

# Effective parameters in heterogeneous and homogeneous transport models with kinetic sorption

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**Abstract.** Transport of dissolved tracers undergoing kinetic sorption in saturated porous media is described on the basis of a dual-porosity model with heterogeneous and cross-correlated sorption parameters, i. e., distribution coefficient and exchange rate. The approach is a conceptual model for reactive transport in a medium with spatially varying reaction capacity, given by the distribution coefficient, and spatially varying accessibility, given by the exchange rate. We treat the sorption parameters as a stochastic process and apply a perturbation approach. From the ensemble-averaged spatial moments of a plume, we analytically derive formal expressions for time-dependent effective transport parameters. For vanishing microdispersion the calculations are carried out up to second order for the effective transport velocity  $u^{\text{eff}}(t)$  and the effective dispersion coefficient  $D^{\text{eff}}(t)$ . For large times the effective retardation is determined by the ensemble-averaged distribution coefficient, whereas the effective dispersion is related to the sorption parameters in a more complicated way depending on the variability of the exchange rate and of the distribution coefficient. Effective sorption parameters are given. For comparison we derive exact expressions for  $u^{\text{eff}}(t)$  and  $D^{\text{eff}}(t)$  in a homogeneous triple-porosity model. Unlike the simpler homogeneous dual-porosity model, the triple-porosity model yields a satisfactory description of the time-dependent dispersion of the heterogeneous model. The appropriate sorption parameters for the triple-porosity model are given as functions of the stochastic parameters.

## 1. Introduction

Homogeneous dual-porosity models with linear kinetic exchange between a mobile and an immobile zone have been studied extensively in the literature. Among the transport situations described by dual-porosity models are solute transport subject to kinetic sorption, diffusion into dead-end pores, and advective exchange into lenses of very low conductivity, as well as transport in fractured media. For the derivation of dual-porosity models and their use see, for example, *Douglas and Arbogast* [1990], *Haggerty and Gorelick* [1995], *Sahimi* [1995], and *Sardin et al.* [1991].

Explicit solutions for the concentration distribution  $c(x, t)$  in one and three dimensions for step and delta inputs are given by *de Smedt and Wierenga* [1979] and *Goltz and Roberts* [1986], respectively. These analytical solutions are based on integral transformations and are limited to homogeneous dual-porosity models. Adding a second immobile region already leads to transformed solutions that can no longer be inverted analytically. Similarly, a heterogeneous distribution of sorption parameters defies an exact analytic treatment. In 1987, *Goltz and*

*Roberts* [1987] presented a detailed analysis of the effective transport velocity and dispersion in homogeneous dual-porosity and diffusion models, calculating both temporal and spatial moments of the concentration distribution. Differences between effective parameters based on spatial and temporal moments have been found.

More recent studies focus on homogeneous multiregion models. The review article of *Sardin et al.* [1991] investigates the breakthrough curve (BTC), i.e., temporal moments of the concentration distribution. The BTC is found to be quite insensitive to the details of the microscopic sorption processes. *Haggerty and Gorelick* [1995] show the equivalence of homogeneous diffusion models and multiregion models and present semianalytical solutions for special flow conditions. Application to Borden data leads to the conclusion that even in a relatively homogeneous aquifer, the mass exchange process is best modeled by a mixture of exchange rates.

Another class of studies investigates kinetic sorption in aquifers with spatially variable conductivity. However, the sorption parameters are still treated as constants. According to numerical calculations by *Selroos and Cvetkovic* [1992], the effects of kinetic sorption on dispersion are similar to macrodispersion resulting from the variability in conductivity, rendering their identification difficult if not impossible. *Dagan and Cvetkovic* [1993] generalize *Dagan's* [1988] theory of macrodispersion by including linear and homogeneous kinetic sorption. Formal expressions for the lower spatial moments are given. The dispersion coefficient consists of a term resulting from the kinetic

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exchange only and of a mixed term including both the sorption kinetics and the variability of conductivity. For transport times large compared to the exchange time and a characteristic heterogeneity time, dispersion of a Fickian type is found. Similar results are given by *Quinodoz and Valocchi* [1993].

*Hu et al.* [1995] take into account a heterogeneous conductivity and a heterogeneous distribution coefficient while treating the exchange rate as constant. They present semianalytical calculations for the effective velocity and dispersion as well as for the skewness.

Our approach is a general conceptual model for reactive transport in a medium with spatially varying reaction capacity, given by the distribution coefficient, and spatially varying accessibility, given by the exchange rate. Hereby we focus on the effects of heterogeneous and correlated sorption parameters on transport in a constant flow field. We choose to keep the flow velocity constant in order to isolate and better assess the effects of the sorption heterogeneity. This assumption is not crucial and the formalism can be extended to account for a heterogeneous flow field. In the case of vanishing cross correlations between the flow and the sorption processes the heterogeneity of the flow field leads to the classical macrodispersion results of *Gelhar* [1993], *Dagan* [1989], and others and superimposes linearly onto the effects of the sorption heterogeneity.

Note that our approach is also a conceptual model for a nonadsorptive medium with very high contrasts in hydraulic conductivity, as for instance, in a sandy aquifer containing low-permeability clay lenses. In this scenario the log conductivity distribution is bimodal and has a variance much greater than unity, defying the applicability of the classical theory of macrodispersion. In a dual-porosity model the sandy soil can be represented by the mobile regions, whereas the slow advective transport through the clay lenses can be modeled as solute exchange into an immobile region. The sorption parameters are then interpreted as "immobile capacity" and "accessibility" to the lenses (see the discussion accompanying (3)).

Using a perturbation approach, we analytically calculate time-dependent effective transport parameters on the basis of the spatial moments of a plume. For comparison with the heterogeneous dual-porosity model we exactly derive the time-dependent effective transport velocity and dispersion coefficient for an equivalent homogeneous triple-porosity model with two immobile zones. We finally derive the parameters of this equivalent triple-porosity model from the statistics of the sorption parameters.

## 2. Description of the Heterogeneous Model

As shown by *Haggerty and Gorelick* [1995], all standard first-order two-region models are essentially the same. For simplicity the following reduced formulation of the basic equations is used.

$$\partial_t g(x, t) + \phi(x) \partial_t g_{im}(x, t) + \hat{u} \nabla g(x, t) - \nabla \hat{D} \nabla g(x, t) = 0 \quad (1a)$$

$$\partial_t g_{im}(x, t) = \alpha(x) [g(x, t) - g_{im}(x, t)] \quad (1b)$$

In this formulation,  $g$  and  $g_{im}$  designate the mobile and the immobile tracer concentrations, respectively. The first equation describes transport in the mobile phase with seepage velocity  $\hat{u}$  and dispersion coefficient  $\hat{D}$ . It also includes an exchange of solute into the immobile phase, a process which is

described by a linear relationship in the second equation. The exchange rate  $\alpha$  sets the fundamental timescale for the sorption or exchange process. We call  $\phi$  the distribution coefficient since in the limit  $\alpha \rightarrow \infty$  the given set of equations reduces to a single transport equation which accounts for linear equilibrium sorption with distribution coefficient  $\phi$ .

The reduced equations can be cast into the form of the standard physical first-order model by choosing

$$g = R_m c_m \quad \hat{u} = \frac{u}{R_m} \quad \hat{D} = \frac{D}{R_m}$$

$$g_{im} = R_m c_{im} \quad \alpha = \frac{\beta}{R_m n_{im}} \quad \phi = \frac{R_m n_{im}}{R_m n_m}$$

The subscripts  $m$  and  $im$  denote the mobile and the immobile phases, respectively. Linear equilibrium sorption in either zone is taken into account by the retardation factors  $R_m$  and  $R_{im}$ . The mobile and the immobile porosities are denoted by  $n_m$  and  $n_{im}$ , and  $\beta$  is the exchange coefficient. To be consistent with (1a) and (1b), the retardation factor in the mobile zone,  $R_m$ , must be constant. The effects of a heterogeneous retardation factor have been extensively investigated [*Garabedian et al.*, 1988; *Dagan*, 1989; *Metzger et al.*, 1996], so the assumption is not crucial (see the above discussion on the homogeneity of the flow).

The sorption parameters  $\alpha$  and  $\phi$  are determined according to the physical or chemical process described by the dual-porosity model. In the case of diffusion into dead-end pores the exchange rate is given by [*van Genuchten*, 1985; *Parker and Valocchi*, 1986; *Rao et al.*, 1980]

$$\alpha = \alpha^*(\phi, T) \frac{D'_m}{a^2} \quad (2)$$

where  $D'_m$  is the diffusion coefficient valid in the porous medium and  $a$  is a typical pore length. The correction factor  $\alpha^*$  depends weakly on the distribution coefficient and an averaging time  $T$ . Typical values in column experiments are  $\phi \approx 0.1$  and  $\alpha \approx 10^2 \cdots 10^3 \text{ d}^{-1}$  [*de Smedt and Wierenga*, 1984].

The advective transport through lenses with very low conductivity with respect to their surroundings can be modeled by a solute exchange between two porosities. In this case one may use [*Kobus et al.*, 1992; *Schäfer*, 1991]

$$\alpha = \frac{1}{n_m \phi} \left( \frac{\phi}{\phi + 1} \right)^{2/3} \frac{3}{2 + \frac{K_{im}}{K_m}} \frac{K_{im} |u|}{K_m L} \quad (3)$$

where  $K_m$  and  $K_{im}$  denote the conductivities of the two regions and  $L$  is a typical length of the lenses. The parameter  $\phi = n_{im}/n_m$  is determined by the ratio of immobile to mobile water content and can be interpreted as immobile capacity, while the exchange rate  $\alpha$  can be thought of as a measure of the accessibility to the lenses. For clay lenses in a sandy aquifer ( $u \approx 0.1 \text{ m/d}$ ,  $n_m \approx 0.2$ ,  $\phi \approx 0.1$ ,  $K_{im}/K_m \approx 10^{-2} \cdots 10^{-3}$ ,  $L \approx 1 \text{ m}$ ), exchange rates  $\alpha \approx 10^{-2} \cdots 10^{-3} \text{ d}^{-1}$  may result.

For an instantaneous unit point source of solute injected into the mobile region of a  $d$ -dimensional infinite medium, (1a) and (1b) is supplemented by the following initial and boundary conditions:

$$g(x, t = 0) = \delta^d(x) \quad \lim_{|x| \rightarrow \infty} g(x, t) = 0 \quad (4)$$

$$g_{im}(x, t = 0) = 0 \quad \lim_{|x| \rightarrow \infty} g_{im}(x, t) = 0 \quad (5)$$

An implicit solution of (1a) and (1b) then is derived by solving the rate equation (1b), inserting  $g_{\text{im}}(x, t)$  into (1a), and transforming the resulting differential equation into an integral equation.

$$g(x, t) = g_0(x, t) - \int dx' \int dt' g_0(x - x', t - t') \phi(x') \partial_{t'} \cdot \int_0^{t'} d\tau \alpha(x') e^{-\alpha(x')(t'-\tau)} g(x', \tau) \quad (6)$$

The propagator  $g_0$  denotes the Green's function for conservative transport without exchange into an immobile region ( $\phi \rightarrow 0$  and  $\alpha \rightarrow \infty$ ). It is a constantly spreading  $d$ -dimensional normal distribution given by

$$g_0(x, t) = \frac{\Theta(t)}{\sqrt{(4\pi t)^d \det \hat{D}}} \exp \left\{ -\frac{1}{4t} (x - \hat{u}t) \hat{D}^{-1} (x - \hat{u}t) \right\} \quad (7)$$

where  $\Theta(t)$  is the Heavyside step function. For negative times,  $g_0$  vanishes; for  $t > 0$  it is normalized to unit mass.

### 3. Definition of Effective Transport Parameters

The heterogeneous structure of the sorption parameters  $\alpha(x)$  and  $\phi(x)$  is modeled by a two-component stationary and ergodic stochastic process. The aquifer is regarded as one realization of an ensemble, reflecting the stochastic properties of the process [Dagan, 1989; Gelhar, 1993; van Kampen, 1981].

To obtain a consistent description of the effective behavior of the solute plume, the quantities of interest are calculated in each realization. We then derive the effective parameters by averaging over the ensemble. Sometimes, the "effective" behavior is derived from the moments of the ensemble-averaged concentration distribution. This approach is mathematically less demanding but contains artificial effects such as dispersion due to the spreading of the center of mass movement in different realizations. For a more detailed discussion, see, for example, [Kitanidis, 1988; Dagan, 1990; Rajaram and Gelhar, 1993; Metzger et al., 1996].

Because of the heterogeneous structure of the sorption parameters, no exact solution of (1a) and (1b) is known. Yet, the calculation of low-order spatial moments of the normalized concentration distribution in the mobile phase provides a crude description of the behavior of the solute plume. The first moment and the second and third central moments in each realization are given by

$$\mu_i^{(1)}(t) \equiv \int x_i p(x, t) dx \quad (8a)$$

$$\mu_{ij}^{(2)}(t) \equiv \int [x_i - \mu_i^{(1)}(t)][x_j - \mu_j^{(1)}(t)] p(x, t) dx \quad (8b)$$

$$\mu_{ijk}^{(3)}(t) \equiv \int [x_i - \mu_i^{(1)}(t)][x_j - \mu_j^{(1)}(t)] \cdot [x_k - \mu_k^{(1)}(t)] p(x, t) dx \quad (8c)$$

with

$$p(x, t) \equiv \frac{g(x, t)}{\int g(x', t) dx'} \quad (9)$$

The effective transport velocity and the effective dispersion coefficient then follow from the time-dependent spatial moments by differentiation with respect to time and averaging the resulting expressions over the ensemble.

$$u_i^{\text{eff}}(t) \equiv \overline{\partial_t \mu_i^{(1)}(t)} \quad D_{ij}^{\text{eff}}(t) \equiv \frac{1}{2} \overline{\partial_t \mu_{ij}^{(2)}(t)} \quad (10)$$

The overbar denotes the ensemble average. Using these effective transport parameters, effective sorption parameters will be derived later.

To describe the asymmetry of the concentration distribution relative to its width, we define a skewness parameter

$$S(t) \equiv \frac{\overline{\mu_{111}^{(3)}(t)}}{[\overline{\mu_{11}^{(2)}(t)}]^{3/2}} \quad (11)$$

where  $\mu_{111}^{(3)}(t)$  denotes the third central moment in the direction of the 1 axis. Negative skewness indicates that the maximum of the concentration distribution is ahead of its center of mass. This situation corresponds to the usually observed tailing.

It is important to note that the effective transport parameters are only illustrating the behavior of the low-order moments of the solute plume. We do not intend to use time-dependent effective transport parameters together with the classical advection-dispersion equation. Rather will we derive effective sorption parameters which can be used in simple homogeneous multiporosity models.

### 4. Perturbation Approach

From (6) we shall construct a perturbation series expansion around  $g_0$  by iteration. Recall that  $g_0$  is the Green's function for transport without sorption. This implies that the sorption process as a whole is treated as a perturbation. In a second step we will then expand the heterogeneous sorption parameters around their mean values. At first glance it might seem more natural to expand around the Green's function of the homogeneous dual-porosity model rather than around  $g_0$ . However, this is not analytically tractable because of the complicated structure of the Green's function of the dual-porosity model [Goltz and Roberts, 1986]. As we shall see later, our double-perturbation approach leads to the same results in the limit of large transport times and to good approximations at finite times (see the discussion accompanying (19) and (20)).

The implicit solution (6) is now expanded into a perturbation series by inserting  $g$  iteratively into the right-hand side. This yields a series

$$g(x, t) = g_0(x, t) + \mathcal{A}(x, t) + \mathcal{B}(x, t) + \mathcal{C}_3 \quad (12)$$

The expressions for  $\mathcal{A}$  and  $\mathcal{B}$  are given in Appendix A. Terms linear in  $\mathcal{A}$  are referred to as first-order terms. Expressions linear in  $\mathcal{B}$  (or quadratic in  $\mathcal{A}$ ) will be called second-order terms. The series (12) is truncated after the second order, and all contributions of third and higher orders in the iteration, denoted by  $\mathcal{C}_3$ , are omitted. Combining (12) with a geometric series expansion of  $1/fg \approx 1/(1 + f\mathcal{A} + f\mathcal{B})$  yields an expansion for the normalized distribution  $p(x, t)$ .

**Table 1.** Dimensionless System Parameters

Parameter	Description	Comments
$\gamma_1 \equiv \hat{D} / \left( \frac{\hat{u}^2 \bar{\phi}}{\bar{\alpha}(1 + \bar{\phi})^3} \right)$	$\frac{\text{microdispersion}}{\text{dispersion from sorption kinetics}}$	in particular $\gamma_1 \ll 1$ interesting
$\gamma_2 \equiv \frac{\bar{\alpha} \ell}{ \hat{u} }$	$\frac{\text{advective time}}{\text{exchange time}}$	$\gamma_2 \ll 1$ necessary for stochastic description at finite $t$

$$\begin{aligned}
p(x, t) = & g_0(x, t) + \left[ \mathcal{A}(x, t) - g_0(x, t) \int \mathcal{A}(x', t) dx' \right] \\
& + \left[ \mathcal{B}(x, t) - g_0(x, t) \int \mathcal{B}(x', t) dx' \right] \\
& + \left[ g_0(x, t) \left( \int \mathcal{A}(x', t) dx' \right)^2 \right. \\
& \left. - \mathcal{A}(x, t) \int \mathcal{A}(x', t) dx' \right] + \mathcal{O}_3
\end{aligned} \quad (13)$$

In a second step we now decompose the sorption parameters into mean values and fluctuations:

$$\alpha(x) = \bar{\alpha} + \eta(x) \quad \phi(x) = \bar{\phi} + \varphi(x) \quad (14)$$

The correlation functions of the fluctuations are given by

$$\begin{aligned}
\overline{\eta(x')\eta(x'')} &= \sigma_\alpha^2 w_{\alpha\alpha}(x' - x'') & \overline{\varphi(x')\varphi(x'')} &= \sigma_\phi^2 w_{\phi\phi}(x' - x'') \\
\overline{\eta(x')\varphi(x'')} &= q w_{\alpha\phi}(x' - x'')
\end{aligned} \quad (15)$$

where the  $w_{(i)}$  are dimensionless functions and normalized at the origin,  $w(0) = 1$ . The relative strength of the cross correlations between  $\alpha$  and  $\phi$  is given by the correlation coefficient, defined as

$$\rho \equiv \frac{q}{\sigma_\alpha \sigma_\phi} \quad (16)$$

The derivation of the spatial moments is now straightforward if we assume that the fluctuations around the mean values are small, i.e.,  $\sigma_\alpha^2 \ll \bar{\alpha}^2$  and  $\sigma_\phi^2 \ll \bar{\phi}^2$ , and if we consequently approximate the stochastic process by the mean values and the correlation functions (15).

Without loss of generality the direction of the 1 axis is chosen parallel to the seepage velocity,  $\hat{u}_i = \hat{u} \delta_{1i}$ . The effective transport velocity will therefore be of the form  $u_i^{\text{eff}} = u^{\text{eff}} \delta_{1i}$ . For simplicity, microdispersion is assumed to be isotropic,  $\hat{D}_{ij} = \hat{D} \delta_{ij}$ . Starting from (13), we derive the spatial moments defined in (8). Expanding these expressions with respect to the random fluctuations of the sorption parameters (14) and averaging over the disorder ensemble, a lengthy but elementary calculation yields the expressions for the moments given in Appendix B. The integral representations given there are valid up to first order in the case of finite microdispersion and up to second order for vanishing microdispersion. From these integral representations the time-dependent effective transport parameters were derived analytically using the algebra software mathematica (Wolfram Research). Exponential

type isotropic correlation functions  $w_{(i)}(x) = \exp(-|x|/\ell_{(i)})$  were used.

## 5. Dimensionless Parameters, Validity at Finite Times

In this section we briefly discuss some necessary conditions to be fulfilled if the perturbation expansion (13) and the stochastic description at finite times are to make sense. By dimensional analysis the expansion parameter of the series expansion (12) is found to be  $\phi(x)\alpha(x)\hat{D}/\hat{u}^2$ . A necessary condition to justify the truncation of this series is therefore the smallness of  $\gamma_0 \equiv \bar{\phi}\bar{\alpha}\hat{D}/\hat{u}^2 \ll 1$ .

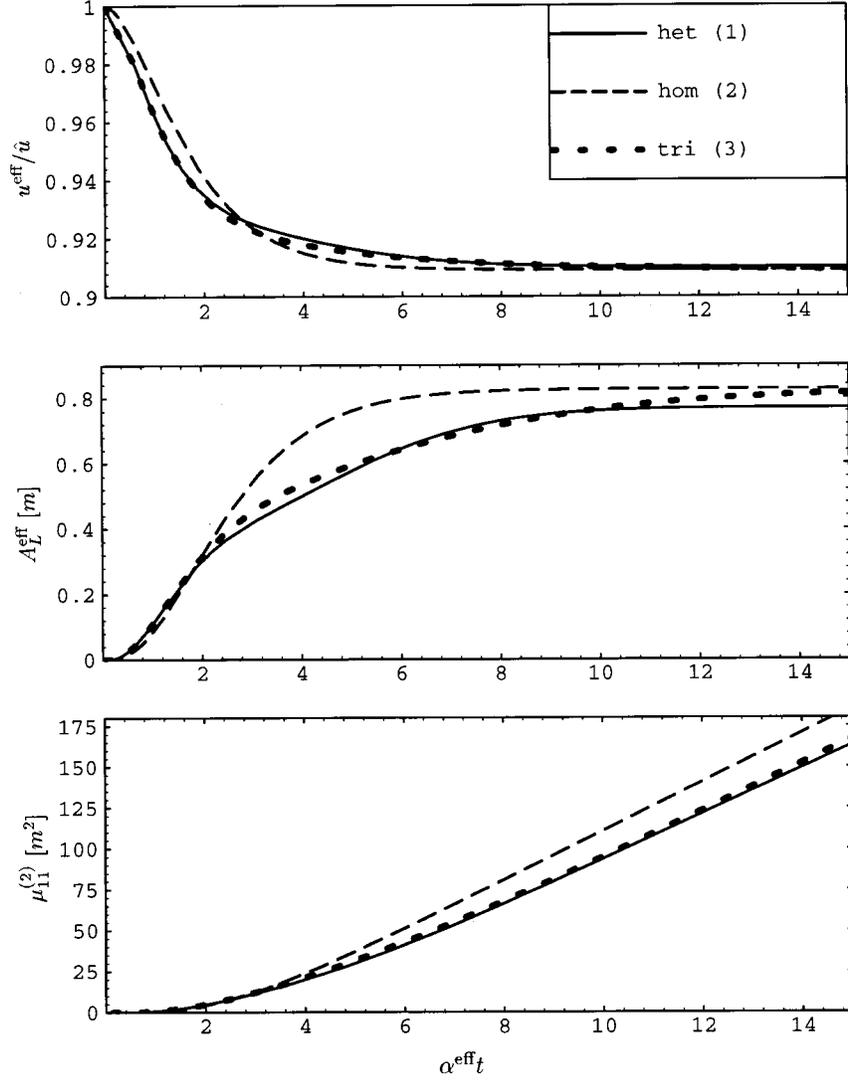
For a further analysis, dimensionless parameters are introduced (Table 1). To simplify the discussion, the correlation lengths of the sorption parameters are set equal to  $\ell$ . In the case of a homogeneous dual-porosity model the large-time longitudinal dispersion coefficient contains the additive term  $\hat{u}^2 \bar{\phi} / [\bar{\alpha}(1 + \bar{\phi})^3]$ , resulting from sorption kinetics [Goltz and Roberts, 1987]. The parameter  $\gamma_1$  compares this dispersive effect to microdispersion. The use of dual-porosity models is especially interesting for relatively strong dispersion resulting from sorption kinetics, i.e.,  $\gamma_1 \ll 1$ . In this case the expansion parameter  $\gamma_0 = \gamma_1 \bar{\phi}^2 / (1 + \bar{\phi})^3$  is small, too.

The time evolution of the transport parameters takes place with a typical timescale, given by the exchange time  $\bar{\alpha}^{-1}$ . For times large compared to  $\bar{\alpha}^{-1}$  the effective transport velocity and dispersion coefficient reach limiting values (see, e.g., Figure 1). To obtain a meaningful time evolution from the stochastic description, the plume has to “experience the aquifer” within times small compared to  $\bar{\alpha}^{-1}$ . Experiencing the aquifer means that the effective quantities become independent of the special realization in which they are calculated or measured. This can strictly be valid only for  $t \rightarrow \infty$ , when the advective transport has covered infinitely many correlation lengths and the plume has thus experienced the entire aquifer. In practice, however, this limit might be reached earlier. The parameter  $\gamma_2$  compares the advective time for transport over one correlation length to the exchange time. If  $\gamma_2 \ll 1$ , the time evolution of the effective transport parameters is slow compared to the advective transport over one correlation length. A stochastic description of the time evolution is then justified. Note that the validity of the results for  $t \rightarrow \infty$  is independent of this restriction.

## 6. Results and Discussion

### 6.1. Heterogeneous Model for $t \rightarrow \infty$

For vanishing microdispersion,  $u^{\text{eff}}(t)$  and  $D^{\text{eff}}(t)$  were calculated as discussed above. The large-time limits of the effective transport parameters are



**Figure 1.** Effective transport velocity, effective dispersivity, and longitudinal second central moment for (1) the heterogeneous model up to second order, (2) the effective homogeneous dual-porosity model, and (3) the triple-porosity model. Correlation between  $\alpha$  and  $\phi$  is assumed to be positive ( $\rho = +1$ ). The other parameters are  $\hat{u} = 0.1m/d$ ,  $\hat{D} = 0$ ,  $\bar{\alpha} = 0.01d^{-1}$ ,  $\bar{\phi} = 0.1$ ,  $\sigma_\alpha^2/\bar{\alpha}^2 = \sigma_\phi^2/\bar{\phi}^2 = 0.3$ ,  $\bar{\eta}^3 = \bar{\eta}^2\bar{\varphi} = 0$ ,  $\ell_{\alpha\alpha} = \ell_{\alpha\phi} = \ell_{\phi\phi} = 1m$ ,  $\alpha^{\text{eff}} = 0.01d^{-1}$ ,  $\phi^{\text{eff}} = 0.1$ ,  $\phi_1 = 0.077$ ,  $\phi_2 = 0.023$ ,  $\alpha_1 = 0.0155d^{-1}$ , and  $\alpha_2 = 0.0045d^{-1}$ .

$$\lim_{t \rightarrow \infty} u^{\text{eff}}(t) = \hat{u}(1 - \bar{\phi} + \bar{\phi}^2) + \mathcal{O}_3 \quad (17)$$

$$\lim_{t \rightarrow \infty} D_L^{\text{eff}}(t) = \frac{\hat{u}^2 \bar{\phi}}{\bar{\alpha}} \left[ 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha \sigma_\phi}{\bar{\alpha} \bar{\phi}} - \frac{\bar{\eta}^3}{\bar{\alpha}^3} + \frac{\bar{\eta}^2 \bar{\varphi}}{\bar{\alpha}^2 \bar{\phi}} \right] - 3\bar{\phi} \left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha \sigma_\phi}{\bar{\alpha} \bar{\phi}} \right) + \mathcal{O}_3 \quad (18)$$

Obviously, (17) and (18) are series expansions in  $\bar{\phi}$  from which we can a posteriori derive the necessary condition  $\bar{\phi} < 1$  for the convergence of these series. In the limiting case of spatially constant sorption parameters, which implies  $\sigma_\alpha^2 = \sigma_\phi^2 = \bar{\eta}^3 = \bar{\eta}^2 \bar{\varphi} = 0$ , the results reproduce the corresponding expansion with respect to  $\phi$  of the exact solution for the homogeneous model [Goltz and Roberts, 1987]. Recollecting these contributions from the homogeneous model allows us to partially sum up the expansion in  $\phi$ . We get

$$\lim_{t \rightarrow \infty} u^{\text{eff}} = \frac{\hat{u}}{(1 + \bar{\phi})} \quad (19)$$

$$\lim_{t \rightarrow \infty} D_L^{\text{eff}} = \frac{\hat{u}^2 \bar{\phi}}{\bar{\alpha}(1 + \bar{\phi})^3} \left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha \sigma_\phi}{\bar{\alpha} \bar{\phi}} - \frac{\bar{\eta}^3}{\bar{\alpha}^3} + \frac{\bar{\eta}^2 \bar{\varphi}}{\bar{\alpha}^2 \bar{\phi}} \right) \quad (20)$$

This procedure amounts to considering the perturbation expansion around the solution of the homogeneous dual-porosity model. One is left with the approximation of small deviations of the sorption parameters from their mean values.

From (19) we see that the effective retardation is given by the ensemble average of the retardation factor  $(1 + \bar{\phi})$  and not by its harmonic mean, which would yield an expansion  $(1 + \bar{\phi})^{-1} \approx 1 - \bar{\phi} + \bar{\phi}^2 + \sigma_\phi^2$ , contrary to (17). This is consistent with most results for equilibrium sorption [Garabedian *et al.*, 1988; Dagan, 1989; Metzger *et al.*, 1996] but contradicts the findings of Kabala and Sposito [1991]. This point is discussed in more detail by Metzger *et al.* [1996].

The corrections to the large-time effective longitudinal dispersion coefficient which are generated by the heterogeneity of the medium are dominated by the fluctuations in the exchange rate. As a result, the dispersion is usually larger than it would be in a homogeneous medium with constant parameters  $\bar{\alpha}$  and  $\bar{\phi}$ . A possible asymmetry in the distribution of exchange rates is taken into account by its third central moment  $\bar{\eta}^3$ . A small portion of very large exchange rates leads to an increase in  $\sigma_\alpha^2$  but also yields a positive  $\bar{\eta}^3$  such that these very large exchange rates have little effect on dispersion. The correlation coefficient  $\rho$ , defined in (16), weakens or strengthens the dispersion according to its sign. If small exchange rates are more likely to appear in combination with large distribution coefficients ( $\rho = -1$ ), then the effective dispersion is enhanced compared to the dispersion in a homogeneous medium with parameters  $\bar{\alpha}$  and  $\bar{\phi}$ . Higher-order cross correlations are taken into account by the term  $\bar{\eta}^2\varphi$ .

In the order of approximation used the correlation lengths and therefore the spatial structure do not explicitly enter the large-time effective transport parameters. Also, note that the absence of microdispersion and the parallel flow field lead to an effectively one-dimensional system with longitudinal mixing due to the kinetic sorption. For  $\alpha \rightarrow \infty$  the results (17) and (18) are consistent with the findings of Metzger *et al.* [1996] for a one-dimensional system with equilibrium sorption. In two and three dimensions, Metzger *et al.* [1996] find additive contributions to  $D_L^{\text{eff}}$  of the form  $\ell_{\phi\phi}\sigma_\phi^2\hat{u}/(1+\bar{\phi})^2$ . We would also expect such terms to appear if we included transverse mixing. However, we focus on the corrections discussed in the previous paragraph which do not contain the correlation lengths explicitly. They are dominant in some cases, for example, in the case of advective transport through clay lenses (see the discussion accompanying (3)).

Nevertheless, this does not mean that one can neglect the inherent spatial structure of the medium and simply deal with an ensemble of media with random but spatially constant sorption parameters. The effective retardation factor in this case would be determined by the harmonic mean, which is wrong as discussed above. Similarly, the ensemble average over the large-time effective dispersion coefficient of these media would lead to

$$\overline{\left(\frac{\phi}{\alpha(1+\phi)^3}\right)} \approx \frac{\bar{\phi}}{\bar{\alpha}} \left[ 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha\sigma_\phi}{\bar{\alpha}\bar{\phi}} - 3\bar{\phi} \left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - 2\rho \frac{\sigma_\alpha\sigma_\phi}{\bar{\alpha}\bar{\phi}} + \frac{\sigma_\phi^2}{\bar{\phi}^2} \right) \right]$$

where we have set  $\bar{\eta}^3 = \bar{\eta}^2\varphi = 0$  for clarity. This expansion differs from our results (equation (18)). It is therefore important to consider the stochastic field as a fixed spatial structure on which the dynamics of the system have to be calculated. In this respect the spatial structure is implicitly contained in our results.

In the large-time limit the results for the heterogeneous model correspond to those of a homogeneous dual-porosity model with appropriately chosen effective sorption parameters  $\alpha^{\text{eff}}$  and  $\phi^{\text{eff}}$ . Comparing (19) and (20) with the exact results for the homogeneous model yields

$$\phi^{\text{eff}} = \bar{\phi} \quad \alpha^{\text{eff}} = \frac{\bar{\alpha}}{\left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha\sigma_\phi}{\bar{\alpha}\bar{\phi}} - \frac{\bar{\eta}^3}{\bar{\alpha}^3} + \frac{\bar{\eta}^2\varphi}{\bar{\alpha}^2\bar{\phi}} \right)} \quad (21)$$

The effective distribution coefficient is given by the ensemble-averaged distribution coefficient, whereas the effective exchange rate includes cross correlations in the case of heterogeneous  $\phi$ . For larger variance  $\sigma_\alpha^2/\bar{\alpha}^2$  the effective exchange rate decreases because of the inverse proportionality between exchange rate and dispersion. For negative correlation between  $\alpha$  and  $\phi$  the effective exchange rate is diminished because the smaller exchange rates  $\alpha(x)$  are more likely to appear in combination with the larger immobile capacities  $\phi(x)$ .

The given effective sorption parameters are not meant to be correct in the sense of strict homogenization. They allow the reproduction of the large-time limits of the effective transport velocity and dispersion coefficient, but no conclusions about time evolution or higher moments can be drawn a priori.

The ensemble average skewness (equation (11)) was calculated up to first order with nonvanishing microdispersion. Note that in first order the spatial correlation structure does not come into play. The asymptotic behavior is given by

$$S(t) \xrightarrow{t \rightarrow \infty} \pm \left( \frac{t_0}{t} \right)^{1/2} \quad (22)$$

with

$$t_0 = \left\{ \left[ 12 \frac{\hat{D}\hat{u}\bar{\phi}}{\bar{\alpha}} \left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha\sigma_\phi}{\bar{\alpha}\bar{\phi}} \right) - 6 \frac{\hat{u}^3\bar{\phi}}{\bar{\alpha}^2} \left( 1 + 3 \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - 2\rho \frac{\sigma_\alpha\sigma_\phi}{\bar{\alpha}\bar{\phi}} \right) \right]^2 \right\} \cdot \left\{ \left[ 2\hat{D}(1-\bar{\phi}) + 2 \frac{\hat{u}^2\bar{\phi}}{\bar{\alpha}} \left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha\sigma_\phi}{\bar{\alpha}\bar{\phi}} \right) \right]^3 \right\}^{-1}$$

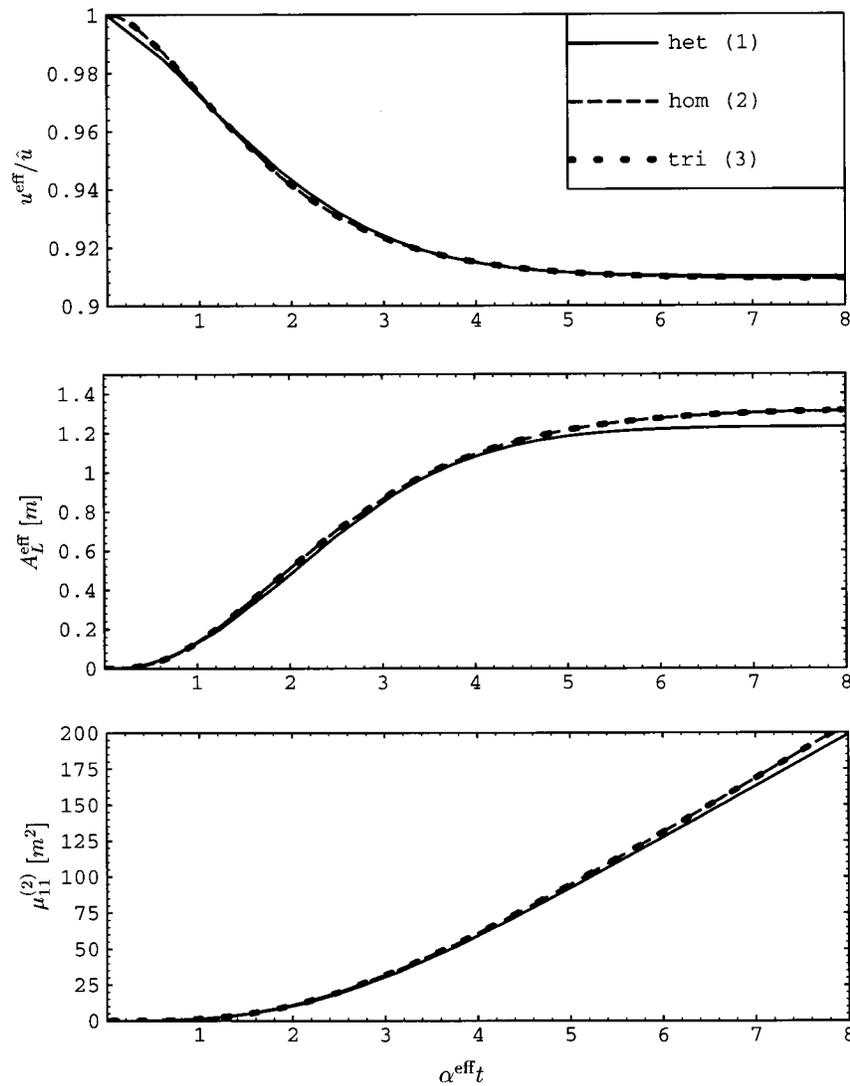
Although reaching zero for infinite times, the skewness vanishes extremely slowly compared with the typical timescale  $\bar{\alpha}^{-1}$  for  $u^{\text{eff}}$  and  $D_L^{\text{eff}}$  to reach their asymptotic values. The sign of the asymptotic skewness is given by the sign of the third central moment of the mobile concentration distribution (square bracket in the numerator). It is negative if the dispersion from sorption kinetics dominates over the microdispersion.

## 6.2. Time Evolution of the Effective Transport Parameters

As outlined in section 4, time-dependent effective transport parameters have been calculated analytically. However, the resulting expressions are lengthy and not very illuminating, so instead of giving the explicit formulae, we discuss the relevant results using the corresponding plots.

For a first set of stochastic parameters, Figure 1 shows the effective transport velocity, the effective longitudinal dispersivity  $A_L^{\text{eff}}(t) \equiv D_L^{\text{eff}}(t)/u^{\text{eff}}(t)$ , and the second central moment of the heterogeneous dual-porosity model, plotted against the dimensionless time  $\alpha^{\text{eff}}t$ . For comparison, exact expressions for an effective homogeneous dual-porosity model with sorption parameters  $\alpha^{\text{eff}}$  and  $\phi^{\text{eff}}$  (21) are also shown. In addition, the plots include the homogeneous triple-porosity model which will be discussed below.

The effective velocity of the solute decreases from its initial value  $\hat{u}$ , the transport velocity in the mobile phase, to the large-time limit as the solute undergoes exchange into the immobile phase where it is retarded. The time for this process to reach equilibrium is  $\sim 10/\alpha^{\text{eff}}$ . With regard to the effective velocity the differences between the heterogeneous and the homogeneous dual-porosity models are small. Moreover, the center of mass position (not shown) is found to be practically



**Figure 2.** Effective transport parameters and longitudinal second central moment. The correlation between  $\alpha$  and  $\phi$  is assumed to be negative ( $\rho = -1$ ). The other stochastic parameters are the same as in Figure 1, but  $\phi_2 = \phi^{\text{eff}} = 0.1$ ,  $\phi_1 = 0$ , and  $\alpha_2 = \alpha^{\text{eff}} = 0.00625d^{-1}$ .

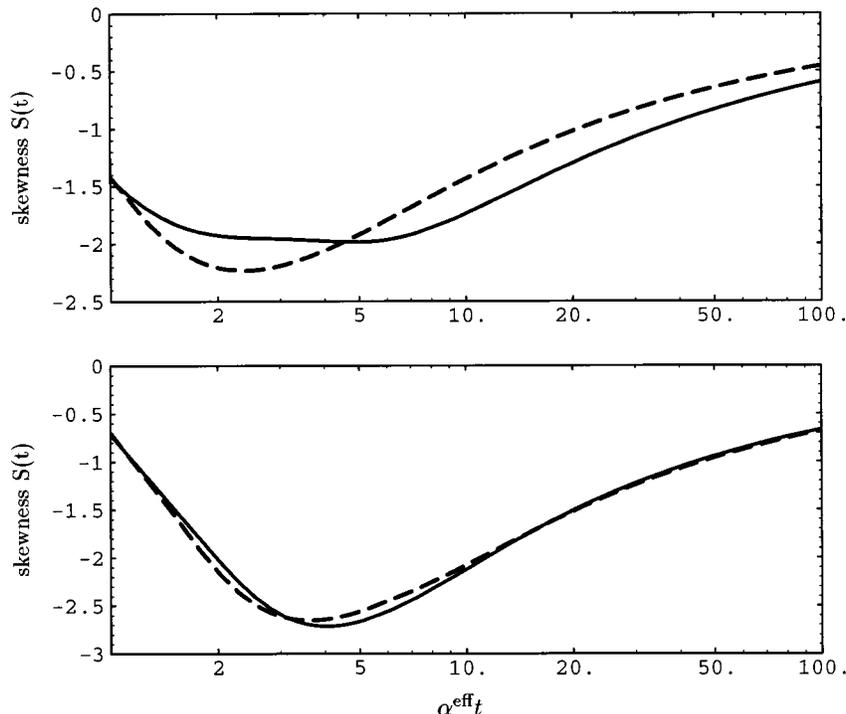
identical. This is due to the fact that for short times the homogeneous dual-porosity model shows smaller retardation than the heterogeneous model, whereas for intermediate times the opposite is true. Integration of the effective velocity to obtain the center of mass position smoothes out the differences. The above statements lead to the conclusion that with respect to effective retardation the heterogeneous model might be replaced by a homogeneous dual-porosity model using the effective sorption parameters given above. However, this is no longer valid if dispersion is considered.

The effective dispersivity increases from zero, microdispersion was assumed to vanish, to its limiting value. Note that for the heterogeneous model the plotted limiting values are given by (17) and (18), not by (19) and (20). Unfortunately, for the general time-dependent effective transport parameters a simple resummation of the series in  $\bar{\phi}$ , as discussed for the large-time limit, cannot be performed. In Figure 1, perfect positive correlation between the exchange rate and the distribution coefficient is assumed ( $\rho = +1$ ). This means that large  $\alpha$  are more likely to appear in combination with large  $\phi$ . Since dis-

persion due to sorption kinetics is proportional to  $\phi/\alpha$ , each pair  $(\alpha(x), \phi(x))$  contributes with about the same amount to the effective dispersion. But this contribution takes effect at different times because the typical timescale is of the order of  $1/\alpha$ . For this reason,  $A_L^{\text{eff}}$  reaches its large-time limit in several steps, a behavior that cannot be reproduced by a homogeneous dual-porosity model.

The second central moment is also shown in Figure 1. This measurable quantity directly describes the spreading of the solute plume. Replacing the heterogeneous model by an effective homogeneous dual-porosity model overestimates the solute spreading.

The situation for perfect negative correlation ( $\rho = -1$ ) between  $\alpha$  and  $\phi$  is shown in Figure 2. Apart from the previously discussed fact of slightly different large-time limits due to the limitations of the perturbation approach,  $u^{\text{eff}}(t)$  and  $A_L^{\text{eff}}(t)$  of the heterogeneous and homogeneous models do not differ significantly. For negative correlation, small exchange rates are more likely to appear in combination with large distribution coefficients. In this case,  $\phi/\alpha$ , and therefore the effective dis-



**Figure 3.** Skewness for the heterogeneous (solid) and the effective homogeneous (dashed) dual-porosity models. The correlation between  $\alpha$  and  $\phi$  is assumed positive ( $\rho = +1$ ) in the upper and negative ( $\rho = -1$ ) in the lower plot. The other parameters are  $\hat{u} = 0.1m/d$ ,  $\hat{D} = 0.01m^2/d$ ,  $\bar{\alpha} = 0.01d^{-1}$ ,  $\bar{\phi} = 0.1$ ,  $\sigma_{\alpha}^2/\bar{\alpha}^2 = \sigma_{\phi}^2/\bar{\phi}^2 = 0.3$ ,  $\phi^{\text{eff}} = 0.1$ ,  $\alpha^{\text{eff}} = 0.01d^{-1}$  for  $\rho = +1$  and  $\alpha^{\text{eff}} = 0.00625d^{-1}$  for  $\rho = -1$ .

persion, is completely dominated by the small exchange rates. Finally, it can be observed that the time needed for the effective transport parameters to fully reach their limiting values is only  $\sim 5/\alpha^{\text{eff}}$ , whereas for  $\rho = +1$  it takes  $\sim 10/\alpha^{\text{eff}}$ . Note that  $\alpha^{\text{eff}}$  is different in both cases.

Figure 3 shows the skewness of the heterogeneous and the effective homogeneous dual-porosity model for perfect positive and negative correlation, respectively. The plots result from the first-order expressions given in Appendix B. Microdispersion has a very strong influence on the skewness for short times. For vanishing microdispersion, skewness diverges toward minus infinity as  $t \rightarrow 0$ . Consequently, a nonvanishing microdispersion was chosen.

In contrast to the previous plots a logarithmic time axis is used to emphasize how slowly the skewness vanishes with time. Maximum skewness prevails until the effective transport parameters have reached their large-time limits. In the analysis of *Hu et al.* [1995], skewness is only plotted up to this time, suggesting that it will remain constant. Since their seepage velocity is random but their exchange rate is constant, the results are not fully comparable. However, a comprehensive explanation of skewness behavior due to sorption kinetics must take larger times into account.

As might be expected from the previous discussion, the effective homogeneous dual-porosity model cannot fully describe the skewness in the heterogeneous model for a positive correlation between  $\alpha$  and  $\phi$ , whereas for a negative correlation the difference between the models is hardly visible.

As a final comment, it should be noted that the analytical solutions were derived for arbitrary values of the correlation coefficient  $\rho$ . Indeed, the correlation can be virtually anything depending on the physical scenario which is described by the

dual-porosity model. Perfect positive and perfect negative correlation scenarios were plotted because they represent limiting cases with respect to the effects on the transport behavior.

### 6.3. Homogeneous Triple-Porosity Model

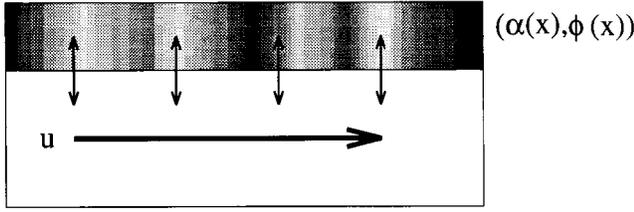
In the section 6.2 we saw that a homogeneous dual-porosity model cannot adequately reproduce the time evolution of the dispersion in the heterogeneous model. Our aim now is to derive more refined homogeneous sorption parameters, related to the stochastic properties of the medium, that allow a better description of the dispersion in the heterogeneous model within a homogeneous framework. We therefore investigate a homogeneous triple-porosity model with two immobile zones in parallel. Figure 4 shows a schematic overview of the models. In the triple-porosity model, exchange takes place from the mobile zone into two immobile zones with constant sorption parameters  $\alpha_1$ ,  $\alpha_2$ ,  $\phi_1$ , and  $\phi_2$ . The basic equations of the parallel triple-porosity model are

$$\begin{aligned} \partial_t g(x, t) + \phi_1 \partial_t g_{\text{im},1}(x, t) + \phi_2 \partial_t g_{\text{im},2}(x, t) \\ = \nabla \hat{D} \nabla g(x, t) - \hat{u} \nabla g(x, t) \end{aligned} \quad (23a)$$

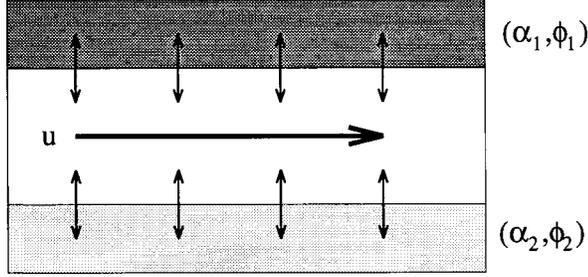
$$\partial_t g_{\text{im},j}(x, t) = \alpha_j [g(x, t) - g_{\text{im},j}(x, t)] \quad j = 1, 2 \quad (23b)$$

The derivation of the effective transport parameters is described in Appendix C. Results for a model with two immobile zones arranged in series can be derived analogously [Reichle, 1996]. The large-time limits for the parallel triple-porosity model are

$$\lim_{t \rightarrow \infty} u^{\text{eff}} = \frac{\hat{u}}{1 + \phi_{\text{im}}^{\text{eff}}} \quad (24)$$



heterogeneous dual porosity model



homogeneous triple porosity model

**Figure 4.** Schematic description of the models.

$$\lim_{t \rightarrow \infty} D_L^{\text{eff}} = \frac{\hat{D}}{1 + \phi_{\text{tri}}^{\text{eff}}} + \frac{\hat{u}^2}{\alpha_{\text{tri}}^{\text{eff}}} \frac{\phi_{\text{tri}}^{\text{eff}}}{(1 + \phi_{\text{tri}}^{\text{eff}})^3} \quad (25)$$

$$\lim_{t \rightarrow \infty} D_T^{\text{eff}} = \frac{\hat{D}}{1 + \phi_{\text{tri}}^{\text{eff}}}$$

with

$$\phi_{\text{tri}}^{\text{eff}} = \phi_1 + \phi_2 \quad \frac{\phi_{\text{tri}}^{\text{eff}}}{\alpha_{\text{tri}}^{\text{eff}}} = \frac{\phi_1}{\alpha_1} + \frac{\phi_2}{\alpha_2} \quad (26)$$

As expected, the large-time effective distribution coefficient is given by the sum of the distribution coefficients of the two immobile regions. Interpretation of  $\alpha^{-1}$  as exchange time leads to the conclusion that the large-time effective exchange time is the weighted mean of the exchange times of the two immobile regions, where the respective distribution coefficients are used as weights. The findings are consistent with the effective parameters derived by *Sardin et al.* [1991] via transfer functions.

Given the large-time effective transport parameters, we can now try to find the homogeneous sorption parameters  $\{\alpha_1, \alpha_2, \phi_1, \phi_2\}$  related to the stochastic properties of the medium. In order to yield the same large-time effective transport parameters the effective sorption parameters (21) and (26) must be identical.

$$\alpha^{\text{eff}} = \alpha_{\text{tri}}^{\text{eff}} \quad \phi^{\text{eff}} = \phi_{\text{tri}}^{\text{eff}} \quad (27)$$

Since from the previous section we know that the correlation coefficient  $\rho$  plays a major role in the time evolution of dispersion in the heterogeneous model, we choose the following additional condition:

$$\phi_1 = \frac{(\bar{\phi} + \sigma_\phi)(1 + \rho)}{2} \quad (28)$$

For perfect negative correlation, (28) assigns a zero distribution coefficient to the first immobile phase, thus reducing the triple-porosity model to a dual-porosity model. For perfect positive correlation both immobile phases contribute comparably to the effective dispersion. The distribution coefficients are then  $\phi_{1,2} = \frac{1}{2}(\bar{\phi} \pm \sigma_\phi)$ . The linear relationship (28) for  $\phi_1$  is a first approximation to match these requirements, and certainly, no exact equivalence of the models is claimed. So far, the choice of  $\alpha_1$  and  $\alpha_2$  is not yet unique. As a last condition, we add

$$\alpha_1 = \bar{\alpha}(1 + \psi) \quad \alpha_2 = \bar{\alpha}(1 - \psi) \quad (29)$$

From (27), (28), and (29) the parameter  $\psi$  can be easily derived.

$$\psi = \frac{-A_2 + \sqrt{A_2^2 - 4A_1A_3}}{2A_1}$$

where

$$A_1 = \left( 1 + \frac{\sigma_\alpha^2}{\bar{\alpha}^2} - \rho \frac{\sigma_\alpha \sigma_\phi}{\bar{\alpha} \bar{\phi}} - \frac{\bar{\eta}^3}{\bar{\alpha}^3} + \frac{\bar{\eta}^2 \bar{\varphi}}{\bar{\alpha}^2 \bar{\phi}} \right)$$

$$A_2 = \left[ 1 - \frac{1}{2} \left( 1 + \frac{\sigma_\phi}{\bar{\phi}} \right) (1 + \rho) \right] \quad A_3 = (1 - A_1)$$

For  $\sigma_\alpha^2 = 0$  we get  $\psi = 0$ , therefore  $\alpha_1 = \alpha_2$ , and the triple-porosity model is identical to a dual-porosity model.

With the given parameter set  $\{\alpha_1, \alpha_2, \phi_1, \phi_2\}$  we can now compare the time-dependent effective transport velocity and dispersivity of the heterogeneous and the homogeneous models. Figure 1 shows that for  $\rho = +1$  the effective transport velocity in the heterogeneous model is better reproduced by the homogeneous triple-porosity model than by the homogeneous dual-porosity model. Moreover, Figure 1 shows that the dispersive behavior of the heterogeneous model for  $\rho = +1$  is adequately described by the triple-porosity model. The dispersivity as well as the second central moment differ only slightly. Finally, from Figure 2 we learn that for  $\rho = -1$  all models show the same effective transport behavior.

## 7. Summary and Conclusions

Within an analytical framework a dual-porosity model with heterogeneous and cross-correlated sorption parameters was investigated. Time-dependent effective transport parameters based on spatial moments were derived using a perturbation approach. The effective transport velocity, dispersion coefficient, and skewness were calculated up to first order. For vanishing microdispersion the effective velocity and dispersion coefficient were calculated up to second order. Our main results are

1. From the large-time effective transport parameters, effective sorption parameters were derived (equation (21)). The effective distribution coefficient is given by the ensemble-averaged distribution coefficient, whereas the effective exchange rate includes cross correlations in the case of heterogeneous  $\phi$ . Effective parameters cannot be obtained by averaging over an ensemble of media with random but spatially constant sorption parameters.

2. For negative correlation between the sorption parameters the effective homogeneous dual-porosity model allows a good description of the heterogeneous model. However, for positive correlation, significant differences between the models

occur at finite times. A better reproduction of the heterogeneous model within a homogeneous framework is provided by a triple-porosity model. The sorption parameters for this model can be expressed as functions of the stochastic properties of the medium.

3. The skewness is found to vanish very slowly compared to the time needed for the effective transport velocity and dispersion coefficient to reach their asymptotic values. The corresponding timescale is given in (22).

Although the analysis of the heterogeneous model is limited to small variability in the sorption parameters, insight was gained into the developing transport velocity, dispersion, and skewness through an analytical approach. In addition, formulae for the conceptual approximation of a heterogeneous medium by effective homogeneous models are given. The assumptions of a constant flow field and a constant retardation factor for the mobile phase are not crucial for the analysis. In future work, cross correlations between a heterogeneous flow field and heterogeneous sorption parameters can be investigated with our approach.

### Appendix A: Some Definitions

The first- and second-order terms in the perturbation series  $g = g_0 + \mathcal{A} + \mathcal{B} + \mathcal{C}_3$  are

$$\begin{aligned} \mathcal{A}(x, t) &\equiv - \int dx' \int dt' g_0(x - x', t - t') \partial_{t'} \\ &\quad \cdot \int_0^{t'} d\tau \phi(x') \alpha(x') e^{-\alpha(x')(t'-\tau)} g_0(x', \tau) \\ \mathcal{B}(x, t) &\equiv + \int dx' \int dt' g_0(x - x', t - t') \partial_{t'} \\ &\quad \cdot \int_0^{t'} d\tau \phi(x') \alpha(x') e^{-\alpha(x')(t'-\tau)} \\ &\quad \cdot \int dx'' \int dt'' g_0(x' - x'', \tau - t'') \partial_{t''} \\ &\quad \cdot \int_0^{t''} d\tau' \phi(x'') \alpha(x'') e^{-\alpha(x'')(t''-\tau')} g_0(x'', \tau') \end{aligned}$$

When averaging the moments, the following terms are encountered.

$$\begin{aligned} \overline{\phi(x') \alpha(x') e^{-\alpha(x')\theta}} &\approx a(\theta) \\ \overline{\phi(x') \alpha(x') e^{-\alpha(x')\theta'} \phi(x'') \alpha(x'') e^{-\alpha(x'')\theta''}} \\ &\approx \{b(\theta', \theta'') + \sum_i c_{(i)}(\theta', \theta'') w_{(i)}(x' - x'')\} \end{aligned}$$

where

$$\begin{aligned} a(\theta) &\equiv e^{-\bar{\alpha}\theta} \left[ \bar{\alpha}\bar{\phi} - \sigma_\alpha^2 \bar{\phi} \left( \theta - \frac{\bar{\alpha}}{2} \theta^2 \right) + q(1 - \bar{\alpha}\theta) \right. \\ &\quad \left. + \frac{\bar{\eta}^3}{\eta^3} \bar{\phi} \left( \frac{\theta^2}{2} - \frac{\bar{\alpha}}{6} \theta^3 \right) - \frac{\bar{\eta}^2}{\eta^2} \bar{\varphi} \left( \theta - \frac{\bar{\alpha}}{2} \theta^2 \right) \right] \end{aligned}$$

$$\begin{aligned} b(\theta', \theta'') &\equiv \bar{\alpha}\bar{\phi} e^{-\bar{\alpha}(\theta'+\theta'')} \\ &\quad \cdot \left\{ \bar{\phi} \left[ \bar{\alpha} - \sigma_\alpha^2 \left( \theta' + \theta'' - \frac{\bar{\alpha}}{2} (\theta'^2 + \theta''^2) \right) \right] \right. \\ &\quad \left. + q(2 - \bar{\alpha}(\theta' + \theta'')) \right\} \\ c_{(\alpha\alpha)}(\theta', \theta'') &\equiv \bar{\phi}^2 \sigma_\alpha^2 e^{-\bar{\alpha}(\theta'+\theta'')} (1 - \bar{\alpha}\theta') (1 - \bar{\alpha}\theta'') \\ c_{(\alpha\phi)}(\theta', \theta'') &\equiv \bar{\alpha}\bar{\phi} q e^{-\bar{\alpha}(\theta'+\theta'')} [2 - \bar{\alpha}(\theta' + \theta'')] \\ c_{(\phi\phi)}(\theta', \theta'') &\equiv \bar{\alpha}^2 \sigma_\phi^2 e^{-\bar{\alpha}(\theta'+\theta'')} \end{aligned}$$

### Appendix B: Integral Representations of the Moments

Up to first order the following integral representations for the moments result.

$$\begin{aligned} \overline{\mu_1^{(1)}(t)} &= +\hat{u} \left[ t - \int_0^t dt' (t - 2t') a(t') \right] + \mathcal{O}_2 \\ \overline{\mu_{11}^{(2)}(t)} &= +2\hat{D} \left[ t - \int_0^t dt' (t - 2t') a(t') \right] \\ &\quad + \hat{u}^2 \int_0^t dt' (t^2 - 2t'^2) a(t') \\ &\quad - \hat{u}^2 \int_0^t dt' \int_0^{t'} dt'' 2(t - t') a(t'') + \mathcal{O}_2 \\ \overline{\mu_{111}^{(3)}(t)} &= +6\hat{D}\hat{u} \int_0^t dt' (t^2 - 2t'^2) a(t') \\ &\quad - 6\hat{D}\hat{u} \int_0^t dt' \int_0^{t'} dt'' 2(t - t') a(t'') \\ &\quad - \hat{u}^3 \int_0^t dt' (t^3 - 2t'^3) a(t') \\ &\quad + \hat{u}^3 \int_0^t dt' \int_0^{t'} dt'' 3(t - t')(t - t' + 2t'') a(t'') + \mathcal{O}_2 \end{aligned}$$

Up to second order and for vanishing microdispersion the following integral representations for the moments result.

$$\begin{aligned} \lim_{\hat{D} \rightarrow 0} \overline{\mu_1^{(1)}(t)} &= +\hat{u} \left[ t - \int_0^t dt' (t - 2t') a(t') \right] \\ &\quad - \hat{u} \int_0^t dt' \int_0^{t'} dt'' (t - 2t'') b(t - t', t' - t'') \\ &\quad + \hat{u} \int_0^t dt' \int_0^{t'} d\tau \int_0^\tau dt'' b(t' - \tau, \tau - t'') \end{aligned}$$

$$\begin{aligned}
& - \hat{u} \int_0^t d\theta \int_0^t d\bar{\theta}(t-2\theta)b(\theta, \bar{\theta}) - \hat{u} \int_0^t dt' \\
& \cdot \int_0^{t-t'} dt''(t'+t'') \sum_{(i)} w_{(i)}[\hat{u}(t-t'-t'')]c_{(i)}(t', t'') \\
& + \hat{u} \int_0^t dt' \int_0^{t'} d\tau \int_0^{t'-\tau} dt'' \sum_{(i)} w_{(i)}[\hat{u}(t'-\tau-t'')] \\
& \cdot c_{(i)}(\tau, t'') + \hat{u} \int_0^t dt' \int_0^{t-t'} dt'' \int_0^{t''} d\theta \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(t-t'-t'')]c_{(i)}(t', \theta) + \hat{u} \int_0^t d\theta \int_0^t d\bar{\theta} \theta \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(\theta - \bar{\theta})]c_{(i)}(\theta, \bar{\theta}) - \hat{u} \int_0^t dt' \int_0^{t'} d\theta \int_0^t d\bar{\theta} \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(\theta - \bar{\theta})]c_{(i)}(t' - \theta, t - \bar{\theta}) + \mathbb{O}_3 \\
& \cdot \int_0^{t''} d\theta 2(t' + \theta) \sum_{(i)} w_{(i)}[\hat{u}(t-t'-t'')]c_{(i)}(t', \theta) \\
& + \hat{u}^2 \int_0^t dt' \int_0^{t'} d\tau \int_0^{t'-\tau} dt'' \int_0^{t''} d\theta 2 \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(t-\tau-t'')]c_{(i)}(\tau, \theta) \\
& - \hat{u}^2 \int_0^t d\theta \int_0^t d\bar{\theta} \theta(\theta + \bar{\theta}) \sum_{(i)} w_{(i)}[\hat{u}(\theta - \bar{\theta})]c_{(i)}(\theta, \bar{\theta}) \\
& + \hat{u}^2 \int_0^t dt' \int_0^{t'} d\theta \int_0^t d\bar{\theta} 2(t+t'-\theta-\bar{\theta}) \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(\theta - \bar{\theta})]c_{(i)}(t' - \theta, t - \bar{\theta}) \\
& - \hat{u}^2 \int_0^t dt' \int_0^{t'} d\theta \int_0^t dt'' \int_0^{t''} d\bar{\theta} \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(\theta - \bar{\theta})]c_{(i)}(t' - \theta, t'' - \bar{\theta}) + \mathbb{O}_3
\end{aligned}$$

$$\begin{aligned}
\lim_{\hat{D} \rightarrow 0} \overline{\mu_{11}^{(2)}(t)} & = +\hat{u}^2 \int_0^t dt'(t^2 - 2t't^2)a(t') \\
& - \hat{u}^2 \int_0^t dt' \int_0^{t'} dt'' 2(t-t')a(t'') \\
& + \hat{u}^2 \int_0^t dt' \int_0^{t'} dt'' [2(t-t'')^2 - t^2]b(t-t', t'-t'') \\
& - \hat{u}^2 \int_0^t dt' \int_0^{t'} d\tau \int_0^{\tau} dt'' 2(t'-2t'')b(t'-\tau, \tau-t'') \\
& - \hat{u}^2 \int_0^t dt' \int_0^{t'} d\tau \int_0^{\tau} dt'' 2(t'-\tau)b(t-t', \tau-t'') \\
& + \hat{u}^2 \int_0^t d\theta \int_0^t d\bar{\theta} [4\bar{\theta}(t-\theta) - 2\theta^2]b(\theta, \bar{\theta}) \\
& - \hat{u}^2 \int_0^t dt' \int_0^{t'} d\theta \int_0^t d\bar{\theta} 2(t-t')b(\theta, \bar{\theta}) + \hat{u}^2 \int_0^t dt' \\
& \cdot \int_0^{t-t'} dt''(t'+t'')^2 \sum_{(i)} w_{(i)}[\hat{u}(t-t'-t'')]c_{(i)}(t', t'') \\
& - \hat{u}^2 \int_0^t dt' \int_0^{t'} d\tau \int_0^{t'-\tau} dt'' 2(\tau+t'') \\
& \cdot \sum_{(i)} w_{(i)}[\hat{u}(t'-\tau-t'')]c_{(i)}(\tau, t'') - \hat{u}^2 \int_0^t dt' \int_0^{t-t'} dt''
\end{aligned}$$

### Appendix C: Triple-Porosity Model

For the derivation of the effective transport parameters of the homogeneous triple-porosity model, Laplace and Fourier transforms are applied to the basic equations (23).

$$f(x, s) = \int_0^\infty e^{-st} f(x, t) dt \quad f(k, t) = \int e^{-ikx} f(x, t) dx \quad (30)$$

Using the initial and boundary conditions (4) and (5) (for both immobile zones), the following transformed solution is obtained:

$$g(k, s) = \frac{s^2 + (\alpha_1 + \alpha_2)s + \alpha_1\alpha_2}{s^3 + ps^2 + qs + r}$$

where

$$p = (k\hat{D}k + i\hat{u}k + \alpha_1 + \alpha_2 + \alpha_2\phi_2 + \alpha_1\phi_1)$$

$$q = (k\hat{D}k + i\hat{u}k)[\alpha_1 + \alpha_2 + \alpha_1\alpha_2 + \alpha_1\alpha_2(\phi_1 + \phi_2)] \quad (31)$$

$$r = (k\hat{D}k + i\hat{u}k)\alpha_1\alpha_2$$

The Laplace transform can be inverted analytically. To this end the denominator of (31) is factorized,  $s^3 + ps^2 + qs + r = (s + A_1)(s + A_2)(s + A_3)$ . Using Cardan's formula [Abramowitz and Stegun, 1972], one finds for  $A_j$

$$\begin{aligned}
A_1 & = -(v+w) + \frac{p}{3} \quad A_{2,3} = \frac{v+w}{2} \mp i\sqrt{3} \frac{(v-w)}{2} + \frac{p}{3} \\
v & = \left( -\frac{p^3}{27} + \frac{pq}{6} - \frac{r}{2} + \sqrt{y} \right)^{1/3} \quad w = \frac{p^2/3 - q}{v} \\
y & = \left( \frac{q - p^2/3}{3} \right)^3 + \left( \frac{p^3}{27} - \frac{pq}{6} + \frac{r}{2} \right)^2
\end{aligned}$$

The inverse Laplace-transform is given by Abramowitz and Stegun [1972]

$$\begin{aligned}
g(k, t) = & \frac{1}{(A_1 - A_2)(A_2 - A_3)(A_3 - A_1)} \\
& \cdot [e^{-A_1 t} [-A_1^2(A_2 - A_3) + (\alpha_1 + \alpha_2)A_1(A_2 - A_3) \\
& + \alpha_1\alpha_2(A_3 - A_2)] \\
& + e^{-A_2 t} [-A_2^2(A_3 - A_1) + (\alpha_1 + \alpha_2)A_2(A_3 - A_1) \\
& + \alpha_1\alpha_2(A_1 - A_3)] \\
& + e^{-A_3 t} [-A_3^2(A_1 - A_2) + (\alpha_1 + \alpha_2)A_3(A_1 - A_2) \\
& + \alpha_1\alpha_2(A_2 - A_1)]] \quad (32)
\end{aligned}$$

From  $g(k, t)$  the spatial moments are calculated by differentiation with respect to the Fourier variable  $k_i$  [Goltz and Roberts, 1987]. With the aid of the algebra software mathematica, we analytically derived the time-dependent effective transport parameters. Plots over time are easily obtained from the rather complex results. However, it seems to be impossible to get explicit expressions for the large-time limits. We therefore followed a different approach in which we examined the Laplace transform of (23) for large times, casting them into a dual-porosity form. Through comparison with the corresponding equations of the homogeneous dual-porosity model we get the expressions (24) and (25) for the effective transport parameters [Reichle, 1996].

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