

Transfer of tracer data to mixing-controlled reactive transport

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Abstract Conservative tracer data are used for the parameterization of mixing-controlled reactive transport. Temporal moments of the tracer breakthrough curve integrated over the outflow boundary of the domain yield the average velocity and the path-averaged macrodispersion coefficient. Analysing the temporal moments of breakthrough curves locally obtained at single points in the domain gives additional information about the dilution of the tracer. We derive an apparent Péclet number of mixing Pe_a from local temporal moments. By interpreting the spatially integrated breakthrough curve as the result of advective-dispersive transport in independent streamtubes with identical Péclet numbers but differing seepage velocity, it is possible to transfer conservative-tracer data to the transport of interacting compounds. The approach is applied to the hypothetical case of a bimolecular reaction in a heterogeneous two-dimensional aquifer.

INTRODUCTION

Chemical interactions between dissolved compounds require that the reacting compounds mix on the pore-scale. If the reaction kinetics are fast compared to the mixing rates, the overall reaction is controlled by mixing. A typical example for this is the aerobic oxidation of well degradable organic compounds that are introduced into the aquifer at different locations (or times) than the oxygen. If the interacting compounds differ significantly in sorption, mixing will be dominated by the chromatographic effect. By contrast, if the compounds hardly undergo sorption or other mass-transfer processes, mixing will be dominated by local-scale dispersion, namely in the transverse direction.

The relevant scale of mixing is the pore-scale. That is, macrodispersion parameters, describing how the second spatial moments of a large-scale plume increases over time, cannot be used to upscale mixing (Ginn *et al.*, 1995; Miralles-Willem *et al.*, 1997). A large second spatial moment of a plume can either be caused by an irregular shape of the plume or by the mass of the plume occupying a large volume. We refer to the former process as spreading, and to the latter as dilution. Only dilution included in macrodispersion is relevant for mixing (Kitanidis, 1994).

Macrodispersion parameters may either be evaluated from spatial moments as indicated above, or from temporal moments. In particular, the second-central temporal moment of the total mass-flux crossing a large observation plane is proportional to the longitudinal macrodispersion coefficient. Additionally, we use concentration measurements at single points, and relate the second-central temporal moment of the point measurements to an apparent dispersion coefficient of mixing (Cirpka &

Kitanidis, 2000a). We use the spatially integrated breakthrough curve and the apparent dispersivity of mixing in order to transfer conservative tracer data to mixing-controlled reactive transport.

TEMPORAL MOMENTS, MACROSCOPIC AND APPARENT PARAMETERS

Let us consider advective–dispersive transport of a tracer in a domain that is heterogeneous but macroscopically one-dimensional. The tracer is introduced instantaneously via the inflow boundary with uniform flux-concentration c^{in} . No dispersive mass-flux is considered at the outflow:

$$\frac{\partial c}{\partial t} + v_i \frac{\partial c}{\partial x_i} - \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right) = 0 \quad (1)$$

$$\begin{aligned} n_i v_i c - n_i D_{ij} \frac{\partial c}{\partial x_j} &= n_i v_i c^{in} \delta(t_0) \quad \text{at } \Gamma_{in} \\ n_i D_{ij} \frac{\partial c}{\partial x_j} &= 0 \quad \text{at } \Gamma_{out} \\ c &= 0 \quad \text{at } t = t_0 \end{aligned} \quad (2)$$

v_i is the seepage velocity vector, D_{ij} the local-scale dispersion tensor, and n_i the unit vector normal to the boundary Γ . Index notation is used. We analyse the resulting concentrations within the domain by their temporal moments:

$$m_k(x_i) = \int_0^\infty t^k c(t, x_i) dt \quad (3)$$

$$m_{kc}(x_i) = \int_0^\infty \left(t - \frac{m_1}{m_0} \right)^k c(t, x_i) dt \quad (4)$$

in which m_k is the k th noncentral and m_{kc} the corresponding central moment. In addition, we consider the temporal moments of the flux-weighted concentrations averaged over the cross-section of the outflow boundary which are related to the local moments at the outflow boundary by:

$$m_k^* = \overline{m}_k \quad (5)$$

$$m_{2c}^* = \overline{m}_{2c} + \sigma_{m_1}^2 \quad (6)$$

in which over-lined quantities are flux-weighted averages and $\sigma_{m_1}^2$ is the flux-weighted variance of the first local moment. From the moments of the spatially integrated breakthrough curves we derive apparent macro-transport parameters:

$$v_{mac} = \frac{x_1 m_0^*}{m_1^*} \quad (7)$$

$$D_{mac} = \frac{x_1^2 m_{2c}^* (m_0^*)^2}{2(m_1^*)^3} \quad (8)$$

which are, in contrast to the standard definition of the macrodispersion coefficient, path-averaged quantities. We apply identical expressions to the moments of the local breakthrough curves to evaluate an apparent velocity v_a and dispersion coefficient of mixing D_a . In the following we use the apparent Péclet number of mixing Pe_a :

$$Pe_a = \frac{2m_1^2}{m_{2c} m_0} \quad (9)$$

Pe_a may be evaluated at several locations and averaged subsequently.

Note that the second central temporal moment of the spatially averaged breakthrough curve reflects macrodispersion (Shapiro & Cvetkovic, 1988), whereas the same moment evaluated for point-wise measurements reflects dilution (Cirpka & Kitanidis, 2000a). We consider a tracer that is introduced by an instantaneous line source. This shape would remain if we neglected local-scale dispersion, and the second central temporal moment would be zero in the entire domain. Local-scale dispersion, however, dilutes the pulse and causes an increase of the second-central moment.

ADVECTIVE-DISPERSIVE STREAMTUBE APPROACH

Although dilution and reactive mixing is caused mainly by the interaction between advective spreading and local-scale *transverse* dispersion (Kitanidis, 1994), we may interpret the breakthrough curve at a point within the domain as if caused by one-dimensional transport (Cirpka & Kitanidis, 2000a). This is the conceptual background of the apparent Péclet number of mixing defined above. If we consider the one-dimensional interpretation of the breakthrough curve for all points at the outflow boundary, we approximate the domain as a bundle of parallel advective-dispersive streamtubes that do not interact with each other. We further simplify the model by assuming an identical Péclet number of mixing Pe_a for all streamtubes at the outflow boundary. Then, we could arrive at the observed spatially averaged breakthrough curve by solving for the one-dimensional advection-dispersion equation in streamtubes with identical dispersivity but varying velocity, and integrating over all velocities after weighting with the probability of the velocity. Similar to the stochastic-convective approach of Simon *et al.* (1995), we need a probability density function (PDF) of advective arrival times τ . For given Pe_a and moments of the spatially integrated breakthrough curve, the variance of the advective arrival times $\sigma_\tau^2 = \sigma_{m_1}^2 / (m_0^*)^2$ is given by:

$$\sigma_\tau^2 = \frac{\sigma_{m_1}^2}{(m_0^*)^2} = \frac{Pe_a}{2 + Pe_a} \frac{m_2^*}{m_0^*} - \frac{(m_2^*)^2}{(m_0^*)^2} \quad (10)$$

We use the inverse Gaussian distribution for the parameterization of the PDF of advective arrival times $p(\tau)$:

$$p(\tau) = \sqrt{\frac{\bar{\tau}^3}{2\pi\sigma_\tau^2\tau^3}} \exp\left(-\frac{\bar{\tau}(\bar{\tau} - \tau)^2}{2\sigma_\tau^2\tau}\right) \quad (11)$$

in which $\bar{\tau} = m_1^* / m_0^*$. The PDF given by equation (11) is used for the transfer of conservative to reactive transport by the following steps:

- Evaluate the moments m_0^* , m_1^* and m_2^* of the integrated breakthrough curve.
- Evaluate the Péclet number of mixing Pe_a from point-related breakthrough curves by equation (9) and take the average.
- Evaluate the variance of the advective arrival times σ_τ^2 by equation (10).
- Derive the PDF of advective arrival times $p(\tau)$ with equation (12).
- Calculate one-dimensional advective–dispersive–reactive transport with differing velocities but identical reactive parameters and dispersivity $\alpha = L/Pe_a$ where L is the length of the domain.
- Weight the reactive breakthrough curve with probability of the velocity $p(L/v)$ and integrate over all velocities.

The approach is an extension of the stochastic-convective model (Simmons *et al.*, 1995) using a parameterization for $p(\tau)$.

APPLICATION TO SOLUTES UNDERGOING BIMOLECULAR REACTION

We apply the approach to a hypothetical case of two solutes A and B undergoing advective–dispersive transport, weak kinetic sorption and a bimolecular irreversible reaction forming a third compound C:



The kinetics of the reaction are proportional to the products of the concentrations $c_A c_B$, and the sorption is described by a linear sorption isotherm combined with a first-order law of mass-transfer:

$$\frac{\partial c_A}{\partial t} + v_i \frac{\partial c_A}{\partial x_i} - \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c_A}{\partial x_j} \right) = -\gamma c_A c_B \quad (13)$$

$$\frac{\partial c_B}{\partial t} + v_i \frac{\partial c_B}{\partial x_i} - \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c_B}{\partial x_j} \right) = -\gamma c_A c_B + \lambda \left(\frac{c_B^s}{K_B} - c_B \right) \quad (14)$$

$$\frac{\partial c_C}{\partial t} + v_i \frac{\partial c_C}{\partial x_i} - \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c_C}{\partial x_j} \right) = \gamma c_A c_B \quad (15)$$

$$\frac{\partial c_B^s}{\partial t} = -\lambda \left(\frac{c_B^s}{K_B} - c_B \right) \quad (16)$$

Only compound B undergoes sorption with the linear partitioning coefficient K_B . γ is the kinetic coefficient for the bimolecular reaction, λ is the mass-transfer coefficient. The values of γ , λ , and K_B are $10^{-4} \text{ l s}^{-1} \text{ mol}^{-1}$, 10^{-5} s^{-1} and 0.1, respectively.

At the initial state, only compound B is present, with sorption at equilibrium. Compound A is introduced continuously from time zero on, via the inflow boundary, with a uniform inflow concentration. The breakthrough curves of all compounds are observed at the outflow boundary of the domain.

The model domain is a two-dimensional heterogeneous aquifer with dimensions of $10.24 \text{ m} \times 5.12 \text{ m}$. A Gaussian covariance model with a mean of $\log(10^{-3}) \text{ m s}^{-1}$, a variance of 1, and integral scales of 0.64 m in the longitudinal direction and 0.16 m in the transverse, has been used for the generation of the log conductivity field shown in Fig. 1. We apply periodic boundary conditions with a mean head gradient of 1% in the x -direction. The calculated flownet is also shown in Fig. 1.

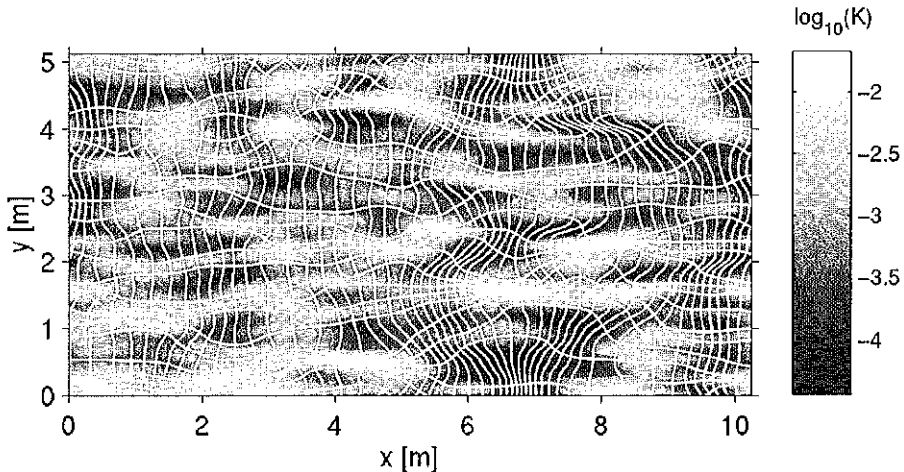


Fig. 1 Distribution of hydraulic conductivity (m s^{-1}) and flownet.

The porosity is 0.2 resulting in a mean seepage velocity of $5.06 \times 10^{-5} \text{ m s}^{-1}$. The local-scale dispersivities are 10^2 m and 10^3 m in the longitudinal and transverse direction, respectively. The molecular diffusion coefficient is set to $10^{-9} \times \text{m}^2 \text{ s}^{-1}$ for all compounds.

After solving directly for the temporal moments of a tracer (Harvey & Gorelick, 1995; Cirpka & Kitanidis, 2000a), we get normalized moments of the integrated breakthrough curve of $m_1^*/m_0^* = 2.02 \times 10^5 \text{ s}$ and $m_{2c}^*/m_0^* = 4.26 \times 10^9 \text{ s}^2$, while the mean second central moment of the local concentrations is $2.49 \times 10^9 \text{ s}^2$. This yields an apparent Péclet number of mixing (Pe_a) of 43.35 compared to a macroscopic Péclet number of 19.24. Substituting the value of Pe_a into equation (10) gives a variance of advective arrival times σ_t^2 of $2.26 \times 10^9 \text{ s}^2$.

The mean value of Pe_a at the outflow boundary was used in the advective-dispersive streamtube approach applied to bimolecular transport in the domain. Figure 2 shows the breakthrough curve integrated over the outflow boundary as calculated with a two-dimensional multicomponent reactive transport model resolving the heterogeneities. Figure 3 shows the prediction by the advective-dispersive streamtube model, which is rather accurate. The mass of the product C is overestimated by only 7%, whereas it was underestimated by 60% when the stochastic-convective model was applied (Cirpka & Kitanidis, 2000b).

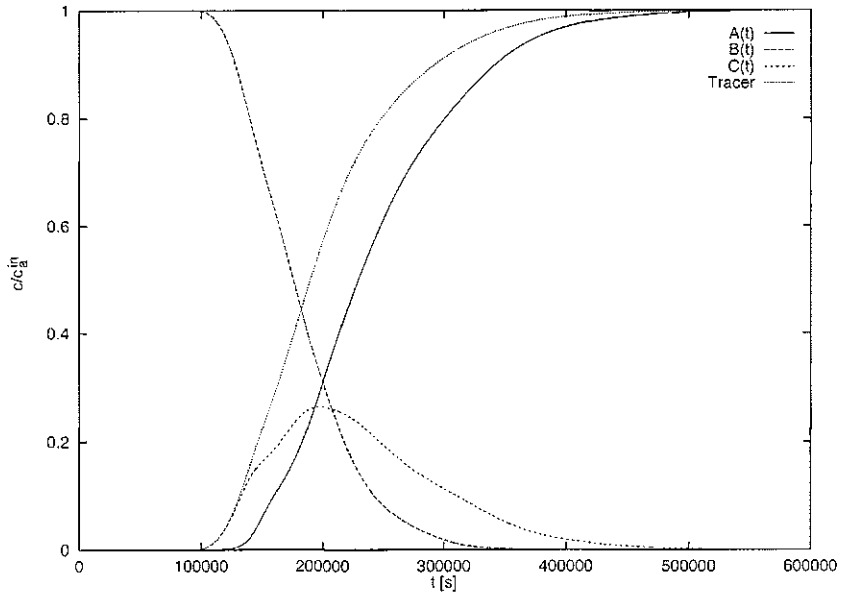


Fig. 2 Breakthrough curves of all compounds for the reactive test case as calculated by 2-D modelling.

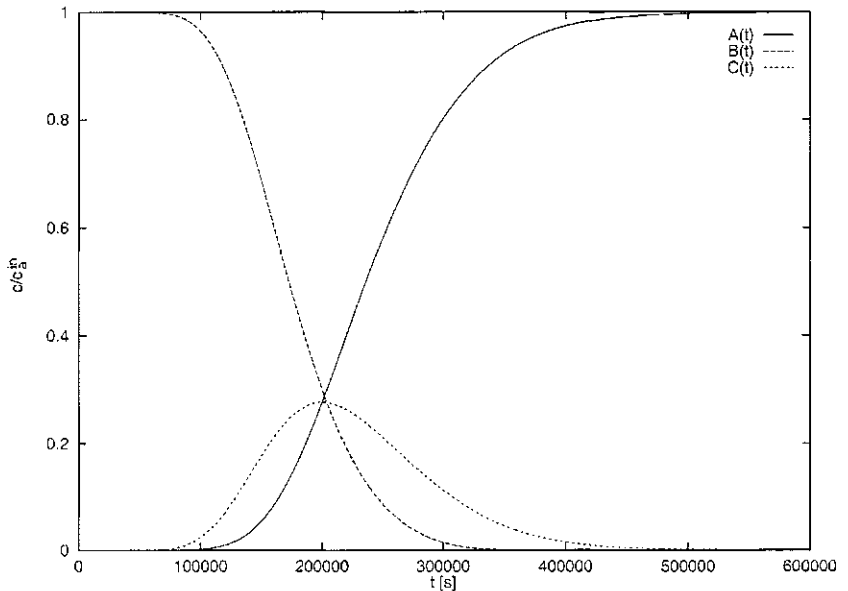


Fig. 3 Breakthrough curves of all compounds for the reactive test case as predicted by the advective-dispersive streamtube model.

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