0^H$  and  $\alpha^S/\alpha^H$  should read  $D_0^H/D_0^S$  and  $\alpha^H/\alpha^S$ . We regret any inconvenience this typographical error may have caused.

## Relationship Between $\alpha$ and $D_0$

Optimized values of  $\omega$  and  $\alpha$  were obtained from single- and dual-parameter fits in the work presented by *Hu and Brusseau* [1995]. The single-parameter optimization involved fitting  $\omega$  and fixing  $\beta$  to the measured value. The two-parameter optimization involved fitting both  $\beta$  and  $\omega$ . *Griffioen et al.* [this issue] suggest that different conclusions regarding the relationship between  $\alpha$  and  $D_0$  can be obtained from the data depending on which fitting approach is used. We will address this issue as follows.

First, the sensitivity to and merits of parameter fits for the dual-porosity model have been more fully evaluated by *Koch and Flühler* [1993]. However, it is clear that the degree of uncertainty associated with parameter values obtained with a

two-parameter fit would generally be greater than that associated with a single-parameter fit, especially if the two fitted parameters are correlated in some manner. Thus one might expect the results obtained from single-parameter fits to be more robust than those obtained from two-parameter fits.

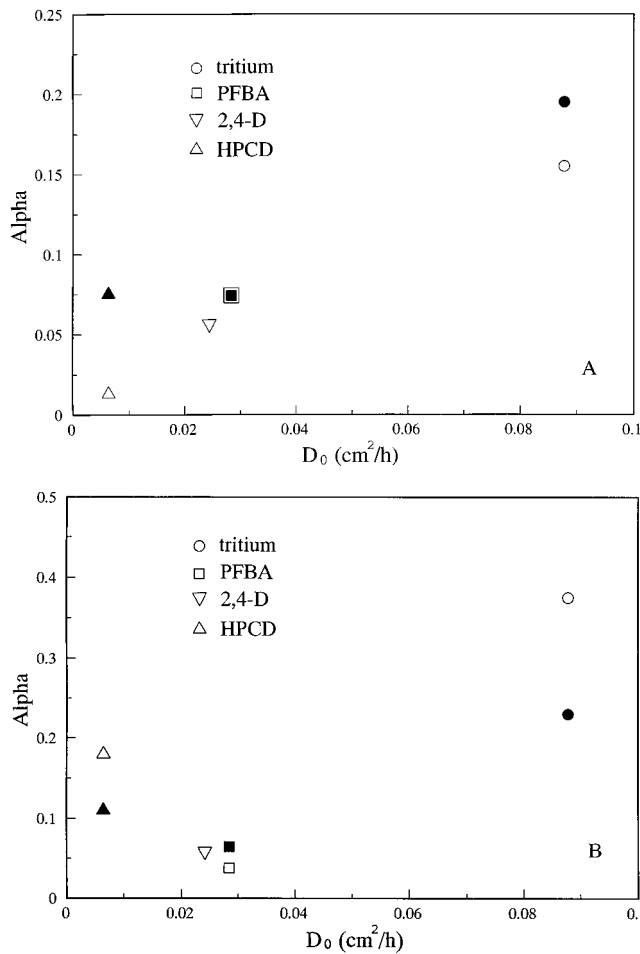
Second, as shown in Table 4 of *Hu and Brusseau* [1995], the fitted  $\beta$  values obtained by optimization in most cases are reasonably close to the measured  $\beta$  values. This is also true for the data reproduced in Table 2 of *Griffioen et al.* [this issue]. The only cases where the fitted values do not match the measured values are those for selected experiments conducted with column WQ13, which had the lowest fraction of "immobile" domains. The fact that fitted and measured values were similar for most cases supports the use of the measured values for all applications. Hence, *Hu and Brusseau* assumed that the  $\beta$  parameter was known for their systems (which, indeed, it was). Thus values of  $\omega$  (and  $\alpha$ ) from the fixed- $\beta$  optimization were used to develop Table 5 of *Hu and Brusseau*.

Third, the statement made by *Griffioen et al.* [this issue] in their conclusion section, that the use of the fitted- $\beta$  data set produces a trend opposite to the one reported by *Hu and Brusseau* [1995] (i.e.,  $\alpha$  varies inversely rather than directly with  $D_0$ ), is not correct. This is apparent from inspection of Figure 1, where fitted  $\alpha$  values are plotted against  $D_0$ . For the case wherein  $\beta$  was fixed,  $\alpha$  decreases essentially uniformly with decreasing  $D_0$  (Figure 1a). For the case wherein  $\beta$  was optimized,  $\alpha$  also decreases with decreasing  $D_0$ , with the exception of the HPCD data (Figure 1b).

It is clear from Figure 1b that the fitted- $\beta$  data set does not exhibit an inverse relationship between  $\alpha$  and  $D_0$ . It is true that the relationship between  $\alpha$  and  $D_0$  is not uniform, as it is for the single fitted-parameter data set shown in Figure 1a. It is possible that this is due, at least in part, to the greater uncertainty associated with two-parameter fits, as discussed above. In summary, considering (1) the data in Figure 1, (2) the generally greater robustness of single-parameter fits versus two-parameter fits, and (3) the important fact that the  $\beta$  parameter was known for the systems used by *Hu and Brusseau* [1995], we suggest that the conclusion put forth by *Griffioen et al.* [this issue] (that the data of *Hu and Brusseau* show that  $\alpha$  is not directly correlated with  $D_0$ ) is not supported by a complete evaluation of the data.

## Velocity Dependency of $\alpha$

The linear relationship between  $\alpha$  and  $D_0$  has been used for quite some time [*Glueckauf*, 1955] and has been derived using different methods. Equation (1), from *van Genuchten* [1985] and *Parker and Valocchi* [1986], was adopted to derive the independent  $\alpha$  values used by *Hu and Brusseau* [1995]:



**Figure 1.** Relationship between  $\alpha$  and  $D_0$  for all solutes: (a)  $\alpha$  from single-parameter fit, (b)  $\alpha$  from dual-parameter fit. Open symbols: WQ 13; filled symbols: WQ14.

$$\alpha = \frac{a \tau D_0 \theta_n}{l^2} \quad (1)$$

This relationship does not take account into the velocity dependency of the  $\alpha$  term, as discussed by many investigators.

Since diffusive mass transfer is a rate-limited process, residence time is expected to affect the magnitude of nonideality for transport of solutes in structured media. For example, the degree of nonideal transport for  $^3\text{H}_2\text{O}$  was smaller at a slower velocity compared to that observed for the faster velocity in the work of *Hu and Brusseau* [1995, Figure 3b]. The optimized simulation based on the dual-porosity model reproduces the experimental data for  $^3\text{H}_2\text{O}$  transport at the slow velocity, and the optimized  $\alpha$  value is smaller than both the optimized  $\alpha$

value obtained for the fast velocity and the predicted  $\alpha$  value obtained with (1) (Table 1). The decrease of  $\alpha$  with a decrease in pore water velocity has been observed and discussed by others [*van Genuchten and Wierenga*, 1977; *Rao et al.*, 1980b; *Nkedi-Kizza et al.*, 1983; *Herr et al.*, 1989; *Brusseau*, 1991; *Kookana et al.*, 1993; *Li et al.*, 1994; *Hu and Brusseau*, 1996]. Because the time available for diffusion into and out of the immobile domain is inversely related to the pore water velocity,  $\alpha$  is expected to decrease with decreasing pore water velocity.

It was reported that  $\alpha$  is dependent upon the aqueous diffusion coefficient, the time of diffusion (e.g., pore water velocity), the sphere radius, and the volumetric water contents inside and outside the sphere [*Rao et al.*, 1980a, b]. *Rao et al.* [1980a] developed equations to account for the time dependence of  $\alpha$  in aggregated media similar to ours:

$$\alpha = \frac{\phi q_1^2}{1-b} \left[ \frac{0.1}{T^*} \right]^b \quad 10^{-4} < T^* \leq 0.1 \quad (2a)$$

and

$$\alpha = \phi q_1^2 \left[ 1 + \frac{0.1b}{(1-b)T^*} \right] \quad T^* \geq 0.1 \quad (2b)$$

where

$$b = 0.14472 \ln(167/\phi q_1^2) \quad (2c)$$

$$T^* = \tau D_0 t_r / l^2 \quad (2d)$$

and  $q_1$  is the empirical constant related to the  $\phi$  value (dimensionless),  $t_r$  is the mean column residence time ( $1/T$ ), and  $l$  is the sphere radius ( $L$ ). The relationship provides an averaged  $\alpha$  value calculated over the mean column residence time.

Using (2), time-averaged  $\alpha$  values are calculated for each miscible displacement experiment reported by *Hu and Brusseau* [1995], given the values of  $\phi$ ,  $q_1$ ,  $\tau$ ,  $D_0$ ,  $l$ , and  $t_r(L/v_a)$ . The predicted  $\alpha$  values for solutes in two columns with different numbers of porous spheres (hence different  $\phi$  values) are close to the optimized  $\alpha$  values for both fast and slow pore-water velocities (see Table 2). Of special note is that the predicted  $\alpha$  value obtained with (2) is very close to the optimized  $\alpha$  value for the slow pore water velocity experiment (experiment 14-5 in Table 2). This has also been observed for data obtained using a column packed with the porous spheres and a loamy soil [*Hu and Brusseau*, 1996]. Thus it appears that accounting for the residence time effect is sufficient to explain the velocity dependence of  $\alpha$  for our aggregated systems [*Hu and Brusseau*, 1996].

### Mass Transfer During Flow Interruption

*Hu and Brusseau* [1995] presented breakthrough curves for transport of  $^3\text{H}_2\text{O}$  and PFBA in the aggregated medium influ-

**Table 1.** Predicted and Optimized Parameter Values for  $^3\text{H}_2\text{O}$  Transport at Slow Velocity for Experiment 14-5

$v_a$ , cm/h	Case	$\beta$	$\omega$		$\alpha$	
			Predicted*	Optimized	Predicted*	Optimized
2.8	$\beta$ varying	0.63 (0.61–0.64)	0.78	1.55 (1.42–1.67)	0.28	0.065 (0.060–0.070)
2.8	$\beta$ constant	0.63	0.78	1.53 (1.48–1.58)	0.28	0.064 (0.062–0.066)

Values in parentheses represent 95% confidence intervals.

\*Predicted by using (1).

enced by flow interruption. It was shown that concentration perturbations for PFBA for three interruption times were different, whereas those for  $^3\text{H}_2\text{O}$  were not. This behavior was related to the influence of their solute size on diffusive mass transfer. No mathematical modeling analysis was presented, however, since this was not the main focus of the paper, as stated above. Such an analysis is presented herein.

The breakthrough curves for transport of  $^3\text{H}_2\text{O}$  and PFBA with flow interruption were optimized with the fitting program FINLLS [Jessup *et al.*, 1989]. Both  $\alpha$  and  $\beta$  are optimized to follow the approach of Griffioen *et al.* [this issue]; all other parameters are fixed to the experiment-determined values. The optimized  $\beta$  values are quite consistent and compare well with the measured  $\beta$  value of 0.64 (Table 3), as observed for the previous cases. For  $^3\text{H}_2\text{O}$ , increasing the interruption time from 2 to 8 hours produces similar  $\alpha$  values. For PFBA, increasing interruption time results in an increasing  $\alpha$  value. Moreover, the optimized  $\alpha$  values for  $^3\text{H}_2\text{O}$  are larger than those for PFBA for all three interruption times. These phenomena are consistent with the statement by Hu and Brusseau [1995]: that the difference in behavior is due to the fact that  $^3\text{H}_2\text{O}$  has a larger aqueous diffusion coefficient than PFBA.

The predicted  $\alpha$  values obtained by using (2) are also presented in Table 3. Note that the time-averaged  $\alpha$  value is calculated using the flow-based residence time ( $L/v_a$ ), and does not include the interruption time. For  $^3\text{H}_2\text{O}$  the optimized  $\alpha$  values compare well with the predicted values. For PFBA there is a trend wherein the optimized  $\alpha$  value approaches the predicted value with increasing time of flow interruption.

## Diffusion-Controlled Mass Transfer

Griffioen *et al.* [this issue] suggest that factors other than diffusion may have contributed substantially to mass transfer of solute between the interaggregate and intra-aggregate domains of the aggregated system used by Hu and Brusseau [1995]. For the aggregated system used by Hu and Brusseau, porous spheres were packed into the column along with silica-glass beads. The glass beads are 212–300  $\mu\text{m}$  in diameter (i.e., medium sand), and the internal pores of the porous spheres are smaller than 1  $\mu\text{m}$ . Given this wide difference in sizes, it

**Table 3.** Predicted and Optimized Parameter Values for Flow Interruption Experiments

Interruption Time, hours	$v_a$ , cm/h	$\beta$ Optimized	$\alpha$ (1/h)	
			Optimized	Predicted*
$^3\text{H}_2\text{O}$				
2	24.6	0.68 (0.68–0.68)	0.16 (0.15–0.16)	0.16
4	24.7	0.68 (0.68–0.69)	0.12 (0.11–0.12)	0.16
8	24.6	0.67 (0.66–0.67)	0.12 (0.12–0.13)	0.16
$\text{PFBA}$				
2	24.6	0.67 (0.67–0.67)	0.028 (0.023–0.032)	0.083
4	24.7	0.67 (0.67–0.68)	0.074 (0.069–0.080)	0.083
8	24.6	0.70 (0.69–0.70)	0.076 (0.072–0.080)	0.083

Values in parentheses represent 95% confidence intervals.

\*Calculated with (2) for the flow-based residence time ( $t_r = L/v_a$ ).

was assumed that advective flow in the internal pores of the porous spheres was insignificant. In addition, the porous spheres were 1.1 cm in diameter. Thus, interregion mass transfer was expected to be predominantly diffusion controlled in this aggregated system. The results discussed by Hu and Brusseau and those presented herein support this assumption:

1. The results of the transport experiments presented by Hu and Brusseau [1995] clearly show that the larger solutes exhibited greater nonideal transport compared to the smaller solutes. Given that all of the solutes are nonreactive, this behavior is consistent only with diffusion-controlled interregion mass transfer.
2. The results of the flow interruption experiments showed that the larger solute required more time to complete mass transfer than did the smaller solute. This again is consistent with diffusion-controlled mass transfer.
3. The measured velocity dependence of  $\alpha$  was accounted for by use of (2). It is important to note that the relationship presented in (2) is based on diffusion-controlled mass transfer between the interaggregate and intra-aggregate domains. This supports the conclusion that diffusion is the primary mass transfer process for the aggregated system.
4. Predicted simulations produced with a model on the basis of the assumption that the interregion mass transfer was diffusion controlled showed good agreement to the measured breakthrough curves for the aggregated system.

## Conclusion

In conclusion, all available evidence indicates that the solute flux into and out of the internal porosity of the aggregates used by Hu and Brusseau [1995] is predominantly diffusion controlled. Thus the suggestion provided by Griffioen *et al.* [this issue] that this may not be the case is not correct for our specific system. We fully agree, however, that processes other than diffusion can contribute to mass transfer in structured soils in general, and that it is important to consider all aspects of a heterogeneous system when attempting analysis and prediction. In addition, we agree that (1) may not always provide a valid representation of  $\alpha$ , even when mass transfer is diffusion controlled.

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**Table 2.** Comparison of Predicted and Optimized  $\alpha$  Values

Experiment	Solute	$v_a$ , cm/h	$\alpha$ (1/h)	
			Predicted*	Optimized†
13-1	$^3\text{H}_2\text{O}$	18.8	0.07	0.15 (0.12–0.18)
13-2	$^3\text{H}_2\text{O}$	18.7	0.07	0.16 (0.14–0.18)
13-3	PFBA	18.4	0.039	0.074 (0.058–0.087)
13-4	HPCD	18.5	0.016	0.013 (0.012–0.013)
13-5	2,4-D	18.5	0.036	0.050 (0.041–0.059)
13-6	2,4-D	18.5	0.036	0.060 (0.048–0.071)
14-1	$^3\text{H}_2\text{O}$	24.1	0.14	0.18 (0.16–0.20)
14-2	$^3\text{H}_2\text{O}$	24.0	0.14	0.21 (0.21–0.21)
14-3	PFBA	17.9	0.067	0.074 (0.073–0.074)
14-4	HPCD	24.8	0.034	0.075 (0.065–0.085)
14-5	$^3\text{H}_2\text{O}$	2.79	0.060	0.064 (0.062–0.067)
18-1	PFBA	24.9	0.083	0.084 (0.074–0.094)

\*Predicted using (2). Value of  $q_1$  is from Rao *et al.* [1980a] for the corresponding  $\phi$  value. Note that the tortuosity factor  $\tau$  (0.15) is obtained from the measured data for  $^{36}\text{Cl}^-$  and  $^3\text{H}_2\text{O}$  diffusion in the porous spheres, as reported by Rao *et al.* [1980a].

†From the fixed- $\beta$  optimization.

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