

## Compound-specific local and effective transverse dispersion coefficients for conservative and reactive mixing in heterogeneous porous media

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**Abstract** Dilution in heterogeneous porous media can be quantified using different measures which lead to the definition of effective dispersion coefficients. These up-scaled parameters should account for both local-scale dispersion and effects of flow variability in heterogeneous formations (e.g. flow focusing in high-conductivity and defocusing in low-conductivity inclusions). The correct quantification of mixing is particularly important in order to model mixing-controlled reactions in porous media. Under steady-state conditions with continuous injection from a line source, 2D conservative and reactive solute transport simulations were performed. It was shown that different parameterizations of local transverse dispersion coefficients significantly affect the quantification of field-scale mixing processes. Bench-scale experiments showed a nonlinear dependence of local transverse dispersion on molecular diffusion over a wide range of flow velocities, implying compound-specific transverse mixing at the local Darcy scale. Heterogeneous field-scale scenarios were considered, characterized by different variability in the conductivity field, and a set of Monte Carlo simulations was performed. We quantified transverse mixing with different measures including effective transverse dispersion coefficients, scalar dissipation rates and the recently introduced flux-related dilution index and flux-related second central spatial moments. It was shown that quantities derived in a flux-related framework are affected by a lower degree of uncertainty and that, in the case of low to moderately heterogeneous porous media, the effective transverse dispersion coefficients are significantly different for different compounds. Effective transverse dispersion coefficients were found to be up to one order of magnitude larger than the local values due to mixing enhancement processes related to flow-focusing in high-permeability inclusions. In the case of mixing-controlled reactive transport, considering instantaneous complete bimolecular reactions, it was shown that compound-specific dispersion coefficients affect the prediction of the length of reactive solute plumes. Furthermore, the recently developed concept of critical dilution index was applied to quantify the amount of mixing required to completely degrade a reactive contaminant plume.

**Key words** mixing; transverse dispersion; dilution index

### INTRODUCTION

Mixing processes (i.e. those physical mechanisms which increase the entropy and decrease the peak concentration of a dissolved species) are particularly important in the description of reactive solute transport in porous media. In fact, if we consider reactions with a fast kinetic, the limiting step in this chemical process is generally mixing between the different reactants. In the case of aged and well developed plumes, originating from a constant source, steady-state flow and transport conditions can be assumed (e.g. Prommer *et al.*, 2009), and dispersion in the transverse direction is the most important mixing process. Hence, a correct parameterization of the transverse dispersion coefficient is required in order to predict quantities of practical interest, such as the length of a steady-state plume (e.g. Liedl *et al.*, 2005).

At the pore-scale, random motion of solute particles can be described by the aqueous diffusion coefficient and this process leads to real physical mixing. Upscaling procedures allow the definition of a local transverse dispersion coefficient at the continuum Darcy scale, which is commonly described as the sum of pore diffusion and a mechanical dispersion term. At the larger field scale, flow focusing or defocusing effects, generated by the heterogeneities in the conductivity fields, may enhance or diminish mixing, respectively.

Since reactions between dissolved contaminants and electron acceptors happen at the narrow fringes of a plume, the quantification of local transverse dispersion is of particular interest. However, a detailed description at the Darcy scale is usually unavailable for field-scale studies,

and hence upscaled (effective) parameters are required in order to capture the macroscopic behaviour of the system.

In this work we investigate how a recently introduced parameterization of the local transverse dispersion coefficient (Chiogna *et al.*, 2010), which is compound-specific even at high flow velocities  $v$  (m/s), affects dilution, the value of the effective transverse dispersion coefficient and reactive transport (i.e. the length of a plume). We extend the outcomes of Chiogna *et al.* (2011b) to heterogeneous flow fields generated using exponential and Gaussian covariance functions with different variances of log hydraulic conductivity (from 0.5 to 2). We quantify mixing (Table 1) using the scalar dissipation rate, the spatial second central moment and two newly defined flux-related quantities, i.e. flux-related dilution index (Rolle *et al.*, 2009) and the flux-related spatial second central moment (Cirpka *et al.*, 2011). It is also shown that considering compound-specific dispersion coefficients affects the estimation of the length of a reactive plume and that the recently introduced concept of critical dilution index (Chiogna *et al.*, 2011a) can be applied to quantify the amount of mixing required to completely extinguish a reactive plume.

**Table 1** Measures of mixing.

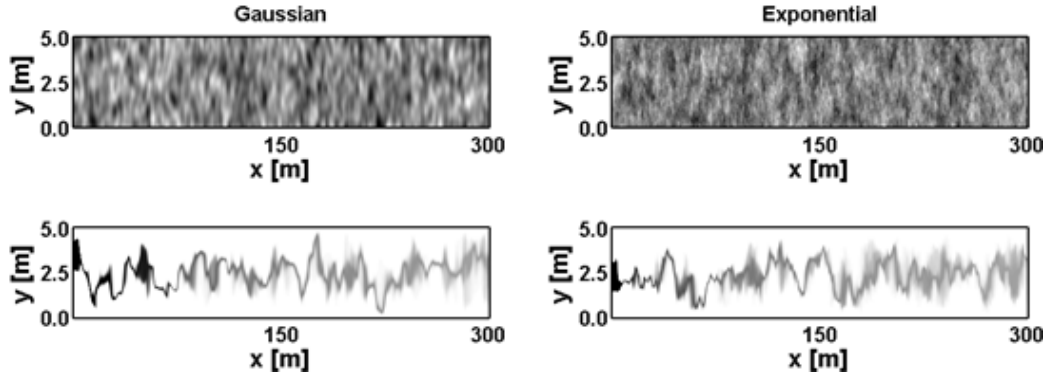
Measure	Mathematical description
Second central moment (e.g. Dentz <i>et al.</i> , 2000)	$M_{2c}(x) = \frac{\int_0^H (y - M_1(x))^2 (z - M_1(x))^2 C(x, y, z) dy}{\int_0^H C(x, y, z) dy}$
Flux-related second central moment (Chiogna <i>et al.</i> , 2011b; Cirpka <i>et al.</i> , 2011)	$M_{q2c}(x) = \frac{\int_0^H (y - M_{q1}(x))^2 (z - M_{q1}(x))^2 C(x, y, z) q_y dy}{\int_0^H C(x, y, z) dy}$
Flux-related dilution index (Kitanidis, 1994; Rolle <i>et al.</i> , 2009)	$E_Q(x) = \exp\left(-\int_0^H p_Q(x, y, z) \cdot \ln(p_Q(x, y, z)) q_y dy\right)$
Scalar dissipation rate (e.g. Bolster <i>et al.</i> , 2010)	$F_{c^2}(x) = -\nabla^T C D \nabla C$

Referring to Table 1,  $H$  (m) indicates the domain dimension in transverse direction  $y$ , while the flow is along the longitudinal direction  $x$ .  $C$  (-) represents the normalized concentration and  $M_1$  and  $M_{q1}$  are the first moment in Cartesian and in flux-related frameworks, respectively. The specific discharge is indicated with  $q$  (m/s), while  $p$  (-) represents the probability density function of the concentration.

## MODEL SET-UP

Conservative and reactive transport simulations are performed in 2D steady-state flow and transport conditions. The solute is continuously injected from a line source with initial normalized concentration  $C_{in} = 1$  (-), as shown in Fig. 1. Considering reactive transport, the injected solute A ( $C_{Ain} = 1$ ) undergoes an instantaneous (i.e. mixing controlled) complete bimolecular reaction ( $f_A A + f_B B \rightarrow f_C C$ , with  $f_A = f_B = f_C = 1$ ) with the ambient fluid B ( $C_{Bin} = C_{Bamb} = 1$ ). We consider heterogeneous hydraulic conductivity fields generated with both Gaussian and exponential covariance functions (e.g. Fig. 1), following the spectral approach of Dykaar & Kitanidis (1992). A set of 100 Monte Carlo realizations was performed for each covariance function and variance of log conductivity considered.

The numerical approach used to solve flow and transport is the following (see also Chiogna *et al.*, 2011b): (a) generation of a conductivity field on a regular grid, (b) simulation of hydraulic head, and stream function values, (c) construction of a streamline-oriented grid (Cirpka *et al.*, 1999a,b), (d) simulation of conservative solute transport on the streamline-oriented grid, (e) simulation of



**Fig. 1** Left: Gaussian conductivity field (top) and computed conservative tracer plume (bottom). Right: Exponential conductivity field (top) and computed conservative tracer plume (bottom).

**Table 2** Model, flow and transport parameters.

Model discretization	
Number of cells ( $n_x, n_y$ )	(1000, 500)
Model dimension (x, y) [m]	(300, 5)
Flow and transport parameters	
Normalized source mass flux [ $\text{m}^3/\text{s}$ ]	$5 \times 10^{-6}$
Seepage velocity $v$ [m/s]	$3.3 \times 10^{-5}$
Mean hydraulic conductivity $K$ [m/s]	$1 \times 10^{-3}$
Variance of log conductivity $\sigma^2$	(0.5, 1, 1.5, 2)
Integral scales ( $I_x, I_y$ ) [m]	(2, 0.5)
Aqueous diffusion coefficients ( $D_{aq}^A, D_{aq}^B$ ) [ $\text{m}^2/\text{s}$ ]	$(0.8, 2.1) \times 10^{-9}$
Tortuosity $\tau$ [-]	2.5
Transverse dispersion coefficient $D_t$ [ $\text{m}^2/\text{s}$ ]	$\frac{D_{aq}^i}{\tau} + v \frac{d}{\sqrt{\text{Pe} + 123}}, \quad i=A, B \quad \text{Pe} = \frac{vd}{D_{aq}^i}$
Mean grain size value in a cell $d$ [m]	$K^{0.5}/100$

reactive solute transport on the streamline-oriented grid using the mixing-ratio approach of Cirpka & Valocchi (2007) and the direct solver UMFPAK (Davis & Duff, 1997), and (f) simulation of reactive solute transport on the streamline-oriented grid using compound specific dispersion coefficients and a Picard iteration (Chiogna *et al.*, 2011b).

Model discretization, flow and transport parameters are briefly summarized in Table 2.

Steady-state conservative solute transport (equation (1)) is solved for two conservative species characterized by different aqueous diffusion coefficients ( $D_{aq}^A, D_{aq}^B$  [ $\text{m}^2/\text{s}$ ]), while the reactive transport problem is solved, first assuming that the aqueous diffusion coefficient of all reaction partners equals  $D_{aq}^A$ , then assuming that the aqueous diffusion coefficient of both reaction partners equals  $D_{aq}^B$ , and in the end considering different aqueous diffusion coefficients for  $A$  and  $B$  (equation (2)), while the aqueous diffusion coefficient for the reaction product  $C$  is assumed to equal  $D_{aq}^A$ .

$$\mathbf{v} \cdot \nabla C - \nabla \cdot (\mathbf{D}_{aq}^i \nabla C) = 0 \quad i=A, B \quad (1)$$

$$C = 1 \quad \text{along } \Gamma_{in}^A$$

$$C = 0 \quad \text{along } \Gamma_{in}^B$$

$$\mathbf{n} \cdot \mathbf{D} \nabla C = 0 \quad \text{along all other boundaries}$$

$$\begin{aligned}
\mathbf{v} \cdot \nabla C_A - \nabla \cdot (\mathbf{D}_A \nabla C_A) &= -f_A \mathbf{r}_A \\
\mathbf{v} \cdot \nabla C_B - \nabla \cdot (\mathbf{D}_B \nabla C_B) &= -f_B \mathbf{r}_B \\
\mathbf{v} \cdot \nabla C_C - \nabla \cdot (\mathbf{D}_C \nabla C_C) &= f_C \mathbf{r}_C
\end{aligned} \tag{2}$$

$$\begin{aligned}
C_A = C_{Ain} \quad C_B = 0 \quad C_C = 0 & \quad \text{along } \Gamma_{in}^A \\
C_A = 0 \quad C_B = C_{Bin} \quad C_C = 0 & \quad \text{along } \Gamma_{in}^B \\
\mathbf{n} \cdot \mathbf{D}_i \nabla C_i = 0 \quad i=A,B,C & \quad \text{along all other boundaries}
\end{aligned}$$

In equations (1) and (2)  $\Gamma_{in}^A$  and  $\Gamma_{in}^B$  are two complementary fractions of the inflow boundary  $\Gamma_{in}$ , and  $\mathbf{r}_i$  are the reaction rates.

## RESULTS AND DISCUSSION

### Conservative transport

Two examples of conservative steady-state plumes in the two different permeability fields are shown in Fig. 1. In Fig. 2 we compare the mean values of the conservative transport results obtained for the normalized second central transverse spatial moments ( $M_{2C}/M_{2Cin}$  [-]), the flux-related second central transverse spatial moments ( $M_{q2C}/M_{q2Cin}$  [-]), the flux-related dilution indices ( $M_Q$  [-]) and the scalar dissipation rates ( $F_{Xz}/F_{Xz_{in}}$  [-]) for fields with  $\sigma^2 = 1$  and different Gaussian and exponential flow fields. The results are shown as a function of a distance normalized by the longitudinal integral scale.

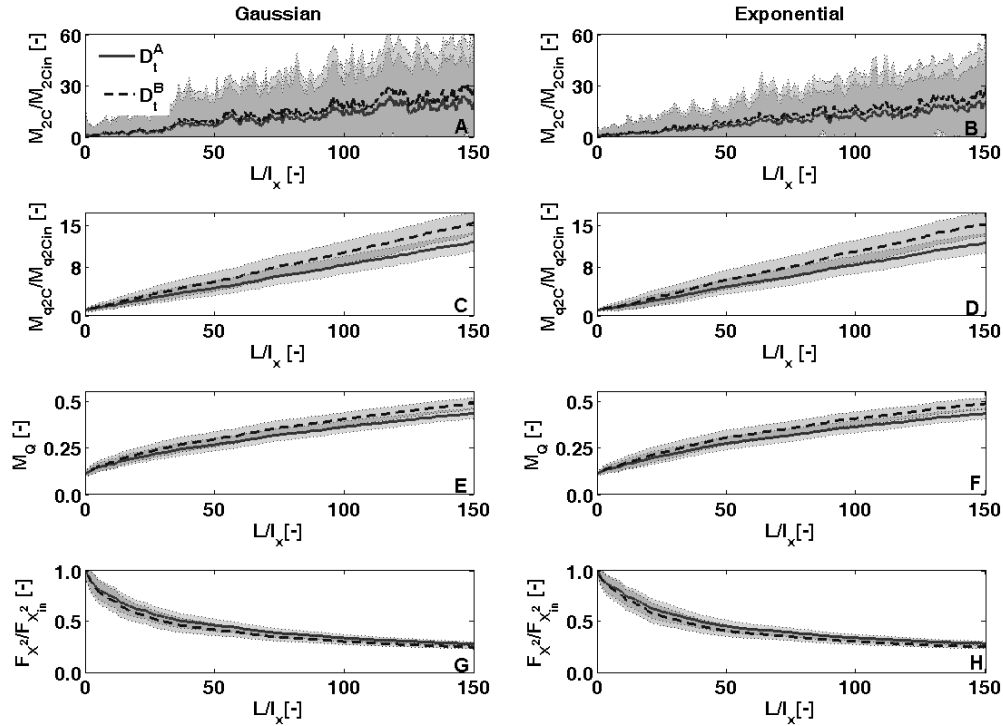
The mean behaviour in the mixing of the two tracers is different; however, the uncertainty in the traditional second central spatial moment analysis is so high that it would be difficult to distinguish the two trends. In contrast, the flux-related quantities, since they are affected by less uncertainty, are able to capture the influence of the aqueous diffusion coefficient on the macroscopic field-scale mixing mechanism. It is necessary to point out that the scalar dissipation rate does not increase with distance as the other quantities, but decreases up to an asymptotic value at which both compounds tend to converge for large distances; therefore the differences in this quantity are significant, even if small in magnitude.

The comparison between the results obtained for the Gaussian flow fields and the exponential ones indicates that, for small variances ( $\sigma^2 \leq 1$ ) the mixing behaviour of the system is practically independent of the choice of the covariance function. In contrast, the increase in the variance of the log hydraulic conductivity has two main effects: it affects the uncertainty of the mixing measures and leads to higher effective transverse dispersion coefficients (e.g. from  $D_{teff} = 2.9 \times 10^{-9}$  m<sup>2</sup>/s for  $\sigma^2 = 0.5$  to  $D_{teff} = 2.7 \times 10^{-8}$  m<sup>2</sup>/s for  $\sigma^2 = 2$ , considering compound A). Furthermore at higher variances of logK the realizations with Gaussian flow fields display less mixing than the one with the exponential flow field.

### Reactive transport

In Table 3 we summarize the results of the plume lengths obtained for the different log conductivity variances and covariance functions. It can be seen that the semi-analytical approach which assumes the same aqueous diffusion coefficient for both reaction partners, leads to systematic errors of over or under estimation of the distance reached by the contaminant.

The analysis of the critical dilution index (CDI) indicates that the amount of mixing required to completely degrade a contaminant plume undergoing an instantaneous complete bimolecular reaction is constant and equals the ratio between the dilution index at the source and the critical mixing ratio of the system, multiplied by the square root of the Euler's number  $e$  (see Chiogna *et al.*, 2011a). Hence this value is independent of the effective transverse dispersion coefficient of the system and on the covariance function used to generate the flow fields and in fact all the simulations confirm that the computed CDI and the theoretical one coincide and equal  $1.68 \times 10^{-5}$ .



**Fig. 2** Normalized second central transverse spatial moments (A–B), flux-related dilution indices (C–D), flux-related dilution indices (E–F) and scalar dissipation rates (G–H) for fields with  $\sigma^2 = 1$ . — shows conservative tracer with low aqueous diffusion coefficient; --- shows conservative tracer with high aqueous diffusion coefficient; shaded regions show 16–84 percentiles.

**Table 3** Median plume lengths [m] and their uncertainties ( $\sigma_{\ln(L)}$ ).

	$\sigma^2 = 0.5$		$\sigma^2 = 1$		$\sigma^2 = 1.5$		$\sigma^2 = 2$	
	Gaussian	Exponential	Gaussian	Exponential	Gaussian	Exponential	Gaussian	Exponential
$D_{aq} = D_{aq}^A$ for all species	>300	>300	$179 \pm 0.3$	$174 \pm 0.3$	$107 \pm 0.3$	$97 \pm 0.3$	$85 \pm 0.3$	$73 \pm 0.4$
$D_{aq}$ compound specific	>300	>300	$143 \pm 0.3$	$146 \pm 0.3$	$90 \pm 0.4$	$77 \pm 0.3$	$69 \pm 0.4$	$60 \pm 0.5$
$D_{aq} = D_{aq}^B$ for all species	>300	>300	$135 \pm 0.3$	$137 \pm 0.3$	$84 \pm 0.4$	$71 \pm 0.3$	$66 \pm 0.4$	$57 \pm 0.5$

## CONCLUSION

In this work we have shown the importance of a correct parameterization of the local transverse dispersion coefficient in order to improve the description of mixing in porous media.

Three main conclusions can be drawn:

- A compound-specific parameterization of the local transverse dispersion coefficient leads to effective transverse dispersion coefficients which are compound-specific and this is relevant in order to correctly estimate the length of a reactive plume.
- The increase in the variance of the log hydraulic conductivity leads to higher values and higher uncertainties in the effective transverse dispersion coefficient. This aspect is relevant in the case of reactive transport because the length of a contaminant plume decreases with increasing variance but the uncertainty on its magnitude increases as well.

- For small variances of the log hydraulic conductivity there is no significant difference between the choice of an exponential or a Gaussian covariance function for the generation of the permeability field. However, our results show that with increasing variances Gaussian permeability fields lead to lower mixing enhancement than exponential ones. The magnitude of mixing and mixing enhancement in different systems is reflected in the value of the effective transverse dispersion coefficient.

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