

MODELING MIXING-CONTROLLED REACTIVE TRANSPORT: IMPORTANCE OF COMPOUND DEPENDENT HYDRODYNAMIC AND (HYDRO)MECHANICAL TRANSVERSE DISPERSION

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1 INTRODUCTION

A correct description of dispersion processes is fundamental in order to model mass transfer, mixing and hence reaction rates during transport of solutes in groundwater. If a plume generated by a continuous source of contamination approaches steady-state conditions, the mixing of reaction partners is mainly controlled by vertical transverse dispersion. The transverse dispersion coefficient therefore determines the extent of the reaction and the length of the contaminant plume^{1,2}. Two different physical mechanisms have to be taken into account in order to describe properly transverse mixing^{3,4}: local dispersion and flow focusing in heterogeneous porous media. Former experimental and modeling investigations carried out at both laboratory and field scales, showed that local vertical transverse dispersion coefficients are typically very small^{5,6}. Mixing of reactants in heterogeneous porous media can be strongly enhanced by flow focusing into high permeability inclusions^{7,8}, leading to an effective dispersion coefficient which is higher than the local one. Unfortunately experimental studies on transverse mixing in heterogeneous media are scarce, and the interpretation of the results is difficult due to the uncertainties of the flow field. In this study, a new compound dependent description of local transverse dispersion coefficient was implemented in a reactive transport numerical code. The code was verified against laboratory scale experiments in quasi two-dimensional flow-through systems. The effects of this compound dependency were hence tested in heterogeneous porous media at the laboratory bench scale and at the field scale. A quantitative evaluation of the modeling results was performed through the calculation of flux related dilution indices and comparing the lengths of reactive plumes determined by mixing-controlled reactions of species characterized by different diffusion/dispersion coefficients.

2 THEORY

2.1 Compound dependent transverse dispersion coefficient

Hydrodynamic dispersion coefficients have been used to describe local dispersion of solutes in porous media. These coefficients are defined as the additive contribution of a pore diffusion

coefficient, D_p [L^2T^{-1}], and a mechanical dispersion coefficient, D_{mech} [L^2T^{-1}]. Therefore the coefficient of hydrodynamic dispersion in transverse direction D_t [L^2T^{-1}] can be written as:

$$D_t = D_p + D_{mech} \quad (1)$$

However a clear separation of the two contributions is rather artificial since hydrodynamic dispersion includes both processes in an inseparable form³.

In this study pore diffusion is approximated as the ratio between the aqueous diffusion coefficient D_{aq} [L^2T^{-1}] of the solute and the tortuosity τ [-] of the medium:

$$D_p = D_{aq} \tau^{-1}, \quad (2)$$

where the tortuosity is assumed to be a function of the porosity¹ n [-] (e.g. $\tau = n^{-1}$).

The mechanical dispersion term, can be described as⁹:

$$D_{mech} = \alpha_t v f(Pe, \delta), \quad (3)$$

in which α_t [L] is the transverse dispersivity, v [LT^{-1}] is the flow velocity in the porous medium, $f(Pe, \delta)$ is a function of the Péclet number ($Pe = (v d) D_{aq}^{-1}$) and of the ratio δ [-] between the length d [L] and the width a [L] of a pore channel. The value of the ratio δ can range between 4 to 20¹⁰. The introduction of the function $f(Pe, \delta)$ was justified⁹ by physical considerations about the relative rate of growth of the volume occupied by a moving elementary mass of solute in a porous medium. The medium is simplified by a conceptual model of channels connected at junctions. Transverse mixing occurs at the pore junctions, due to molecular diffusion¹¹. Bear and Bachmat introduced the function $f(Pe, \delta)$ using a mass balance approach over a representative elementary volume (REV) of the porous medium⁹. The introduction of a function based on Pe implies a compound-dependency of the mechanical dispersion term and clearly points out that molecular diffusion is a key process inseparable from mechanical dispersion. Bear and Bachmat also considered the possibility of deriving other forms for $f(Pe, \delta)$ in order to reproduce nonlinear effects observed in experimental studies^{3,10} and hence to determine experimentally this function. Chiogna et al.¹⁰ demonstrated experimentally the compound dependency of mechanical dispersion through multitracer experiments, and using a best fit procedure they computed the function $f(Pe, \delta)$, obtaining the following parameterization for the transverse dispersion coefficient:

$$D_t = D_p + D_{aq} \sqrt{\frac{Pe^2}{Pe + 2 + 4 \cdot (5.5)^2}} = D_p + v \frac{d}{\sqrt{Pe + 123}} \quad (4)$$

2.2 Flux related dilution index

The flux related dilution index⁸ is a useful measure to quantify mixing in case of a continuous source. Kitanidis⁵ first introduced the concept of dilution index to measure mixing and defined it as the exponential of the entropy of the system. The flux related dilution index

$E_Q(x)$ expresses dilution as the act of distributing a given solute mass flux over a larger water flux and it is defined as:

$$E_Q(x) = \exp\left[-\int_A p_Q(\mathbf{x}) \cdot \ln(p_Q(\mathbf{x})) \cdot q_x(\mathbf{x}) dydz\right], \quad (5)$$

where p_Q is the density function defined as:

$$p_Q(\mathbf{x}) = \frac{c(\mathbf{x})}{\int_A q_x(\mathbf{x}) \cdot c(\mathbf{x}) dydz} \quad (6)$$

In a bounded domain, a normalized measure of mixing, the reactor ratio, can be obtained dividing the flux related dilution index by the total discharge:

$$M(x) = \frac{E(x)}{Q} \quad (7)$$

2.3 Reactive transport

The reactive system we want to describe undergoes an instantaneous complete bimolecular reaction of the kind $aA + bB \rightarrow cC$, with a , b , c stoichiometric coefficients of the reaction. At steady state the system is described by the following system of equations:

$$\begin{aligned} \mathbf{v} \cdot \nabla C_A - \nabla \cdot (\mathbf{D}_A \nabla C_A) &= -aR \\ \mathbf{v} \cdot \nabla C_B - \nabla \cdot (\mathbf{D}_B \nabla C_B) &= -bR \\ \mathbf{v} \cdot \nabla C_C - \nabla \cdot (\mathbf{D}_C \nabla C_C) &= cR \end{aligned} \quad (8)$$

in which R [$M/(TL^3)$] denotes the reaction rate, \mathbf{D} is the dispersion tensor [L^2/T] and C is the concentration [M/L^3]. In case of conservative transport the reaction term is zero. The reaction takes place in the pore space between two different aqueous species A and B and gives as a product a third aqueous specie C .

3 MATERIAL AND METHODS

We performed two kinds of numerical experiments at different scales. In the first one a laboratory scale experiment^{8,10} was simulated both in homogeneous and heterogeneous conditions, where inclusions of rectangular blocks with high hydraulic conductivity K [L/T] were inserted in the model domain (Fig. 1A). In the second numerical experiment we performed field scale simulations in heterogeneous systems (Fig. 1B). In this case the high conductivity lenses are stochastically generated. Both at the laboratory and at the field scale, fixed head boundary conditions were used with a hydraulic gradient of 0.0025 and 0.003, respectively. In the larger scale simulation, the generated heterogeneous system is binary, since the hydraulic conductivity can assume just two values (i.e. a high conductivity for the inclusions and a lower value for the surrounding matrix). Furthermore a line source of 100 cells with constant concentration is placed in the middle of the left boundary. In the laboratory scale experiments the aquifer is unconfined, while in the field scale the aquifer is a confined system. The numerical code is based on a cell-centered finite volume method¹².

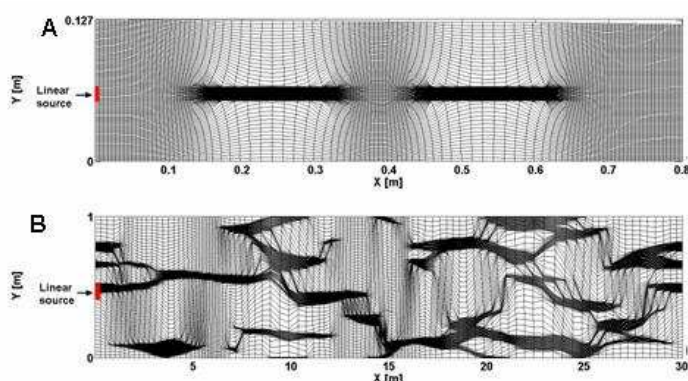


Figure 1: Conductivity fields for the heterogeneous laboratory scale model (A) and for the heterogeneous field scale model (B).

The structure of the code can be summarized in the following steps: (a) generation of a conductivity field on a regular grid as described in Werth et al.⁷ (inclusions of defined rectangular shape for the laboratory scale models, random, auto-correlated conductivity field for the field scale model); (b) simulation of hydraulic head and stream function values; (c) construction of a streamline-oriented grid; (d) simulation of conservative and reactive solute transport.

The streamline oriented grid was constructed following Cirpka¹². In the first step, the streamlines are traced by applying the contouring routine of Matlab[®] to the stream-function field. Because the stream-function range is discretized regularly, the discharge is identical in all streamtubes. As shown in Fig. 1A and 1B, in case of a high conductivity zone the streamlines are focused in the inclusion, leading to narrow, elongated cells in that region. Then, the potential values for all points describing the streamlines are determined. Potential values, according to a regular discretization of the potential range, are sought for along the streamlines by linear interpolation between neighboring points on the streamlines. Finally, pairs of adjacent potential values in neighboring streamlines are selected defining quadrilaterals bounded by isopotential lines and streamlines. Orienting the grid in the flow direction avoids numerical transverse dispersion caused by diagonal fluxes between the cells, which pose problems especially in case of flow in heterogeneous fields.

The transport problem in the streamline oriented grid was solved using the UMFPACK implicit solver implemented in Matlab[®]. This solver uses pivoting procedures in order to accelerate the factorization of the matrices and hence the convergence to the solution. The system of equations given by Eq. 8 has been first solved in the conservative case ($R_i=0$). A Picard iteration is then conducted in order to compute the solution for the reactive species. To determine the reactive fringe of the plume the necessary conditions to be fulfilled for the existence of A and B for the instantaneous bimolecular reaction where used¹³ and the reactive term has to be considered as a sink term for the reactants and as a source for the product which equals the fluxes across interfaces of the cells in which the reaction takes place. In the reactive case we model a line source of a compound A , while the reaction partner (compound B) is present in the aquifer domain with constant concentration and injected from the left

boundary of the domain in the cells where A is not present. In our case we set the stoichiometric coefficients to $a=1$, $b=9$ and $c=1$. In order to simulate a realistic scenario, the aqueous diffusion coefficient of A is close to that of many organic pollutants, while the one of B is close to the one of oxygen¹⁰. Flow and transport parameters are given in Table 1.

Laboratory scale domain dimension [m ³]	0.8×0.01×0.13 (L×W×H)	n [-]	0.4
Field scale domain dimension [m ³]	30×1×1 (L×W×H)	α_L [m]	2×10 ⁻⁴
Discretization [cells]	600×1×900	D_{aq} fluorescein [m ² s ⁻¹]	0.48×10 ⁻⁹
d coarse sand [m]	1.25×10 ⁻³	D_{aq} bromide [m ² s ⁻¹]	1.96×10 ⁻⁹
d fine sand [m]	0.275×10 ⁻³	D_{aq} A [m ² s ⁻¹]	0.8×10 ⁻⁹
K coarse sand [ms ⁻¹]	1.27×10 ⁻²	D_{aq} B [m ² s ⁻¹]	2.1×10 ⁻⁹
K fine sand [ms ⁻¹]	6.14×10 ⁻⁴	D_{aq} C [m ² s ⁻¹]	0.8×10 ⁻⁹

Table 1 Flow and transport parameters for the model.

5 RESULTS AND DISCUSSION

5.1 Conservative Transport

Figure 2 shows that our model is able to reproduce the laboratory experiments of Chiogna et al.¹⁰. A comparison between measured concentrations and simulated profiles shows a good agreement between the observations and forward numerical modeling. The values for the transverse dispersion coefficients were computed using Eq.4 and no calibration for the model was required.

Based on the outcomes of the conservative simulations in both the homogeneous and the heterogeneous setup, we calculated the flux related dilution index for fluorescein and bromide. Since fluorescein is characterized by a lower aqueous diffusion coefficient its dilution index is always lower than the one of bromide (Fig. 3). Furthermore we can notice that, as shown by Rolle et al.⁸, the presence of heterogeneities enhances the mixing producing a steep increase in the dilution index of both compounds.

5.2 Reactive Transport

Figure 4A, 4B show the results for the reactive simulations at the laboratory scale, while panel C presents a conservative tracer transported in the heterogeneous field scale aquifer which was used for the reactive simulation presented in panel D.

In the laboratory scale homogeneous simulation the inlet concentration of A and B were 0.2 mg/l and 1 mg/l, while in the heterogeneous one they were 0.83 mg/l and 1 mg/l, respectively. In both cases we can notice that, if we assume all the reactive partners to be characterized by the same high aqueous diffusion coefficient $D_{t,high}$ (i.e. all the species have the same aqueous diffusion coefficient as B), we obtain the shortest plume, while the longer is obtained assuming all the compounds with the diffusion properties of compound A (Table 2) and hence the transverse dispersion coefficient $D_{t,low}$. The real case, in which A and B have their own

diffusion coefficients as implemented in the reactive model according to Eq.4 ($D_{t,model}$), lays in-between.

Increasing the dimension of the system, from the laboratory to the field scale, using as inlet concentration of A and B 0.2 mg/l and 1 mg/l, respectively, we obtained consistent results showing different plume lengths corresponding to different transverse dispersion coefficients (Table 2). In particular, despite the plume encounters more heterogeneities and mixing is enhanced during its meandering pathway in the field scale aquifer (Fig. 4C), we can still observe the effect of compound-specific transverse dispersion resulting in different plume lengths.

The differences in the length of the reactive plumes of compound A computed with different values for D_t shown in figure 4A, 4B and 4D, clearly demonstrate the importance of the compound dependent parameterization for the local transverse dispersion coefficient. A model with the same dispersion coefficients for all the reactive species can lead in fact to an over (cases with $D_{t,low}$) or under (cases with $D_{t,high}$) estimation of the plume length.

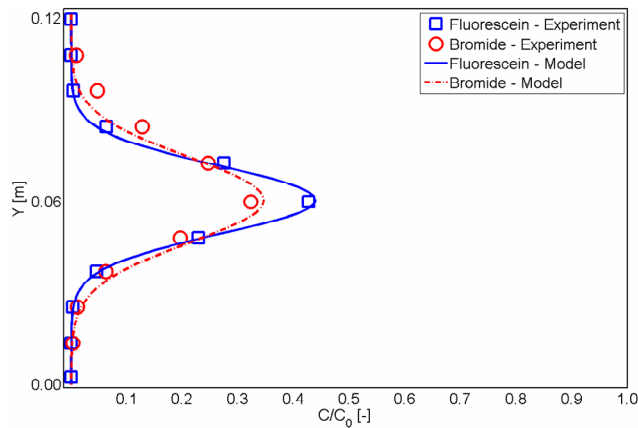


Figure 2: Measured and simulated concentrations of fluorescein and bromide for a tracer experiment conducted at a seepage velocity of 1 m/d.

	Plume length [m] $D_{t,high}$	Plume length [m] $D_{t,model}$	Plume length [m] $D_{t,low}$
Homogeneous laboratory scale	0.49	0.56	0.77
Heterogeneous laboratory scale	0.32	0.44	0.49
Heterogeneous field scale	14.34	16.10	20.10

Table 2 Length of the reactive plumes

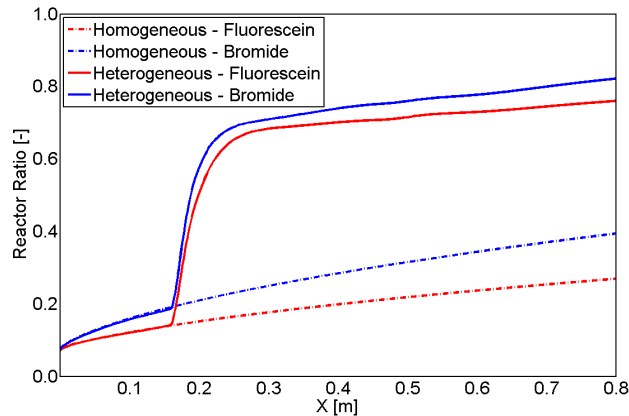


Figure 3: Reactor ratio for the homogeneous and heterogeneous laboratory scale experiment with conservative tracers (blue lines bromide, red dash-dot lines fluorescein).

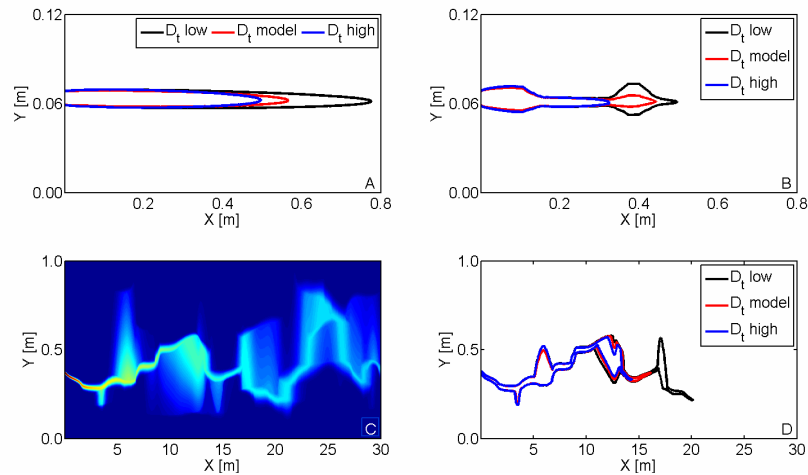


Figure 4: Zero-concentration isolines for the reactive specie A in the homogeneous laboratory scale problem (A), in the heterogeneous laboratory scale problem (B) and in the heterogeneous field scale domain (D). Concentration of a conservative tracer in the heterogeneous field scale domain (C).

5 CONCLUSIONS

In this work we showed that a compound dependent formulation of transverse dispersion is relevant in order to describe in a correct way mixing and reactions in porous media. The presence of heterogeneities may even magnify this effect. The difference in the plume length of the reactive specie A between the real case, in which both reactive compounds are characterized by their own aqueous diffusion coefficient, and the cases in which we assume that they have the same D_{aq} , is between 10% and 30%. Semi-analytical methods to perform reactive transport simulations using the concept of mixing ratio^{13,14} are based on the assumption that all the reactive species are characterized by the same aqueous diffusion coefficient and hence the same dispersion. Moreover, numerical transport codes implement a linear parameterization of transverse dispersion¹⁵ in which the mechanical dispersion term is

considered independent of the transported species. This study shows that a more accurate description of mixing-controlled reactive transport should include a compound-specific description of the transverse dispersion term.

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