Observations of the Impact of Rock Heterogeneity on Solute Spreading and Mixing

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Key Points:

- We have imaged transverse spreading and mixing in 3-D in heterogeneous rock cores using X-ray CT
- Spatially resolved observations of solute in 3-D rock samples show an increase of D_t with Pe and rock heterogeneity
- Reactor ratio and scalar dissipation rate show either Fickian or non-Fickian behavior depending on heterogeneity

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Abstract

Rock heterogeneity plays an important role in solute spreading and mixing in hydrogeologic systems. Few observations, however, have been made that can spatially resolve these processes in 3-D, in consolidated rocks. We make observations of the spatially resolved steady state concentration of a sodium iodide solute while flowing brine through cylindrical rock cores using X-ray CT imaging. Three rocks with an increasing level of heterogeneity are chosen: Berea sandstone, Ketton carbonate and Indiana carbonate. The impact of heterogeneity on solute transport is analyzed by: 1., quantifying spreading and mixing using metrics such as the transverse dispersion coefficient, the dilution index, the reactor ratio and the scalar dissipation rate, and 2., visualizing and analyzing flow structures such as meandering, flow-focusing and flow-splitting using iso-concentration contour maps. The transverse dispersion coefficient, D_t , and the variation in D_t throughout the rock core, increases with Peclet number (Pe) and rock heterogeneity. The reactor ratio indicates that mixing is Fickian for the Berea sandstone and Ketton carbonate, but diverges for the Indiana carbonate. The temporal evolution of the scalar dissipation rate, a measure of the mixing rate, remains close to that of Fickian mixing for the Berea and Ketton rocks but not for the Indiana. Heterogeneous rock features are observed to cause meandering, focusing or splitting of the plume depending on Pe.

1 Introduction

Spreading and mixing of solutes in rocks are two important processes in characterizing reactive transport in hydrogeologic systems. Spreading delineates the spatial extent of a solute plume and is important in a number of engineering and scientific fields. It describes the movement of dissolved CO₂ after subsurface injection [Xiao *et al.*, 2009; Wang *et al.*, 2016; Nakanishi *et al.*, 2016], and the extent of a contaminant groundwater plume [Mayer *et al.*, 2002; Kitanidis and McCarty, 2012]. Mixing describes dilution, or the interaction of separate chemical components by concentration gradients and diffusion. Mixing can be conservative or reactive when compounds upon mixing react with each other. Reactive mixing exhibits a key control in the remediation of contaminant groundwater [Kitanidis and McCarty, 2012] and in enhanced oil recovery [Stalkup, 1983].

Rock heterogeneity has a primary control on the spreading and mixing of solutes in permeable rocks. There are still many uncertainties in evaluating the impact of rock heterogeneity on conservative and reactive transport, both experimentally and in terms of

mathematical and numerical modeling [Dentz *et al.*, 2011; Le Borgne *et al.*, 2014]. One source of difficulty is that the impact that heterogeneity has on solute spreading and mixing is not easily accounted for using the conventional continuum model describing flow and transport, the advection-dispersion equation (Equation 3). This approach assumes both spreading and mixing are Fickian processes that can be described by using an average parameter, the dispersivity [Lichtner and Kang, 2007; Dentz *et al.*, 2011; Boso and Battiato, 2013]. However, recent modeling approaches show that both incomplete mixing [Gramling *et al.*, 2002; Edery *et al.*, 2009, 2010; Sanchez-Vila *et al.*, 2010; Bolster *et al.*, 2013; Chiogna and Bellin, 2013; Alhashmi *et al.*, 2015] and incomplete spreading [Alhashmi *et al.*, 2015] need to be taken into account to fully describe transport and reaction rates in porous systems. At larger spatial scales heterogeneity can lead to a number of three dimensional flow structures such as flow-focusing, splitting, meandering, and spiraling [Werth *et al.*, 2006; Rolle *et al.*, 2009; Cirpka *et al.*, 2015; Chiogna *et al.*, 2015; Ye *et al.*, 2015a,b; Chiogna *et al.*, 2011b,a; Cirpka *et al.*, 2011]. These can result in enhanced chemical mixing. Hence, further experimental studies are needed to examine the impact of rock heterogeneity on solute spreading and mixing with spatially resolved observations in three dimensions. This is one of our main objectives.

Observational techniques to derive dispersion coefficients are standardized [Grane, 1961; Harleman and Rumer, 1963; Perkins and Johnston, 1963; Blackwell, 1962; Hasinger and Von Rosenberg, 1968; Han *et al.*, 1985; Robbins, 1989; Seagren *et al.*, 1999; Klenk and Grathwohl, 2002; Eberhardt and Grathwohl, 2002; Cirpka *et al.*, 2006; Benekos *et al.*, 2006; Massabo *et al.*, 2007; Fripiat *et al.*, 2008]. However, observations that can distinguish between spreading and mixing and identify larger scale transport processes are restricted to unconsolidated sand or bead pack models. These are limited in their ability to provide spatially resolved observations in three dimensions [Rahman *et al.*, 2005; Rolle *et al.*, 2009; Castro-Alcala *et al.*, 2012; Ye *et al.*, 2015a,c,b; Pini *et al.*, 2016].

This work builds on the technique developed by Boon *et al.* [2016], using X-ray tomography to obtain three dimensional observations of the steady state distribution of non-reactive NaI solute in a brine flowing through consolidated rock cores. In Boon *et al.* [2016] the technique is demonstrated on a homogeneous rock and the analysis is focused on different approaches to quantifying transverse dispersion, one measure of spreading. Here the observations and analysis are extended to heterogeneous rocks and descriptions of commensurately complex transport processes. The key measures of spreading and mix-

ing - the dispersion coefficient, the dilution index, and the scalar dissipation rate - are compared at a range of transport regimes on three rock cores: Berea sandstone, Ketton carbonate and Indiana carbonate. The rocks have distinct pore structure and flow heterogeneity characteristics. The detailed spatial resolution allows for an analysis of dependencies of these properties on solute travel time, transport regime, and the character of rock heterogeneity. To aid in the analysis of time and Pe -dependent plume behavior we use a 2-D numerical model. Furthermore, the imagery allows for identification and analysis of complex flow structures such as meandering, flow-focusing, and flow-splitting, and their impacts on plume spreading and mixing.

2 Experimental apparatus

A detailed description of the experimental apparatus used in this study can be found in *Boon et al.* [2016]. A medical X-ray CT scanner is used to visualize the steady state distribution of a NaI aqueous solution continuously injected into cylindrical rock cores. The cores are 2×10^{-1} m long and 7.62×10^{-2} m in diameter. An aqueous solution of NaI is injected in the middle annular region, whereas in the center and outer annular region deionized water is injected, as illustrated in Figure 1. The inner (ρ_1) and outer (ρ_2) radius of the middle annular region are 2.31×10^{-2} m and 2.77×10^{-2} m, respectively. The concentrations of the NaI solution used for each of the experiments can be found in Table 1.

Due to its novelty, there are a number of design elements in the experimental test worth noting. The cylindrical geometry of the rock samples is the most accurate for tomographic imaging and allows for the use of conventional core holder flow cells commonly used in subsurface rock characterization. The annular geometry of the inlet where solute is introduced is chosen primarily for two reasons. First, maintaining symmetry within the cylindrical geometry of the rock samples facilitates the use of analytic models in the design and benchmarking the interpretation of resulting observations (This is described in more detail in §3.3). Secondly, the annulus allows for a larger sampling of the rock structure than would be available from, e.g. a point injection. Solute concentration is measured after the system has reached steady state to allow for accuracy in the imaging. The medical X-ray CT-scanner can image at resolutions of 1 mm^3 but there is significant random noise in the CT-numbers produced by a given scan. Accuracy in the spatially resolved concentration calculation is significantly enhanced if multiple repeat scans can be per-

98 **Figure 1.** Schematic of the experimental apparatus - Deionized water is injected in the center and outer
 99 annular region. A NaI solution is injected between ρ_1 and ρ_2 . The arrows represent the flow direction.

Figure 2. Cumulative mercury saturation distributions as a function of pore throat radius for the rocks used in this work obtained by mercury intrusion porosimetry (MIP) [Lai *et al.*, 2015].

formed and averaged [Pini *et al.*, 2012; Boon *et al.*, 2016]. The timescales involved in scanning are such that the system must be at steady state. (Approximately 10 minutes are needed to scan and another 50 minutes for the X-ray CT machine to cool before the next scan can be made.)

Three rock cores with varying degrees of heterogeneity are obtained from quarries for the observations: The Berea sandstone is a homogeneous subarkosic sandstone with a narrow pore throat size distribution. The Ketton carbonate is a homogeneous ooidal grainstone with a bimodal pore throat size distribution. The Indiana carbonate is a heterogeneous bioclastic grainstone with a wide ranging continuous pore throat size distribution. Pore throat size distributions obtained by mercury intrusion porosimetry (MIP) measurements are presented in Figure 2 [Lai *et al.*, 2015]. In addition, the distribution of fluid velocity through pore space presented by Bijeljic *et al.* [2013a,b] give a clear indication of the varying degrees of flow and transport heterogeneity of the three rocks.

To create a steady and uniform flow field at the inlet, a ceramic porous plate is placed between the inlet end cap and the core for some of the experiments (Table 1). This leads to a more dispersed tracer boundary condition at the inlet of the core due to radial dispersion within the porous plate. The experiments are carried out for Pe ranging from 0.5 to 210 representing the restricted diffusion, transition and power-law transport regimes (Table 1). The characteristic length L in Pe is taken as the grain size calculated from micro-CT images, (150×10^{-6} m) [Rabbani and Jamshidi, 2014] for Berea, (320×10^{-6} m) [Bijeljic *et al.*, 2013a] for Ketton and (300×10^{-6} m) [Bijeljic *et al.*, 2013a] for Indiana and the molecular diffusion coefficient (D_m) of NaI is 1.33×10^{-9} m²/s. At steady state, X-ray scans are taken every 2×10^{-3} m along the core. For the low Pe experiments (Pe=1 and

Table 1. Experimental conditions - air entry pressure of porous plate and concentration of NaI solution. [-]

indicates that no porous plate is used.

Berea			Ketton			Indiana		
Pe	plate	[NaI]	Pe	plate	[NaI]	Pe	plate	[NaI]
	(bar)	(wt %)		(bar)	(wt %)		(bar)	(wt %)
0.5	1	15	1.1	1	15	1	-	30
2	1	15	4.3	1	15	4	-	30
10	-	30	21	1	30	20	-	30
20	-	30	43	1	30	40	-	30
30	-	30	64	0.5	30	60	-	30
40	-	30	86	0.5	30	80	-	30
60	-	30	128	0.5	30	120	-	30
100	-	30	214	0.5	30	200	-	30

Pe=4) on the Indiana carbonate, the radial boundaries are reached after a short distance,

therefore, X-ray scans are taken of just the upstream half of the core.

3 Measures of spreading and mixing

Spreading (dispersion) and mixing are the result of two processes: 1) mechanical spreading due to small scale variations in the velocity field of the advective flux, and 2) molecular diffusion. The relative effect of each of these processes is characterized by the Peclet number (Pe) as the ratio between the time needed for solutes to travel a characteristic length L by diffusion t_{dif} , and the time needed for solutes to travel the same length by advection t_{adv} :

$$Pe = \frac{t_{dif}}{t_{adv}} = \frac{\frac{L^2}{D_m}}{\frac{L}{v}} = \frac{vL}{D_m}, \quad (1)$$

where D_m is the molecular diffusion coefficient [$\text{m}^2 \text{s}^{-1}$] and v is the magnitude of the average fluid velocity in the pores [m s^{-1}]. This velocity is the interstitial velocity and is defined by $v = Q/(A\phi)$ where Q is volumetric flow rate [$\text{m}^3 \text{s}^{-1}$], A is the cross-sectional area [m^2], and ϕ is porosity [Bijeljic and Blunt, 2007].

3.1 Spreading

Spreading in the direction of flow is measured as the longitudinal dispersion coefficient, D_l [$\text{m}^2 \text{s}^{-1}$], while spreading perpendicular to the flow direction is measured as the transverse dispersion coefficient, D_t [$\text{m}^2 \text{s}^{-1}$]. The dispersion coefficient is defined as

$$\sigma^2 = 2Dt, \quad (2)$$

where D is either the longitudinal dispersion coefficient or the transverse dispersion coefficient, $\sigma^2 = \langle x_i - \bar{x} \rangle^2$ is the second central spatial moment (spatial variance) of the solute in either the flow direction or perpendicular to the flow, t is time, x_i is the position of the particle, and $\bar{x}$ is the mean solute location in either the flow direction or perpendicular to the flow. Dispersion coefficients can be incorporated in the diffusive term of the concentration evolution equation to model the transport of conservative solutes due to advective and dispersive mechanisms:

$$\frac{\partial c}{\partial t} = -\mathbf{v} \cdot \nabla c + \nabla \cdot (D \nabla c), \quad (3)$$

where c is the solute concentration and D is the dispersion tensor. Equation (3) is known as the advection-dispersion equation.

In this study, the transverse dispersion coefficient and dispersivities are calculated as a measure of spreading. The dispersion coefficient is the combined effect of molecular diffusion and mechanical dispersion due to variations of velocity in the advective flux,

$$D_t = D_m + \alpha_t v. \quad (4)$$

Here α_t is the transverse dispersivity [m], which is defined under the assumption of complete mixing at the pore scale.

For laminar flow, the dependence of transverse dispersion on Pe can be divided into four different regimes [Sahimi, 1995; Bijeljic and Blunt, 2007; Delgado, 2007]: (1) restricted diffusion ($Pe \ll 1$), (2) transition ($0.3 < Pe < 5$), (3) power-law ($5 < Pe < 300$) and (4) mechanical dispersion ($Pe > 300$). The power-law regime is defined by,

$$\frac{D_t}{D_m} = \beta \text{Pe}^\delta \quad 5 < \text{Pe} < 300, \quad (5)$$

in which β and δ are fitting parameters obtained from experimental or model results. Sub-linear behavior where $\delta < 1$ in the power-law regime is observed both experimentally [Carvalho de and Delgado, 2000; Klenk and Grathwohl, 2002; Olsson and Grathwohl, 2007; Boon et al., 2016] and in pore-scale modeling [Sahimi et al., 1986; Bijeljic and Blunt, 2007]. The obtained power-law coefficients are significantly lower for bead- and sand packs, 0.5 - 0.72 [Carvalho de and Delgado, 2000; Klenk and Grathwohl, 2002; Olsson and Grathwohl, 2007] than for consolidated rock, 0.84 - 0.95 [Sahimi et al., 1986; Bijeljic and Blunt, 2007; Boon et al., 2016]. This sub-linear behavior is explained by incomplete mixing at the pore throats [Klenk and Grathwohl, 2002] or the more pronounced effect of the decrease of D_t with distance due to flow-focusing [Boon et al., 2016].

By incorporating the dispersion coefficient as defined by Equations (2) and (4) in the concentration evolution equation (Equation 3) the implication is made that spreading is a Fickian process. This definition is correct once the asymptotic dispersion regime is reached [Bijeljic and Blunt, 2007]. In the initial pre-asymptotic dispersion regime, the concentration plume will not be Gaussian and transverse dispersion coefficients obtained using Equation (2) will appear to increase with the travel time of the solute. Once all the velocity variations within the flow-field are sampled the concentration distribution becomes Gaussian and the transverse dispersion coefficient remains constant. The time it takes to transition from pre-asymptotic to asymptotic dispersion corresponds to the asymptotic length and depends on the heterogeneity of the rock. For very heterogeneous rocks with a wide range in fluid velocities, higher order heterogeneities might be encountered before all velocity variations are sampled. In these cases the asymptotic dispersion regime might never be reached [Bijeljic and Blunt, 2007]. The use of an asymptotic dispersion coefficient leads to an overestimation of spreading for systems in the pre-asymptotic regime, and results in an overestimation of mixing and the effective reaction rates [Alhashmi et al., 2016].

3.2 Mixing

Mixing is the process which leads to the homogenization of concentration fields within a spreading plume due to advection and molecular diffusion. It increases the ac-

tual volume taken in by the solute. Spreading and mixing are strongly coupled. Spreading, driven by advective mechanisms, tends to enhance concentration contrasts, which in turn enhances mixing. Most continuum transport models do not separate the two, assuming that the spatial variance (σ^2) is indicative of both solute spreading and dilution. However, this is only the case for homogeneous rocks where the solute plumes are close to exhibiting Fickian behavior and can be fully characterized by a mean position and spatial variance. For a heterogeneous rock, where the plume is non-Gaussian, the spatial variance can still reasonably describe spreading, (although with limitations [Bijeljic *et al.*, 2013a]) but it significantly overestimates dilution [Gramling *et al.*, 2002; Raje and Kapoor, 2000; Luo *et al.*, 2008]. This is in agreement with the results of Le Borgne *et al.* [2010] who show that even in cases of Fickian spreading, mixing can be non-Fickian.

3.2.1 Mixing state

The dilution index is a measure of the mixing state. Two different definitions of the dilution index exist that describe mixing for the case of steady state continuous injection into cylindrical rock cores: 1., the cross-sectional dilution index [Kitanidis, 1994], 2., the flux-related dilution index [Rolle *et al.*, 2009; Chiogna *et al.*, 2011a]. We use a variation of the flux-related dilution index, the mass-weighted dilution index, with a derivation provided in Appendix A. The applicability of each of the methods depends on the inlet configuration, the heterogeneity of the rock, and the information available. The cross-sectional dilution index can only be used to describe mixing in homogeneous porous media. The flux-related dilution index requires information about the local specific discharge which cannot be obtained from our core-flood data. Therefore, in this study the mass-weighted dilution index, which describes mixing in both homogeneous and heterogeneous media, is used to measure the mixing state. The mass-weighted dilution index, E_{mw} [m³] is given by,

$$E_{mw} = E_{cs} \frac{M_{ave}}{M_{cs}}, \quad (6)$$

where M_{cs} and M_{ave} are the cross-sectional and average cross-sectional mass, respectively. E_{cs} [m³], is the cross-sectional dilution index [Kitanidis, 1994],

$$E_{cs}(t) = \exp \left[- \int_V P(z,t) \ln(P(z,t)) dV \right]. \quad (7)$$

231 Here the density function of the solute mass $P(z,t)$ [m^{-3}] is given by,

$$P(z,t) = \frac{c(z,t)}{\int_V c(z,t) dV}, \quad (8)$$

232 where $c(z,t)$ [$kg\ m^{-3}$] is the concentration of the tracer solution at time $t = z/v$ where
 233 z [m] is the distance along the core and v [$m\ s^{-1}$] is the fluid velocity, and V [m^3] is the
 234 volume of the cross-section. The cross-sectional dilution index can be calculated using a
 235 discrete form of Equation (7),

$$E_{cs}(t) = \Delta V \exp \left(- \sum_{k=1}^m P_k(t) \ln(P_k(t)) \right), \quad (9)$$

236 where,

$$P_k(t) = \frac{M_k}{M_{cs}}, \quad (10)$$

237 which is the ratio of the solute mass in voxel k (M_k) to the total solute mass in the cross-
 238 section (M_{cs}) at time t , and m is the number of voxels in the cross-section. ΔV is the vol-
 239 ume of the cross-sectional domain divided by the number of voxels (three dimensional
 240 pixels) used to discretize the cross-sectional domain. A 2-D mass-weighted dilution index
 241 with dimensions [m^2] is obtained by dividing by the thickness of the cross-section.

242 To evaluate the evolution of the dilution index with solute travel time in the rock
 243 cores, the observations are compared with the behavior expected for a purely Fickian
 244 spreading process. *Kitanidis* [1994] shows that the dilution index for instantaneous point
 245 injection in a 1-D homogeneous medium, with constant velocity and dispersion coefficient
 246 is given by,

$$E(t) = \sqrt{(2\pi)} \exp(1/2) \sqrt{2D_t} \sqrt{t}. \quad (11)$$

247 By taking the natural logarithm on both sides, the following expression is obtained:

$$\ln(E) = \left[\frac{1}{2} \ln(2\pi) + \frac{1}{2} + \frac{1}{2} \ln(2D_t) \right] + \frac{1}{2} \ln(t). \quad (12)$$

This expression shows that the increase of the dilution index has a $t^{\frac{1}{2}}$ scaling. Because of the axisymmetric conditions of the inlet boundary condition, and the fact that longitudinal dispersion does not influence the steady state concentration profile, each radial transect can be viewed as a 1-D medium with a solute source of finite width ($w = \rho_2 - \rho_1$ [m]) at a travel time $t = 0$ where $t = (z/v)$. To account for the initial solute width, an initial dilution index, E_0 , is calculated. For this we use the symmetry of the system where the ratio of the 2-D dilution index over the 2-D area of the cross-section is the same as the 1-D dilution index over the 1-D length:

$$E_0 = R \frac{\pi \rho_2^2 - \pi \rho_1^2}{\pi R^2}. \quad (13)$$

The initial dilution index is added to the dilution index resulting in,

$$E(t) = E_0 + \sqrt{(2\pi)} \exp(1/2) \sqrt{2D_t} \sqrt{t}. \quad (14)$$

By taking the natural logarithm and rearranging terms,

$$\ln(E) = \ln(\sqrt{(2\pi)} \exp(1/2) \sqrt{2D_t} \sqrt{t}) + \ln\left(\frac{E_0}{\sqrt{(2\pi)} \exp(1/2) \sqrt{2D_t} \sqrt{t}} + 1\right). \quad (15)$$

The first term on the right is the same as the right hand side of Equation (12) and shows the $t^{\frac{1}{2}}$ scaling. The second term will go to zero with time, resulting in the re-emergence of the square-root of time scaling. Due to the radial symmetry, Equation (14) can be extended to calculate a cross-sectional dilution index by multiplying the right hand side of Equation (14) by a factor πR . This model is compared with the observed dilution index, Equation (6).

For plumes that are heterogeneous and non-Gaussian the entropy increases faster resulting in faster smoothing of the concentration gradients. In these cases observations would exhibit a dependence with travel time greater than that of Equation (15). Amongst plumes with the same total mass and mean concentration, the Gaussian plume has the highest degree of dilution. The ratio of the dilution index of a plume and its equivalent Gaussian plume can be used as a measure of plume deformation and is called the reactor

ratio [Kitanidis, 1994; Thierrin and Kitanidis, 1994]. In this work the reactor ratio is obtained by calculating the reactor ratio for each cross-sectional slice and then average over all the slices.

3.2.2 Mixing rate

A measure of local conservative mixing is the mixing factor [Bolster *et al.*, 2011],

$$m(x, y, z, t) = \left[\frac{\partial c(t)}{\partial x} \right]^2 + \left[\frac{\partial c(t)}{\partial y} \right]^2 + \left[\frac{\partial c(t)}{\partial z} \right]^2. \quad (16)$$

A global measure of mixing can be obtained by integrating the mixing factor (Equation 16) over space, Ω [m^3],

$$\chi(t) = \int_{\Omega} m(x, y, z, t) d\Omega, \quad (17)$$

where $\chi(t)$ is known as the scalar dissipation rate and is a measure of the mixing rate of a system [Kapoor and Anmala, 1998; Pope, 2000; Fedotov *et al.*, 2005; Le Borgne *et al.*, 2010]. Le Borgne *et al.* [2010] show that the scalar dissipation rate can be determined from the integral of the squared concentration. For this we first average over the voxels which are at the same radial distance from the center. Next, the scalar dissipation, S , is calculated from the sum of the squared concentration, c , of each radial voxel, k ,

$$S(t) = \sum_{k=1}^m c_k^2, \quad (18)$$

where m is the number of radial voxels.

The scalar dissipation rate is then given by,

$$\chi = -\frac{1}{2} \frac{dS}{dt}. \quad (19)$$

The scalar dissipation rate decreases with time due to the smoothing of concentration gradients.

3.3 Methods for determination of transverse dispersion coefficient, dilution index and scalar dissipation rate

Boon et al. [2016] derived analytical solutions to the advection-dispersion equation for the annular inlet configuration used in the experiments. It was shown that longitudinal dispersion does not influence the steady state concentration profile. The solution ignoring longitudinal dispersion is given by:

$$C(r, t) = \frac{C_0}{R^2} (\rho_2^2 - \rho_1^2) + \frac{2}{R^2} \sum_{n=1}^{\infty} C_0 \left(\frac{\rho_2}{\lambda_n} J_1(\lambda_n \rho_2) - \frac{\rho_1}{\lambda_n} J_1(\lambda_n \rho_1) \right) \exp(-D_t \lambda_n^2 t) \frac{J_0(\lambda_n r)}{|J_0(\lambda_n R)|^2}, \quad (20)$$

where C_0 is the concentration of the injected solute, D_t is the transverse dispersion coefficient, R is the radius of the core, ρ_1 is the inner radius of the annular source, ρ_2 is the outer radius of the annular source. λ_n is the Finite Hankel transform parameter which is determined by,

$$\frac{dJ_0(\lambda_n R)}{dr} = 0.$$

J_0 is the zero order Bessel function of the first kind and J_1 is the first order Bessel function of the first kind. The derivation of this equation can be found in *Boon et al.* [2016].

The transverse dispersion coefficients in this study are calculated using three separate techniques: (1) By fitting Equation (20) to the steady state concentration profile (C profile), (2) by fitting Equation (20) to the second-central moment (σ_t^2) length profile (M_2 profile) and (3) by fitting Equation (20) to the mass-weighted dilution index (Equation 6) length profile (E profile). For the first method, the core is divided in radial transects. For each radial transect at the inlet, the area of $\pi(\rho_2^2 - \rho_1^2)$ is calculated. This area is kept constant throughout the fitting but ρ_1 and ρ_2 can vary to allow for meandering in the radial direction. For the second and third method the spatial variance and the mass-weighted dilution index are calculated for each cross-section, respectively. Equation (20) is fitted to the obtained length profiles using an average ρ_1 location and the average thickness of the solute ring at the inlet of each experiment. A detailed description of these methods can be found in *Boon et al.* [2016].

The mass-weighted dilution index and scalar dissipation for a pure Gaussian plume are determined from the analytical model of Equation (20) using the values of D_t obtained with the dilution index method. For each experiment the average ρ_1 location and

the average thickness of the solute ring at the inlet are obtained and used as initial condition. The thickness of the porous plate is taken into account for the experiments where a porous plate was used.

3.4 Numerical analysis of flow structures

To aid in the analysis of the experimental results a simple 2-D numerical model is developed using the reactive transport code CrunchFlow [Steefel *et al.*, 2014] which is based on the advection-dispersion equation. The model allows for the analysis of the impacts of flow structures such as flow-splitting and focusing on the spatial variance and cross-sectional dilution index. It also enables us to develop better understanding of the use of concentration iso-contour maps in the identification of such structures. The model medium is 5.00×10^{-2} m by 1.50×10^{-1} m with a voxel size of 1.25×10^{-3} m by 1.25×10^{-3} m. The model medium contains several low permeability zones on each side and one high permeability zone in the center (Figure 7). A constant flow boundary is created at the inlet and no-flow boundaries are created on both sides. A NaI tracer is continuously injected over 1.25×10^{-3} m at the center of the inlet. Simulations are run for $Pe=0.5$, 2, 10 and 100 representing a wide range of transport regimes. The model input parameters can be found in Table 2. The spatial variance and the cross-sectional dilution index are calculated from the concentration profiles and later in §4 used in aiding the interpretation of the experimental results.

4 Results and Discussion

We provide experimental measurements of spreading and mixing in §4.1 and §4.2, respectively, and analyze the dispersion coefficient, mass-weighted dilution index and scalar dissipation rate. In §4.3 we show how flow structures such as flow-focusing, splitting and meandering can impact plume migration and how this affects spreading and mixing.

4.1 Spreading

Figure 3 shows the steady-state concentration profiles, experimentally observed for the injection of a NaI aqueous solution into a Berea sandstone, Ketton carbonate and Indiana carbonate. The values of the dispersion coefficient and its variation with solute travel

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Table 2. Input parameters of the 2-D numerical model.

Porosity	0.22	
Tortuosity	0.34	
α_l	1.6×10^{-4}	m
α_t	1.6×10^{-5}	m
Permeability - default	0.35×10^{-12}	m ²
Permeability - high	0.35×10^{-7}	m ²
Permeability - low	0.35×10^{-22}	m ²
ΔP Pe=0.5	1.24×10^2	Pa
ΔP Pe=2	4.95×10^2	Pa
ΔP Pe=10	2.50×10^3	Pa
ΔP Pe=100	2.50×10^4	Pa

time (or distance along the length of the core) increase with rock heterogeneity and Peclet number (Figure 4 A, B and C). The transition from a pre-asymptotic to an asymptotic dispersion regime is not observed in any of the experiments. The variations in D_t are small for the Berea sandstone and Ketton carbonate. The use of a single D_t to describe spreading in transport models appears justified in these cases. For the Indiana carbonate, however, the variations are large and the use of a single D_t based on laboratory observations would not allow for predictive modeling of the local spreading.

The core averaged transverse dispersion coefficients and associated dispersivities, obtained with the different methods for the range of Pe studied are provided in Table 3. The values for dispersion coefficient obtained with the mass-weighted dilution index method (E profile) are plotted in Figure 5. All three methods (concentration (C profile), second central moment (M_2 profile), and mass-weighted dilution index (E profile) method) give similar results for dispersion coefficients in the Berea sandstone. For the Ketton, the dispersion coefficient obtained by fitting the second central moment (Equation 2) or mass-weighted dilution index (Equation 9) are of the same order of magnitude but fitting the concentration profile with Equation (20) gives slightly higher estimates of D_t . For the Indiana, the mass-weighted dilution index method results in the lowest estimates of D_t , whereas the highest values are obtained when the concentration profile is used for the fit-

Figure 3. at steady state for Berea ($Pe=0.5, 10$ and 100), Ketton ($Pe=1.1, 21$ and 214) and Indiana ($Pe=1$). Flow is from left to right. For Indiana $Pe=1$, the radial boundaries are reached after a short distance, therefore, X-ray scans were taken of just the upstream half of the core.

Figure 4. D_t/D_m vs distance along the core for (A) Berea, (B) Ketton and (C) Indiana for the range of Pe studied. D_t was obtained from fitting the analytical solution to the concentration profile.

Figure 5. Core-average D_t for Berea, Ketton and Indiana obtained for the range of Pe studied by fitting the analytical model (Equation 20) to the mass-weighted dilution index length profile (E profile).

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Table 3. Core average D_t/D_m and 95% confidence bounds in parentheses and $\alpha_t \times 10^{-5}$ m obtained with

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the different methods described in §3.

<i>C</i> profile			<i>E</i> profile			<i>M</i> ₂ profile			
Berea									
Pe	<i>D_t/D_m</i>		<i>α_t</i> (m)	<i>D_t/D_m</i>		<i>α_t</i> (m)	<i>D_t/D_m</i>		<i>α_t</i> (m)
0.5	0.517	(0.463 - 0.571)		0.400	(0.375 - 0.425)		0.427	(0.404 - 0.450)	
2	0.836	(0.772 - 0.900)		0.603	(0.574 - 0.631)		0.651	(0.629 - 0.673)	
10	3.71	(3.62 - 3.80)	4.06	3.61	(3.58 - 3.64)	3.92	3.79	(3.76 - 3.83)	4.19
20	6.85	(6.69 - 7.01)	4.39	5.78	(5.68 - 5.89)	3.59	5.97	(5.89 - 6.05)	3.73
30	9.25	(9.05 - 9.45)	4.12	8.36	(8.24 - 8.47)	3.68	8.46	(8.35 - 8.57)	3.73
40	13.3	(12.9 - 13.6)	4.60	11.0	(10.9 - 11.2)	3.75	12.7	(12.5 - 13.0)	4.39
60	18.8	(18.3 - 19.3)	4.45	13.9	(13.7 - 14.2)	3.23	15.3	(15.1 - 15.6)	3.58
100	28.6	(27.6 - 29.7)	4.14	23.1	(22.3 - 23.9)	3.32	25.4	(24.3 - 26.5)	3.66
Ketton									
Pe	<i>D_t/D_m</i>		<i>α_t</i> (m)	<i>D_t/D_m</i>		<i>α_t</i> (m)	<i>D_t/D_m</i>		<i>α_t</i> (m)
1.1	1.23	(-)		0.657	(0.547 - 0.768)		0.528	(0.496 - 0.560)	
4.3	2.85	(2.55 - 3.15)		1.45	(1.33 - 1.58)		1.47	(1.44 - 1.51)	
21	10.2	(9.31 - 11.1)	13.8	6.05	(5.78 - 6.32)	7.58	7.01	(6.79 - 7.22)	9.00
43	17.2	(15.6 - 18.7)	12.1	10.5	(10.1 - 11.0)	7.15	10.5	(10.4 - 10.7)	7.16
64	26.3	(24.5 - 28.1)	12.6	19.2	(18.4 - 20.0)	9.11	18.3	(18.0 - 18.6)	8.63
86	34.5	(32.2 - 36.7)	12.5	23.2	(22.3 - 24.0)	8.31	23.3	(22.9 - 23.8)	8.37
128	48.7	(45.6 - 51.8)	11.9	34.9	(33.6 - 36.1)	8.47	31.8	(31.2 - 32.3)	7.70
214	78.5	(72.9 - 84.0)	11.6	57.7	(55.4 - 59.9)	8.50	44.6	(44.0 - 45.3)	6.55
Indiana									
Pe	<i>D_t/D_m</i>		<i>α_t</i> (m)	<i>D_t/D_m</i>		<i>α_t</i> (m)	<i>D_t/D_m</i>		<i>α_t</i> (m)
1	3.78	(2.23 - 5.32)		1.17	(1.02 - 1.33)		1.82	(1.58 - 2.05)	
4	11.4	(9.74 - 13.1)		3.97	(3.55 - 4.39)		5.85	(5.53 - 6.17)	
20	50.8	(41.8 - 59.8)	74.7	11.3	(10.2 - 12.4)	15.4	27.2	(24.3 - 30.2)	39.4
40	118	(102 - 134)	87.9	25.4	(23.1 - 27.8)	18.3	47.8	(43.9 - 51.7)	35.1
60	155	(44.5 - 265)	77.0	33.8	(30.4 - 37.3)	16.4	69.5	(62.6 - 76.5)	34.3
80	202	(170 - 233)	75.2	42.4	(38.7 - 46.1)	15.5	53.3	(49.6 - 57.0)	19.6
120	294	(253 - 336)	73.4	68.4	(62.6 - 74.2)	16.9	123	(114 - 132)	30.4
200	428	(402 - 453)	64.0	129	(119 - 139)	19.2	202	(195 -209)	30.2

ting. The values of D_t estimated with the second central moment method lie in between the values obtained by the dilution index method and the method using the concentration profile. The analytical model of the concentration distribution, Equation (20), used for fitting the concentration profile is based on the advection-dispersion equation which assumes a Gaussian distribution in concentration. For more heterogeneous rocks, where the concentration distribution is not Gaussian, this assumption results in an overestimation of the spreading.

The calculated values for dispersivity with each method are relatively constant for different Pe for the Berea sandstone and Ketton carbonate. For the Indiana carbonate, the values of the dispersivity are relatively constant with Pe when calculated using the model (Equation 20) fit to the concentration profile, or inferred from the dilution index (Equation 9) but not when calculated using the second central moment (Equation 2). This suggests that dispersion coefficients derived using the dilution index are the most accurate for describing spreading when using a continuum advection-dispersion model of solute transport since the concentration profile method overestimates the spreading.

The dependence of the transverse dispersion coefficient on Pe for the power-law regime ($5 < \text{Pe} < 300$) is investigated by fitting Equation (5) to the data. The values for β and δ can be found in Table 4. Both Berea and Ketton show sub-linear behavior of D_t with $0.86 < \delta < 0.89$ [Boon *et al.*, 2016] and $0.78 < \delta < 0.98$, respectively. Similar values have been found in previous theoretical studies in sandstones [Sahimi *et al.*, 1986; Bijeljic and Blunt, 2007]. Our measured power-law coefficient is highest for Indiana with $\delta=1.1$ using the dilution index method. The mechanisms that determine power-law scaling behavior are: incomplete mixing by diffusion at the pore-throats, flow-focusing, and flow-splitting. The lowest values for δ (0.5 - 0.72) are observed for bead- and sand packs [Carvalho *de and Delgado*, 2000; Klenk and Grathwohl, 2002; Olsson and Grathwohl, 2007], implying that incomplete mixing at the pore throats is the mechanism responsible for this scaling behavior. We still observe sub-linear behavior for Berea and Ketton but with larger δ values than in the bead packs. This could be due to both flow-focusing and flow-splitting starting to have an impact on spreading. The highest scaling is observed for Indiana where flow-splitting seems to have a larger impact as we discuss later in §4.3.

The use of a single D_t does not allow for predictive modeling of the local spreading for the Indiana on the cm scale due to the large variations in D_t . However, the relatively constant dispersivities obtained with the dilution index method indicate that on the scale

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Table 4. β and δ values and 95% confidence bounds in parentheses from the fit to Equation (5)

Berea	β	δ
<i>C</i> profile	0.49 (0.34 - 0.63)	0.89 (0.82 - 0.96)
<i>E</i> profile	0.47 (0.27 - 0.67)	0.84 (0.74 - 0.94)
<i>M</i> ₂ profile	0.48 (0.2 - 0.76)	0.86 (0.72 - 1.0)
Ketton	β	δ
<i>C</i> profile	0.6 (0.49 - 0.72)	0.91 (0.87 - 0.95)
<i>E</i> profile	0.30 (0.20 - 0.40)	0.98 (0.91 - 1.0)
<i>M</i> ₂ profile	0.68 (0.33 - 1.0)	0.78 (0.68 - 0.89)
Indiana	β	δ
<i>C</i> profile	5.2 (3.0 - 7.5)	0.83 (0.75 - 0.92)
<i>E</i> profile	0.32 (0.088 - 0.56)	1.1 (0.98 - 1.3)
<i>M</i> ₂ profile	0.94 (-0.77 - 2.6)	1.0 (0.65 - 1.4)

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of the core (20cm) the use of a single D_t will provide a good estimate of the spreading of
 405 the plume. This shows that the ADE model can predict spreading reasonably well as long
 406 as the scale of interest is larger than the scale of heterogeneity.

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4.2 Mixing

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The evolution of the observed mass-weighted dilution index, scalar dissipation, and
 scalar dissipation rate with solute travel time are shown in Figure 6. The experimental
 data for the scalar dissipation rate is obtained by using a spline fitting to the scalar dis-
 sipation data. Also shown are the values of these properties calculated when using the
 analytical model, Equation (20). The values of dilution index obtained with the dilution
 index equation (Equation 14) are also plotted in the dilution index graphs of Figure 6 and
 are very similar to the results obtained using the analytical model, Equation (20).

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As expected, the dilution index and scalar dissipation evolve in opposite directions
 with solute travel time. When the dilution increases, the concentration gradients smooth
 out which results in a decrease of the scalar dissipation and scalar dissipation rate. The
 mass-weighted dilution index is based on entropy concepts and, therefore, increases mono-

416 **Figure 6.** Temporal evolution of the experimental (mass-weighted) and analytical dilution index (left),
 417 scalar dissipation (center) and scalar dissipation rate (right) for Berea (top), Ketton (middle) and Indiana
 418 (bottom) for a range of Pe .

Table 5. Reactor ratios for Berea, Ketton and Indiana for the range of Pe studied.

Berea		Ketton		Indiana	
	reactor		reactor		reactor
Pe	ratio	Pe	ratio	Pe	ratio
0.5	0.81 ± 0.06	1.1	0.97 ± 0.03	1	0.93 ± 0.05
2	0.94 ± 0.04	4.3	0.98 ± 0.02	4	0.90 ± 0.06
10	0.95 ± 0.03	21	0.97 ± 0.02	20	0.86 ± 0.1
20	0.93 ± 0.04	43	0.97 ± 0.02	40	0.85 ± 0.1
30	0.96 ± 0.03	64	0.95 ± 0.03	60	0.86 ± 0.1
40	0.96 ± 0.03	86	0.95 ± 0.03	80	0.87 ± 0.06
60	0.96 ± 0.03	128	0.96 ± 0.02	120	0.87 ± 0.08
100	0.95 ± 0.03	214	0.95 ± 0.02	200	0.86 ± 0.08

tonically with time. However, the dilution index results of the Indiana at later times when the radial boundaries are reached do not clearly appear monotonically increasing. This is due to increased experimental error at the final state of dilution when local concentrations are very low.

The temporal evolution of the dilution index of the Berea and Ketton follows the analytical model, indicating Fickian behavior. For the Indiana, the experimentally obtained dilution index increases more quickly than predicted by the model. This is characteristic of solute transport in heterogeneous systems. In heterogeneous media deformation of the solute front occurs due to preferential flow paths which increases the concentration gradients and therefore the mixing [Le Borgne *et al.*, 2014]. This is in agreement with the values obtained for the reactor ratios (Table 5). The reactor ratios for Berea and Ketton are close to one. Much lower values are found for the Indiana indicating significant plume deformation.

The values of scalar dissipation in the Berea sandstone follow the analytical model. For the Ketton the values of scalar dissipation are slightly below the results of the analytical model for the entire experiment and follow a slightly steeper scaling with travel time. For the Indiana, the difference between the experiment and model is much larger. Lower values of scalar dissipation show that the smoothing of concentration gradients is faster in

the experiment than predicted by the model. As with the dilution index, this is characteristic of heterogeneous solute transport, in which preferential flow paths form, leading to enhanced mixing. The experimentally obtained scalar dissipation rates for the Berea follow closely those of the model as seen by the slopes of the scalar dissipation. The scalar dissipation rates for Ketton are initially slightly higher than predicted by the model but eventually start to follow the model. For the Indiana the values for scalar dissipation rate are initially larger but eventually fall below the values for scalar dissipation rate of the model because the boundaries are reached and the plume is fully mixed.

At the cm scale of our experiment with 1mm resolution, Fickian transport behavior is observed for the Berea and Ketton. Fickian behavior in mixing occurs when local concentration gradients have been erased by diffusion. However, incomplete mixing might still exist at the pore-scale in both homogeneous and heterogeneous porous media [Al-hashmi *et al.*, 2015, 2016] and, therefore, should be taken into account in modeling of reactive transport.

4.3 Flow structures and their impact on spreading and mixing

To aid in the analysis, a 2-D numerical model is created using CrunchFlow [Steefel *et al.*, 2014]. A number of features are seen in the simulations that are useful in interpreting the experimental observations. Figure 7 shows the transport results from the simulation, including spatial variance and cross-sectional dilution index profiles, alongside the permeability map of the model. It can be seen that a low permeability zone in the rock can have a varying impact on the spatial variance depending on Pe . The low permeability zones cause plume-focusing for the high Pe resulting in a decrease in the spatial variance and the dilution index. However, for the low Pe , the plume flows around both sides of the low permeability zones which increases the variance and the cross-sectional dilution index, although the impact on the spatial variance is much higher than on the cross-sectional dilution index. The different response is a result of the difference in length scales associated with spreading at a given Pe and location in the permeability field, and the length scales associated with the location and size of the heterogeneity. Thus the different response at different values of Pe provides a measure of the length scales of heterogeneity affecting flow and transport.

Similar features are seen in the experimental observations. Figure 8 shows the spatial variance versus distance graphs for the three rocks for the range of Pe studied. It is

Figure 7. Numerical model showing the impacts of heterogeneity. From left to right: Spatial variance (σ^2) vs distance graphs, cross-sectional dilution index (E) vs distance graphs, permeability field with flow lines, permeability field with iso-concentration contours for $Pe=0.5, 2, 10$, and 100 . The arrow shows the flow direction.

Figure 8. From left to right: Spatial variance (σ^2) vs distance graphs for Berea, Ketton and Indiana.

likely that the variation and change in variation with Pe is a result of similar features as presented in the simulation. The different nature of each profile as a function of Pe gives an indication of the length scale of heterogeneity.

It can also be seen from the simulation that iso-concentration contour maps can be used to visualize the impact of heterogeneity of the rocks used in the experiments. Iso-concentration contour lines clearly converge where there is flow-focusing and diverge when there is flow-splitting due to permeability heterogeneities. Iso-concentration contour maps from the experimental observations are shown in Figure 9 for Berea ($Pe=0.5, 2, 100$), Ketton ($Pe=1.1, 4.3, 214$) and Indiana ($Pe=1, 4, 200$), alongside with spatial pro-

Figure 9. From left to right: Spatial variance (σ^2) vs distance graph, cross-sectional dilution index (E) vs distance graph and iso-concentration contours for Berea (Pe=0.5, 2 and 100)(top), Ketton (Pe=1.1, 4.3 and 214)(middle) and Indiana (Pe=1, 4, 200)(bottom). The yellow arrows indicate flow-focusing. The blue arrows indicate flow-splitting.

files of the second central moment and the cross-sectional dilution index. The yellow arrows indicate locations where there is flow-focusing while the blue arrows point to areas of flow-splitting. It can be seen that the length scale of heterogeneity is very small for the Berea but slightly higher for the Ketton where more transverse spreading in combination with meandering and plume-splitting is observed. The scale of heterogeneity is much larger for the Indiana where a combination of meandering, plume-splitting and plume-focusing causes the transverse spreading to be so large that the radial boundaries are reached even for the highest Pe .

The spatial variance and the cross-sectional dilution index length profiles show a clear decrease in regions where the plume is focusing and a clear increase in locations where plume-splitting is observed although the impact is much more pronounced for the spatial variance. When a low permeability zone is reached and the plume splits in two the spatial variance increases dramatically, indicative of an increase in plume spreading, whereas the cross-sectional dilution index only exhibits a modest increase, indicating that the amount of volume taken in by the solute has not increased as significantly. A clear example of this is the plume-splitting seen for Indiana at $Pe=1$. Furthermore, it can be seen that the low permeability zone results in plume-splitting at $Pe=1$ whereas the same heterogeneity results in meandering and plume-focusing for the advection dominated $Pe=4$ and 200. This shows that the impact of heterogeneity on solute spreading and mixing depends on the interplay between length scales associated with advection, dispersion, and rock heterogeneity and therefore on Pe .

5 Conclusions

We present observations resolving spreading and mixing of solutes in three dimensional consolidated rocks by using X-ray CT. The transverse dispersion coefficient, D_t , and the variation in D_t with solute travel time, increases with Pe and rock heterogeneity. The variations in D_t are relatively small for the homogeneous Berea sandstone and Ketton carbonate and the use of a single D_t to describe spreading in reactive transport models might be justified. For the more heterogeneous Indiana carbonate, however, the variations are large and the use of a single value of D_t would not be accurate in describing local solute spreading but can give a reasonable prediction at the scale of the core length. For homogeneous media, D_t can be obtained from the concentration-, second central moment- or mass-weighted dilution index profiles. For heterogeneous rocks the dilution index method

is most suitable since the assumption of a Gaussian concentration profile overestimates the spreading and the spatial variance is very sensitive to heterogeneities that cause flow-splitting.

A sub-linear correlation is observed between D_t and Pe for the homogeneous Berea sandstone and Ketton carbonate but not for the more heterogeneous Indiana carbonate. The power-law coefficient δ shows an increasing trend with pore space heterogeneity. In bead- and sand packs incomplete mixing by diffusion at the pore-throats is the key control on the scaling behavior [Klenk and Grathwohl, 2002]. However, in sandstones and carbonates both flow-focusing and flow-splitting seem to play an important role resulting in higher δ values.

The evolution of the mass-weighted dilution index, scalar dissipation and scalar dissipation rate with solute transport time exhibits behavior close to Fickian for the Berea sandstone and Ketton carbonate but not for the heterogeneous Indiana carbonate. In heterogeneous media mixing occurs more rapidly. This is consistent with theory showing that more preferential flow paths form in heterogeneous systems which increase concentration gradients and therefore the mixing. This is also in agreement with values of the reactor ratio which are found to be close to one for the Berea and Ketton. However, much lower values are found for the Indiana where significant plume deformation occurs.

Iso-concentration contours can be used to visualize heterogeneities and the impact of flow structures such as flow-splitting and focusing. The impact of heterogeneity on the transport of solutes depends on Pe . Depending on the size of the plume, the same heterogeneity can result in meandering, plume-focusing or plume-splitting. Plume-splitting increases the spreading dramatically but not the amount of volume that is taken in by the solute.

Our methodology based on experimental and modeling analysis provides a quantitative description of the transport of solutes in three dimensional consolidated rocks of varying degrees of heterogeneity. It provides a detailed observational basis for understanding the relationships and divergences of spreading and mixing processes. Some observations show clear cases in which the conventional model of Fickian transport can be used to describe both spreading and mixing. In other cases, they provide some of the first insights into transport in complex flow structures that emerge in the presence of natural rock heterogeneity.

A: Derivation of the mass-weighted dilution index and the relationship between the flux-related and mass-weighted dilution index

Two different definitions of the dilution index exist that describe mixing for the case of steady state continuous injection into cylindrical rock cores. The first definition is the dilution index proposed by *Kitanidis* [1994] applied to each cross-section (cross-sectional dilution index), E_{cs} [m^3] (Equation 7). The cross-sectional dilution index defines how much of the volume of the cross-section is occupied by the solute. This definition correctly describes mixing in the case of homogeneous rock cores. This should not be used to describe mixing in heterogeneous media since the cross-sectional area over which the solute flux is distributed may decrease due to areas of flow focusing. The second definition is the flux-related dilution index, $E_Q(z)$ [m^3s^{-1}] [*Rolle et al.*, 2009; *Chiogna et al.*, 2011a]. Assuming that flow is generally oriented in the z -direction, the flux-related dilution index can be defined as,

$$E_Q(z) = \exp\left[-\int_A P_Q(z) \ln(P_Q(z)) q_z(z) dx dy\right], \quad (\text{A.1})$$

with the flux-related density function of the solute mass $P_Q(z)$ [s m^{-3}] given by:

$$P_Q(z) = \frac{c(z)}{\int_A q_z(z) c(z) dx dy}, \quad (\text{A.2})$$

where $c(z)$ [kg m^{-3}] is the concentration of the tracer solution, q_z [m s^{-1}] is the z -component of the specific discharge normal to the cross-sectional $x - y$ plane with area A [m^2]. The flux-related dilution index shows how much of the water flux contains solute and can therefore correctly describe mixing in homogeneous and heterogeneous media. However, information about the local specific discharge is required which is not easily obtained from core-flood data. We use a variation of the flux-related dilution index, the mass-weighted dilution index, E_{mw} [m^3] (Equation 6). The mass-weighted dilution index can be used for both homogeneous and heterogeneous media. The mass-weighted dilution index is based on the principle of mass conservation and the assumption that the average concentration in each slice stays constant.

A.1 Derivation of mass-weighted dilution index

As a result of the annular configuration, the tracer samples a wide area of the face of the core. This, together with the fact that the volumetric flow rate, Q [m^3s^{-1}], is constant during the experiments, allows for the assumption that the total mass flow rate, $Q_m = Qc_{ave}$ [kg s^{-1}], stays constant as well as the average solute concentration in the cross-section, c_{ave} [kg m^{-3}]. This average concentration can be obtained from the tracer/water distribution at the inlet. The experiments are carried out at steady state, which means that the cross-sectional mass, M_{cs} [kg] stays constant with time. The mass in each cross-section can be used to compute the volume of fluid, V_f [m^3], in the cross-section:

$$V_f = \frac{M_{cs}}{c_{ave}}. \quad (\text{A.3})$$

The cross-sectional dilution index (Equation 9) is calculated using the volume of the full cross-section with ΔV given by the volume of the cross-sectional domain divided by the number of voxels used to discretize the cross-sectional domain. With this approach the dilution index measures how much of the total cross-sectional volume is taken in by the solute but this does not represent mixing in case of heterogeneous rocks. To represent mixing, the reduction in volume over which the solute flux is distributed due to flow-focusing needs to be taken into account. This is done by using the volume of fluid, V_f (Equation A.3), in Equation (9) instead of the total cross-sectional volume. Here ΔV_f is given by,

$$\Delta V_f = \frac{M_{cs}}{mc_{ave}}, \quad (\text{A.4})$$

The dilution index in this form shows how much of the fluid volume in the cross-section is taken in by the solute and can therefore be used as a measure of mixing. Because the number of voxels to discretize the domain, m , stays constant, ΔV_f , changes for each cross-section. To be able to compare the dilution index obtained for the different cross-sections, ΔV_f needs to be normalized. This can be done by using the linear relationship between ΔV_f and the mass in the cross-section (Equation A.4) resulting in the mass-weighted dilution index, E_{mw} [m^3],

$$E_{mw} = E_{cs} \frac{M_{ave}}{M_{cs}}, \quad (\text{A.5})$$

where M_{ave} is the average cross-sectional mass.

A.2 Relationship between the flux-related and mass-weighted dilution index

From our measurements it is impossible to calculate the specific discharge in each voxel in the cross-section but we can look at the cross-sectional average specific discharge, q_{cs} .

By dividing V_f (Equation A.3) by the thickness of the cross-section, z_{cs} [m], an area is obtained over which the solute is observed to flow, $\bar{A}$ [m²],

$$\bar{A} = \frac{V_f}{z_{cs}} = \frac{M_{cs}}{c_{ave} z_{cs}}. \quad (\text{A.6})$$

The cross-sectional average specific discharge depends on the volumetric flow rate, Q , and the cross-sectional area over which the solute is observed to flow, $\bar{A}$,

$$q_{cs} = \frac{Q}{\bar{A}}. \quad (\text{A.7})$$

In the experiments Q stays constant but in the heterogeneous rocks $\bar{A}$ (Equation A.6) varies for each cross-section. By substituting Equation A.6 in Equation A.7 we obtain,

$$q_{cs} = \frac{Q z_{cs} c_{ave}}{M_{cs}} = \frac{q_{ave} A_{ave} z_{cs} c_{ave}}{M_{cs}} = \frac{M_{ave}}{M_{cs}} q_{ave}, \quad (\text{A.8})$$

where q_{ave} is the specific discharge and M_{ave} the cross-sectional mass for $\bar{A} = A_{ave}$, where A_{ave} is the average cross-sectional area where the solute is observed to flow. The relationship between the flux-related dilution index and the cross-sectional dilution index for steady-state continuous injection in homogeneous media is given by [Chiogna *et al.*, 2011a],

$$E_{cs}(z) = \frac{E_Q(z)}{q_z}. \quad (\text{A.9})$$

Here, the cross-sectional dilution index can be written as a function of z by using $z = tv$. By substituting Equation (A.8) in Equation (A.9) the following relation between the flux-related dilution index and the mass-weighted dilution index is obtained:

$$E_Q(z) = E_{cs}(z) \frac{M_{ave}}{M_{cs}} q_{ave} = E_{mw}(z) q_{ave}. \quad (\text{A.10})$$

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Figure 1.

Figure 2.

Figure 3.

Berea

Ketton

Indiana

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.