Modeling Dual-Domain Solute Transport with MT3D

Christopher J. Neville
S.S. Papadopulos & Associates, Inc.
Last update: July 13, 2006

Overview

The capability to simulate dual-domain transport was added to MT3D with the release of MT3DMS. Dual-domain transport is also referred to as dual-porosity, or two-region transport.

The first-order mass transfer coefficient approach is phenomenological, which means that it has a relatively weak physical basis and the mass transfer coefficient is less a physical quantity than a curve-fitting parameter. However, this approach has two important virtues:

- It is simple to understand and implement; and
- It is sufficiently general to provide approximate representations of physical situations.

These notes have been prepared to describe in detail the interpretation of the first-order mass transfer coefficient, with the specific aim of assisting in the appropriate use of the dual-domain capability in solute transport simulations. The notes are divided into three main sections:

- Implementation of the dual-domain model in MT3D;
- Interpretation of the dual-domain mass transfer coefficient; and
- Discussion of limiting cases for dual-domain transport.

1. Implementation of the dual-domain model in MT3D

Dual-domain transport is simulated with MT3D as a first-order mass transfer reaction:

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \varsigma \left(C_m - C_{im} \right)$$

where:

θ_{im} porosity of the immobile domain [volume of immobile domain/volume of porous medium];

C_m dissolved concentration in the mobile domain [mass of solute/volume of water in the mobile domain];

C_{im} dissolved concentration in the immobile domain [mass of solute/volume of water in the immobile domain]; and

ζ first-order mass transfer coefficient [time^{-1}];

The mass transfer coefficient ζ is phenomenological. Although the mass transfer coefficient should be regarded primarily as a curve-fitting parameter, it is possible to attach some physical consideration to the asymptotic behavior of the mass transfer relation. The derivations in the next section is included to set the stage for a consideration of the limiting cases for solute transport with dual domain mass transfer.

2. Interpretation of the dual-domain mass transfer coefficient

The mass transfer coefficient ζ controls how quickly mass is exchanged between the mobile and immobile domains. In order to appreciate its significance, let us consider a hypothetical batch experiment in which an immobile region with an initial concentration of zero comes in contact with a mobile region with constant concentration C_m^o.

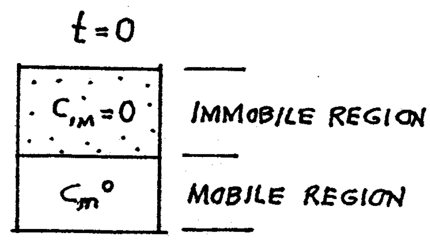
SOLUTION:

— Governing equation for concentration in the immobile region:

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \zeta \left(C_m^o - C_m \right)$$

SUBJECT TO:

$$C_m(t=0) = 0$$



— Apply the Laplace transform to the mass transfer relation.

$$\theta_{im} \left[p\bar{C}_{im} - \cancelto{0}{C_{im}(0)} \right] = \zeta \left(\frac{C_m^o}{p} - \bar{C}_{im} \right)$$

Substituting for the initial conditions and collecting terms:

$$\theta_{im}\, p\, \bar{C}_{im} + \zeta \bar{C}_{im} = \zeta \frac{C_m^o}{p}$$

Solving for $\bar{C}_{im}$ yields :

$$\bar{C}_{im} = \frac{\frac{\zeta C_m^0}{p}}{(\theta_{im} p + \zeta)}$$

- Apply the inverse Laplace transform

$$C_{im} = \mathcal{L}^{-1}\left[\frac{\frac{\zeta C_m^0}{p}}{(\theta_{im} p + \zeta)}\right]$$

$$= C_m^0 \zeta \; \mathcal{L}^{-1}\left[\frac{1}{p(\theta_{im} p + \zeta)}\right]$$

Factoring θ_{im} :

$$C_{im} = C_m^0 \frac{\zeta}{\theta_{im}} \mathcal{L}^{-1}\left[\frac{1}{p\left(p + \frac{\zeta}{\theta_{im}}\right)}\right]$$

The inverse is :

$$\mathcal{L}^{-1}[\cdot] = \frac{1}{a}\left[1 - EXP\{-at\}\right] \qquad \text{Hantush (1964)}$$

where $a = \dfrac{\zeta}{\theta_{im}}$

$$\therefore \quad C_{im} = \frac{C_m^0 \zeta}{\theta_{im}} \left(\frac{\theta_{im}}{\zeta} \left[1 - EXP\left\{ -\frac{\zeta}{\theta_{im}} t \right\} \right] \right)$$

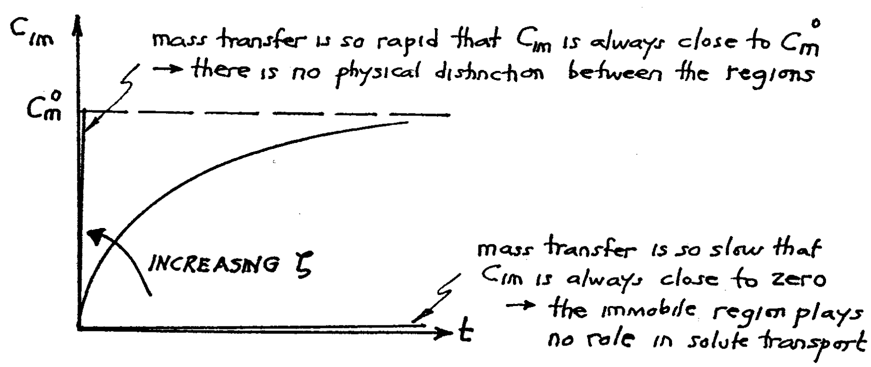
Simplifying:

$$\boxed{C_{im} = C_m^0 \left[1 - EXP\left\{ -\frac{\zeta}{\theta_{im}} t \right\} \right]}$$

Limiting cases:

i) $\zeta \rightarrow 0$: $C_{im} \rightarrow 0$

ii) $\zeta \rightarrow \infty$: $C_{im} \rightarrow C_m^0$



EXTENSION FOR TIME-VARYING MOBILE CONCENTRATION

- Apply the Laplace transform to the mass transfer reaction:

$$\theta_{im}\, p\, \bar{C}_{im} + \zeta \bar{C}_{im} = \zeta \bar{C}_m$$

$$\therefore \quad \bar{C}_{im} = \frac{\zeta \bar{C}_m}{(\theta_{im} p + \zeta)}$$

- Apply the inverse Laplace transform:

$$C_{im} = \mathcal{L}^{-1}\left[\frac{\zeta \bar{C}_m}{\theta_{im} p + \zeta}\right]$$

$$= \zeta\, \mathcal{L}^{-1}\left[\bar{C}_m \cdot \frac{1}{\theta_{im} p + \zeta}\right]$$

The inverse can be evaluated using the convolution theorem:

$$C_{im} = \zeta \int_0^t F(\tau)\, g(t-\tau)\, d\tau$$

If we let $\bar{f}(p) = \bar{C}_m \rightarrow f(t) = C_m(t)$

$$\bar{g}(p) = \frac{1}{\theta_{im} p + \zeta} \rightarrow g(t) = \mathcal{L}^{-1}\left[\frac{1}{\theta_{im} p + \zeta}\right]$$

$$= \frac{1}{\theta_{im}}\, \mathcal{L}^{-1}\left[\frac{1}{p + \frac{\zeta}{\theta_{im}}}\right]$$

The inverse is given by:

$$\mathcal{L}^{-1}[\cdot] = \text{EXP}\left\{-\frac{\zeta}{\theta_{im}} t\right\}$$

$$\therefore \quad g(t) = \frac{1}{\theta_{im}} \text{EXP}\left\{-\frac{\zeta}{\theta_{im}} t\right\}$$

$$\therefore \quad \boxed{C_{im} = \frac{\zeta}{\theta_{im}} \int_0^t C_m(\tau)\, \text{EXP}\left\{-\frac{\zeta}{\theta_{im}}(t-\tau)\right\} d\tau}$$

<u>CHECK</u>: For $C_m(t) = C_m^o$, a constant.

$$C_{im} = C_m^o \frac{\zeta}{\theta_{im}} \int_0^t \text{EXP}\left\{-\frac{\zeta}{\theta_{im}}(t-\tau)\right\} d\tau$$

Letting $\chi = t - \tau \rightarrow d\tau = -d\chi$

$\tau = 0 \rightarrow \chi = t$

$\tau = t \rightarrow \chi = 0$

$$\therefore \quad C_{im} = C_m^o \frac{\zeta}{\theta_{im}} \int_t^0 \text{EXP}\left\{-\frac{\zeta}{\theta_{im}} \chi\right\} (-d\chi)$$

$$= C_m^o \frac{\zeta}{\theta_{im}} \int_0^t \text{EXP}\left\{\frac{-\zeta}{\theta_{im}} \chi\right\} d\chi$$

$$= C_m^o \frac{\zeta}{\theta_{im}} \left(\frac{-\theta_{im}}{\zeta}\right) \text{EXP}\left\{-\frac{\zeta}{\theta_{im}} \chi\right\} \Bigg|_0^t$$

$$= -C_m^o \left(\text{EXP}\left\{-\frac{\zeta}{\theta_{im}} t\right\} - 1\right)$$

$$= C_m^o \left(1 - \text{EXP}\left\{-\frac{\zeta}{\theta_{im}} t\right\}\right) \qquad \checkmark$$

3. Limiting cases for dual-domain solute transport

This section examines the limiting cases for dual-domain solute transport. The results highlight the correct forms of the single domain solutions that arise for very low and very high mass transfer coefficients. It is particularly important to examine these limiting cases because they hold the key to understanding how the dual-domain approach is related to conventional solute transport modeling.

The limiting cases of solute transport with physical nonequilibrium are:

- Very slow mass transfer between the immobile and mobile regions; and
- Very fast slow mass transfer between the immobile and mobile regions.

To investigate these cases we consider an idealized example of three-dimensional transport from an instantaneous point source, with neither sorption nor transformation reactions. Groundwater flow is assumed to be steady and uniform, parallel to the *x*-direction.

The governing equations for dual-domain transport are:

$$\theta_m \frac{\partial C_m}{\partial t} = -q \frac{\partial C_m}{\partial x} + \theta_m D_{Lm} \frac{\partial^2 C_m}{\partial x^2} + \theta_m D_{THm} \frac{\partial^2 C_m}{\partial y^2} + \theta_m D_{TVm} \frac{\partial^2 C_m}{\partial z^2} - \alpha \left(C_m - C_{im} \right) + M\delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{1}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha \left(C_m - C_{im} \right) \tag{2}$$

We can write the first governing equation in an alternate form, by adding Equations (1) and Equation (2) to yield a statement for the total mass balance:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = -q \frac{\partial C_m}{\partial x} + \theta_m D_{Lm} \frac{\partial^2 C_m}{\partial x^2} + \theta_m D_{THm} \frac{\partial^2 C_m}{\partial y^2} + \theta_m D_{TVm} \frac{\partial^2 C_m}{\partial z^2} + M\delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{1b}$$

3.1 Limiting case for low mass transfer coefficient, α

For a very low mass transfer coefficient, that is, $\alpha \to 0$, there is no transport into the immobile region. Therefore, the dual domain solution collapses to a LEA (i.e., single porosity) model with the effective porosity being the mobile porosity. The problem reduces to a single governing equation:

$$\theta_m \frac{\partial C}{\partial t} = -q \frac{\partial C}{\partial x} + \theta_m D_{Lm} \frac{\partial^2 C}{\partial x^2} + \theta_m D_{THm} \frac{\partial^2 C}{\partial y^2} + \theta_m D_{TVm} \frac{\partial^2 C}{\partial z^2} + M \delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{3}$$

We can re-write (3) in an alternate form by dividing through by θ_m:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D_{Lm} \frac{\partial^2 C}{\partial x^2} + D_{THm} \frac{\partial^2 C}{\partial y^2} + D_{TVm} \frac{\partial^2 C}{\partial z^2} + \frac{M}{\theta_m} \delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{3b}$$

The effective velocity v is given by q/θ_m.

This simple theoretical argument suggests that for cases with low values of the mass transfer coefficient, solute transport models that incorporate dual domain collapse to single domain models with the effective porosity given by the mobile porosity and the effective groundwater velocity given by q/θ_m, where q is the Darcy flux.

3.2 Limiting case for high mass transfer coefficient, α

For a very high mass transfer coefficient, that is, $\alpha \rightarrow \infty$, there is instantaneous transport between the mobile and immobile regions. Therefore, the concentrations in the two domains are identical. The problem reduces to a single governing equation from (1b):

$$(\theta_m + \theta_{im})\frac{\partial C}{\partial t} = -q\frac{\partial C}{\partial x} + \theta_m D_{Lm}\frac{\partial^2 C}{\partial x^2} + \theta_m D_{THm}\frac{\partial^2 C}{\partial y^2} + \theta_m D_{TVm}\frac{\partial^2 C}{\partial z^2} + M\delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{4}$$

Let us again divide through by θ_m:

$$\left(1+\frac{\theta_{im}}{\theta_m}\right)\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D_{Lm}\frac{\partial^2 C}{\partial x^2} + D_{THm}\frac{\partial^2 C}{\partial y^2} + D_{TVm}\frac{\partial^2 C}{\partial z^2} + \frac{M}{\theta_m}\delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{4b}$$

Equation (5b) is identical to (4b), except for the leading coefficient in the mass accumulation term. If we re-write (4b) as:

$$R\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D_{Lm}\frac{\partial^2 C}{\partial x^2} + D_{THm}\frac{\partial^2 C}{\partial y^2} + D_{TVm}\frac{\partial^2 C}{\partial z^2} + \frac{M}{\theta_m}\delta(t-0)\delta(x-0)\delta(y-0)\delta(z-0) \tag{4c}$$

This simple theoretical argument suggests that for cases with high values of the mass transfer coefficient, solute transport models that incorporate dual domain again collapse to single domain models, but this time with the effective porosity given by the mobile porosity, and with an effective retardation factor given by an "effective" retardation factor R given by:

$$R = 1+\frac{\theta_{im}}{\theta_m} \tag{5}$$

3.3 Example calculations

We will consider three-dimensional transport from an instantaneous point source in an infinite domain. For this problem we neglect molecular diffusion and calculate the dispersion coefficients according to:

$$D_{Lm} = \alpha_L \frac{q}{\theta_m} \tag{6}$$

$$D_{THm} = \alpha_{TH} \frac{q}{\theta_m} \tag{7}$$

$$D_{TVm} = \alpha_{TV} \frac{q}{\theta_m} \tag{8}$$

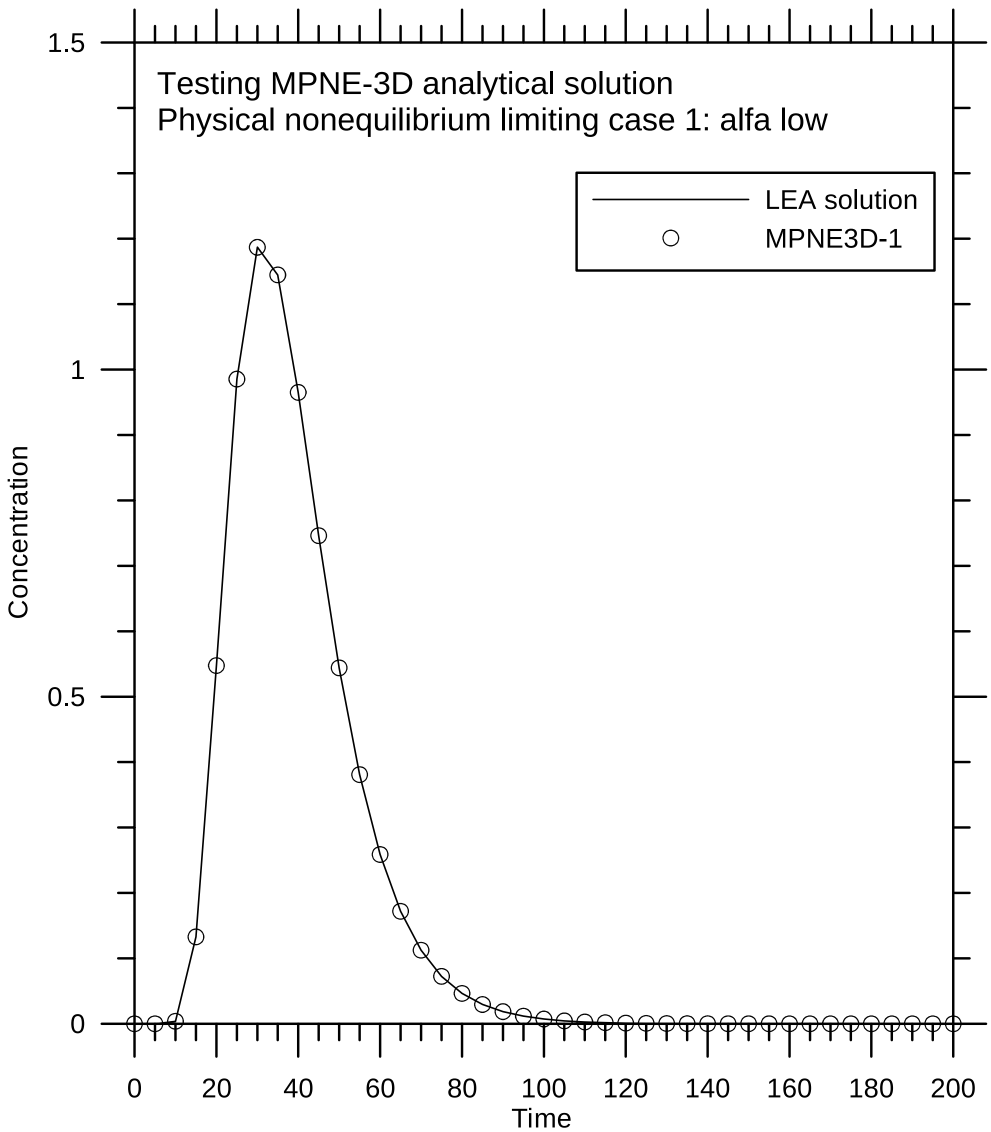
The parameters for the example are derived from the Stanford-Waterloo tracer test:

Parameter	**Value**
Darcy flux, q	0.02138 cm/d
Total porosity, θ	0.33
Mobile porosity, θ_m (ϕ = 0.50)	0.165
Immobile porosity, θ_{im} (1-ϕ = 0.50)	0.165
Longitudinal dispersion coefficient, D_x	0.045 cm^2/d
Horizontal transverse dispersion coefficient, D_y	0.0045 cm^2/d
Vertical transverse dispersion coefficient, D_z	0.000198 cm^2/d
Mass of slug, M	0.3610

Limiting case #1: Very slow mass transfer between mobile and immobile regions

For $\alpha \rightarrow 0$, the dual-domain solution should collapse to a single porosity problem (LEA) with the effective porosity equal to the mobile porosity, 0.165. For the LEA solution we use the following "effective" parameters:

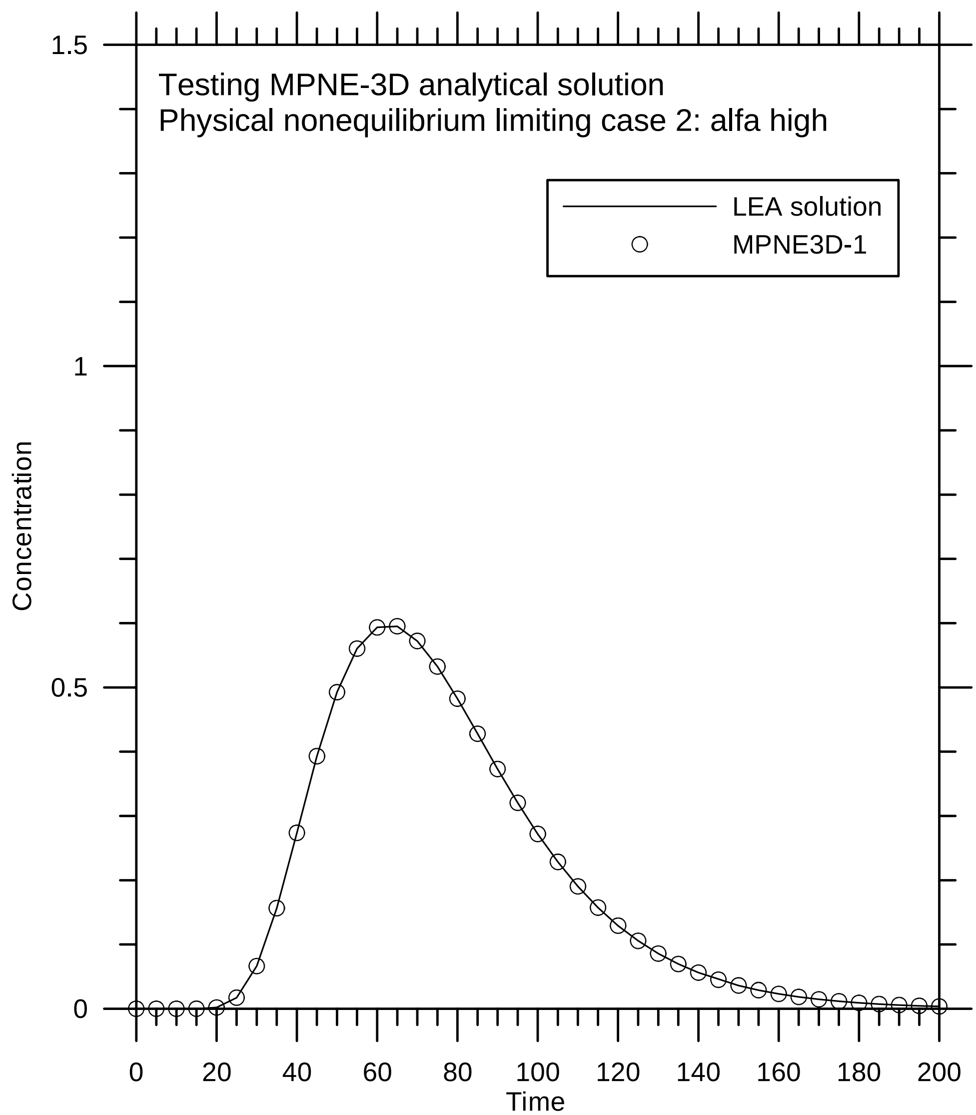
Parameter	**Value**
Avg. linear groundwater velocity, v	0.12958 cm/d
Longitudinal dispersion coefficient, D_x	0.3473 cm^2/d
Horizontal transverse dispersion coefficient, D_y	0.03473 cm^2/d
Vertical transverse dispersion coefficient, D_z	0.00153 cm^2/d



Limiting case #2: Very fast mass transfer between mobile and immobile regions

For $\alpha \rightarrow \infty$, the dual-domain solution should collapse to a single porosity problem (LEA) with the effective porosity equal to the mobile porosity, 0.165, and an "effective retardation coefficient of 2.0. For the LEA solution we use the following "effective" parameters:

Parameter	**Value**
Avg. linear groundwater velocity, v	0.12958 cm/d
Longitudinal dispersion coefficient, D_x	0.3473 cm^2/d
Horizontal transverse dispersion coefficient, D_y	0.03473 cm^2/d
Vertical transverse dispersion coefficient, D_z	0.00153 cm^2/d
Retardation factor, R	2.0



4. Conclusions

Although the first-order mass transfer coefficient is a curve-fitting parameter that in general cannot be estimated independently, it is possible to assign physical meaning to asymptotic conditions.

1. When the mass transfer coefficient is relatively low, mass transfer between the mobile and immobile domains is negligible and the model responds as if there is a single porosity corresponding to the mobile porosity. The effective groundwater velocity is given by q/θ_m, where q is the Darcy flux.

2. When the mass transfer coefficient is relatively high, mass transfer between the mobile and immobile domains is rapid and the concentrations in the two domains equilibrate rapidly. For very high values of the mass transfer coefficient, solute transport models that incorporate dual domain again collapse to single domain models, with the effective porosity given by the mobile porosity, but with an effective retardation factor given be:

$$R = 1 + \frac{\theta_{im}}{\theta_m}$$