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2-D vs. 3-D flow-through systems

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Experimental Investigation of Compound-Specific Dilution of Solute Plumes in Saturated Porous Media: 2-D vs. 3-D Flow-Through Systems

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Highlights

- Experimental study on plume dilution in saturated porous media
- Direct comparison of dilution and transverse dispersion in quasi 2D and 3D setups
- Compound-specific transverse dispersion effects are more pronounced in 3D transport
- Semi-analytical solutions proposed to quantify dilution of steady-state plumes
ABSTRACT

Dilution of solute plumes in groundwater strongly depends on transverse mixing. Thus, the correct parameterization of transverse dispersion is of critical importance for the quantitative description of solute transport. In this study we perform flow-through laboratory experiments to investigate the influence of transport dimensionality on transverse mixing. We present a high-resolution experimental setup to study solute dilution and transverse dispersion in three-dimensional porous media. We conduct multi-tracer experiments in the new 3-D setup and compare the results with the outcomes of analogous tracer experiments performed in a quasi 2-D system. We work under steady-state flow and transport conditions and consider a range of velocities relevant for groundwater flow (0.5-8 m/day). Transverse dispersion coefficients are determined from high-resolution concentration profiles at the outlet of the flow-through chambers (7×7 ports in the 3-D setup and 7 ports in the quasi 2-D system), considering conservative tracers with significantly different aqueous diffusion coefficients, namely fluorescein and dissolved oxygen. To quantify dilution in the 2-D and 3-D systems, we experimentally determine the flux-related dilution index using the flow rates and the concentrations measured at the inlet and outlet ports, and we propose semi-analytical expressions to predict its evolution with travel distance in uniform groundwater flow. The experimental results in the quasi 2-D and 3-D flow-through systems are consistent and show a compound-specific behavior of the transverse dispersion coefficient and its non-linear dependence on the seepage velocity in both setups. The degree of dilution and the compound-specific effects of transverse dispersion are considerably more pronounced in 3-D than in quasi 2-D transport systems.

Keywords: dilution, transverse dispersion, mixing, flux-related dilution index, laboratory experiments
1. INTRODUCTION

The characterization of transverse mixing is critical for the understanding and quantitative assessment of solute transport and reactions in groundwater. Especially for continuously emitted contaminant plumes, transverse mixing represents the principal process of mass exchange between the polluted plume and the clean ambient water (e.g., Cirpka et al., 1999). This mechanism is necessary for biodegradation processes occurring at the plume fringes that require the simultaneous availability of multiple substrates such as dissolved electron donors and acceptors. Steep concentration gradients and favorable conditions for microbial activity at the fringes of groundwater plumes have been identified in a number of high-resolution field investigations of contaminated aquifers (e.g., Amos et al., 2011; Anneser et al., 2008; Davis et al., 1999; Thornton et al., 2001; Tuxen et al., 2006). Furthermore, modeling studies have shown the importance of transverse mixing for transport and natural attenuation of organic contaminant plumes at the field scale (e.g., Cirpka et al., 2012; Herrera et al., 2009; Herrera et al., 2010; Liedl et al., 2005; Maier and Grathwohl, 2006; Prommer et al., 2009; Zarlenaga and Fiori, 2013). Although at the field-scale effective dispersion parameters are often needed for the interpretation and modeling of contaminant plumes, their definition requires a correct parameterization of the processes occurring at the smaller Darcy and pore-scales (e.g., Chiogna et al., 2011a; Rolle et al., 2013b). Indeed, biogeochemical reactions take place at the microscopic (pore) scale and local diffusive/dispersive processes are important and often limit the overall contaminant degradation (e.g., Bauer et al., 2009; Rolle et al., 2010; Steefel et al., 2005). Therefore, the detailed investigation of transverse mixing at the pore and Darcy scales is instrumental for the understanding and the accurate parameterization of the interactions between the fundamental physical processes of advection and diffusion, which are necessary to obtain up-scaled dispersion coefficients relevant in field applications.

At the pore scale, transverse mixing has been studied in microfluidic experiments (e.g., de Anna et al., 2014; Willingham et al., 2008; Zhang et al., 2010) and numerical simulations
(e.g., Acharya et al., 2007; Bijeljic and Blunt, 2007; Hochstetler et al., 2013; Knutson et al., 2007; Porter et al., 2010). At the Darcy scale, flow-through laboratory experiments have been conducted to study lateral displacement of conservative and reactive solutes in homogeneous and heterogeneous porous media (e.g., Chiogna et al., 2010; Delgado, 2006; Olsson and Grathwohl, 2007; Rolle et al., 2013a; Seagren et al., 1999). Most of these pore-scale studies and laboratory experiments were performed in two-dimensional computational domains or in quasi two-dimensional experimental setups (e.g., Castro-Alcala et al., 2012; McNeil et al., 2006). These investigations showed the importance of the fundamental interactions between advection and diffusion at the pore scale resulting in incomplete dilution in the pore channels (e.g., Klenk and Grathwohl, 2002; Rolle et al., 2012) and demonstrated the controlling role of transverse mixing for a number of abiotic and microbially-mediated reactions (e.g., Hochstetler et al., 2013; Knutson et al., 2007; Zhang et al., 2010).

Three-dimensional simulations of pore-scale transport are computationally very expensive and have not been performed very often (e.g., Molins et al., 2012; Scheibe et al., 2013). To the best of our knowledge, these studies have not addressed the question of transverse mixing. Likewise, most existing 3-D laboratory-scale experiments have focused on the development of non-invasive concentration measurement techniques and longitudinal dispersion (e.g., Danquigny et al., 2004; Gheith and Schwartz, 1998; Klise et al., 2008; Oswald et al., 1997; Oswald and Kinzelbach, 2004; Stohr et al., 2003).

In this work, we study transverse mixing and plume dilution in a three-dimensional laboratory setup. We performed conservative multi-tracer experiments using fluorescein and dissolved oxygen, which differ significantly in their aqueous diffusion coefficients, and considered a range of seepage velocities (0.5-8 m/day) representative of groundwater flow. The 3-D setup was designed to collect high-resolution measurements of concentration and flow rates in a dense network of sampling points at the outlet of the flow-through system (7×7 ports). This allows the accurate experimental determination of the solute mass flux and the
dilution of steady-state plumes. The outcomes of the 3-D experiments were compared with
the results of analogous multi-tracer experiments performed in a more conventional quasi 2-D
setup at the same scale. The main objective of this study is to experimentally evaluate the
effect of transport dimensionality on transverse dispersion and on steady-state plume dilution
in homogeneous saturated porous media and to show the increased importance of compound-
specific effects, arising from distinct incomplete mixing of different solutes in the pore
channels, for three-dimensional solute transport. Furthermore, we propose semi-analytical
solutions to quantify plume dilution at different cross-sections and we test their predictive
capability with the experimental results in the 2-D and 3-D systems.

2. MATERIAL AND METHODS

In this section we describe the new three-dimensional and the quasi two-dimensional setups
used to measure solute concentrations and flow rates in the steady-state multi-tracer
experiments performed in this study. In addition, we provide the description of the analytical
models applied to estimate the transverse dispersion coefficients and the flux-related dilution
index for the different experimental runs.

2.1 Bench-Scale Experiments

Multi-tracer experiments of solute transport in porous media were performed in quasi 2-D
and 3-D flow-through systems in a temperature-controlled room at 22 °C. The selected tracers
were fluorescein and oxygen, which have significantly different aqueous diffusion
coefficients: $4.8 \times 10^{-10}$ m$^2$s$^{-1}$ and $1.97 \times 10^{-9}$ m$^2$s$^{-1}$, respectively, at $T=22$ °C (e.g., Atkins, 1990;
Worch, 1993). Fig. 1 shows a schematic overview of the quasi 2-D and 3-D experimental
setups. A photograph of the new 3-D experimental apparatus is shown in Fig. 2.
Both flow-through chambers are made of acrylic-glass. The quasi two-dimensional setup has inner dimensions of 28 cm × 1.1 cm × 14 cm while the three-dimensional system has inner dimensions of 30 cm × 7.7 cm × 10 cm. The 2-D setup is equipped with 11 equally-spaced ports (1.27 cm) at the inlet and at the outlet. The 3-D setup has an array of 5×5 injection ports at the inlet and 7×7 extraction ports at the outlet. The ports at the inlet are equally-spaced with a distance of 1.54 cm, while at the outlet the distance between the ports is 1.1 cm. All ports are plugged by rubber septa; syringe needles (ID 0.9 mm) are inserted into the septa for liquid injection and extraction. Peristaltic pumps (IPC and IPC-N, Ismatec, Glattbrugg, Switzerland) were used to obtain constant flux boundary conditions. For the 2-D setup 14 ports (7 at the inlet and 7 at the outlet, counting from the bottom) were active and connected to an IPC-N pump. This allows for a direct comparison of the outlet measurements with the 3-D system that also has at the outlet arrays of 7 ports in the vertical direction. In both systems a similar height of the water table was established. The 25 inlet ports of the 3-D
setup were connected to an IPC-N-12 (P1 in Fig. 2) and an IPC-N-18 (P2 in Fig. 2) pump. At the outlet, 48 ports were connected to two 24-channel IPC-N pumps (P3 and P4 in Fig. 2) and one port (right corner in the bottom row) was left free to maintain a stable water table. Fluran pump tubings (ID 0.64 mm, Ismatec, Glattbrugg, Switzerland) and stainless steel capillaries were used for the connections between the injection and extraction needles and the pumps. Both flow-through systems were homogeneously filled with glass beads (Sigmund Lindner, Germany) with a grain size of 0.4-0.6 mm (saturated hydraulic conductivity $K=2.1\times10^{-3}$ m/s, Haberer et al., 2013). A wet-packing procedure was applied to avoid air entrapment within the water-saturated medium (e.g., Haberer et al., 2012). The porosity of the homogeneous media was 0.4 in both setups. The multi-tracer experiments were performed in a range of flow velocities between 0.5 m/day and 8 m/day in both flow-through systems.

An oxygen-depleted sodium fluorescein solution was used as tracer solution, thus allowing the simultaneous detection of the two tracers (i.e., fluorescein and oxygen) in the saturated porous medium. The oxygen concentration of the solution at the inlet was kept below 1.0 mg/l, while the inlet concentration of fluorescein was in the range of 10-20 mg/l. The solution was stored in a gastight Tedlar bag (Alltech, Germany). After establishing steady-state flow conditions, the tracer solution was injected through the central inlet port (red in Fig. 1), while tap water with no fluorescein and oxygen concentration of 8.5 mg/L was injected from the surrounding inlet ports. Steady-state plumes were obtained after the injection of at least two pore volumes.
Fig. 2 Photograph of the 3-D experimental setup, with high-resolution injection (25 ports) and extraction (49 ports) of the tracers and of the ambient solution. P1-P4 are the multi-channel pumps at the inlet and at the outlet, and V1-V2 denote the flow-through vials for oxygen measurement shown in detail in the inset.

Oxygen concentrations were measured in the vials right after the outlet pumps (Fig. 2) and at the central inlet port, to check the effectiveness of oxygen stripping from the inlet solution, using the non-invasive optode technique (PreSens, Germany) described by Haberer et al. (2011). The technique is based on the dynamic luminescence quenching of a luminophore by molecular oxygen. Samples were also collected at the outlet ports and fluorescein concentrations were measured using a UV-spectrometer (Perkin Elmer LS-3B) with extinction wavelength of 492 nm and absorbance wavelength of 513 nm. The flow rate at the outlet ports was determined by weighing the samples collected at each port.

2.2 Evaluation of Transverse Dispersion Coefficients

Analytical solutions of the advection-dispersion equation are useful to estimate transport parameters in laboratory experiments in porous media (e.g., Robbins, 1989). We estimated the
effective transverse dispersion coefficients for the quasi 2-D and 3-D experimental setups by fitting the analytical solutions of the advection-dispersion equation for uniform flow to the experimental data. Under steady-state transport conditions, the contribution of longitudinal dispersion becomes negligible compared to the one of transverse dispersion (e.g., Cirpka et al., 2011) and the governing equations can be written as:

2-D:
\[
v \frac{\partial c}{\partial x} - D_t \frac{\partial^2 c}{\partial^2 z} = 0
\] (1)

3-D:
\[
v \frac{\partial c}{\partial x} - D_t \frac{\partial^2 c}{\partial^2 y} - D_r \frac{\partial^2 c}{\partial^2 z} = 0
\] (2)

where \( c \) [ML^{-3}] is the concentration, \( x \) [L], \( y \) [L] and \( z \) [L] are the spatial coordinates in longitudinal, lateral and vertical directions, respectively, \( v \) [LT^{-1}] is the average flow velocity and \( D_t \) [L^2T^{-1}] denotes the transverse dispersion coefficient. Since the porous medium is assumed homogeneous and isotropic, lateral and vertical dispersion coefficients are assumed to be identical.

In the two-dimensional case, we consider a line source as boundary condition:

2-D:
\[
c(x = 0, z) = \begin{cases} 
c_0 & \forall |z| < \frac{Z}{2} 
c_{bg} & \forall |z| \geq \frac{Z}{2} \end{cases}
\] (3)

where \( c_0 \) [ML^{-3}] is the concentration of the injected tracer solution, \( c_{bg} \) [ML^{-3}] is the background concentration in the ambient solution and \( Z \) [L] is the source thickness. The analytical solution of the two-dimensional problem, adapted after Domenico and Palciauskas (1982) and satisfying the conditions pointed out by Srinivasan et al. (2007), reads as:

2-D:
\[
c_{norm}(x, z) = \frac{c - c_{bg}}{c_0 - c_{bg}} = \frac{1}{2} \left\{ \operatorname{erf} \left[ \frac{z + Z/2}{2(D_t x/v)^{1/2}} \right] - \operatorname{erf} \left[ \frac{z - Z/2}{2(D_t x/v)^{1/2}} \right] \right\}
\] (4)
which is formulated here for an infinitely high domain. The solution is valid if \( Z + 2(D_x v)^{1/2} \) remains significantly smaller than the height of the domain; otherwise image sources are needed to account for no-flux conditions at the bottom and top boundaries of the domain.

In the 3-D case we consider a rectangular source of width \( Y \) and thickness \( Z \) as boundary condition:

\[
c(x = 0, y, z) = \begin{cases} 
  c_0 & \forall |y| < \frac{Y}{2} \cup \forall |z| < \frac{Z}{2} \\
  c_{bg} & \forall |y| \geq \frac{Y}{2} \cup \forall |z| \geq \frac{Z}{2}
\end{cases}
\]  

(5)

The analytical solution of the three-dimensional, steady-state transport problem reads as:

\[
c_{\text{norm}}(x, y, z) = \frac{c - c_{bg}}{c_0 - c_{bg}} 
= \frac{1}{4} \left\{ \text{erf} \left[ \frac{y + Y/2}{2(D_x v)^{1/2}} \right] - \text{erf} \left[ \frac{y - Y/2}{2(D_x v)^{1/2}} \right] \right\} 
- \left\{ \text{erf} \left[ \frac{z + Z/2}{2(D_x v)^{1/2}} \right] - \text{erf} \left[ \frac{z - Z/2}{2(D_x v)^{1/2}} \right] \right\}
\]  

(6)

Like Eq. 4, the expression of Eq. 6 does not account for no-flux boundaries in a domain of finite width and height. Eq. 4 and Eq. 6 were used to interpret the experimental results in the quasi 2-D and in the 3-D flow-through systems, respectively. These analytical solutions are simplified models of the experimental flow-through systems. However, for the permeable and uniformly packed porous media considered in our study, they allow a satisfactory interpretation of the experimental results. This was also verified in previous studies (e.g., Rolle et al., 2009) where the outcomes of simplified analytical solutions were shown to be in good agreement with those of more complex and detailed numerical models. In the quasi 2-D system the observed source thickness was 1.27 cm, and the concentration was uniform within the thin width of the flow-through chamber (1.1 cm). Thus, the 2-D analytical solution with a line source thickness \( Z \) equal to of 1.27 cm was used to evaluate the vertical concentration...
profiles measured at the outlet. In the 3-D setup Eq. 6 with a square source \((Y=Z=1.54 \text{ cm})\) was used to fit the concentration measurements at the 49 outlet ports.

The trust-region-reflective method for the minimization of non-linear least squares problems implemented in the Matlab function \texttt{lsqnonlin} (e.g., Coleman and Li, 1996) was adopted to fit the experimental results with the analytical solutions (Eq. 4 and Eq. 6), using \(D_t\) as fitting parameter. The hydrodynamic transverse dispersion coefficient was estimated for each seepage velocity tested in the experiments and for each tracer in both the quasi two-dimensional and three-dimensional laboratory setups. These values of \(D_t\) were also used to obtain a parameterization of transverse dispersion. We consider a nonlinear, compound-specific parameterization that was inspired by an earlier statistical model (Bear and Bachmat, 1967) and validated in previous studies in quasi two-dimensional experimental setups (e.g., Chiogna et al., 2010; Rolle et al., 2012) and in two-dimensional pore-scale domains (e.g., Hochstetler et al., 2013; Rolle et al., 2012):

\[ D_t = D_p + D_{aq} \left( \frac{Pe^2}{Pe + 2 + 4\delta^2} \right)^\beta \]  

(7)

where \(D_p \, [\text{L}^2/\text{T}]\) is the velocity-independent pore diffusion coefficient given by the ratio of the aqueous diffusion coefficient and the tortuosity of the porous medium and approximated as \(D_p = nD_{aq}\), with \(n\) [-] representing the porosity of the medium. \(Pe = vd/D_{aq} \, [-]\) is the grain Péclet number, \(d \, [\text{L}]\) is the average grain size, \(\delta \, [-]\) is the ratio between the length of a pore channel and its hydraulic radius and \(\beta \, [-]\) is an empirical exponent that captures the degree of incomplete mixing within the pore channels (e.g., Chiogna and Bellin, 2013; Tartakovsky et al., 2009). Compared to the traditional linear parameterization (e.g., Scheidegger, 1961), Eq. 7 describes more accurately the interactions between the fundamental processes of advection and diffusion at the pore scale. In fact, in this compound-specific parameterization, \(D_t\) retains an explicit dependence of the mechanical dispersion term on the aqueous diffusion coefficient.
of the transported tracers at all velocities and a (possibly) non-linear relationship with the
average seepage velocity, quantified by the exponent β in the mechanical dispersion term.

The same fitting procedure described above for the estimation of \( D_t \) in each experimental
run was adopted to determine the values of the empirical exponent β and the geometrical
parameter δ of the transverse dispersion parameterization (Eq. 7) from the outcomes of all
multi-tracer experiments in both the quasi 2-D and the 3-D flow-through systems.

2.3 Evaluation of Plume Dilution

Dilution of conservative tracers in porous media can be quantified using different metrics
such as the scalar dissipation rate (e.g., Bellin et al., 2011; Bolster et al., 2010; De Simoni et
al., 2005) and the dilution index (e.g., Kitanidis, 1994). The dilution index is defined as the
exponential of the Shannon entropy. It was introduced to quantify true mixing in porous
media, as opposed to plume spreading, which is associated with the deformation and
stretching of a solute plume due to the variability of the velocity field. For steady-state
transport problems, a modified version of the dilution index, the flux-related dilution index,
was proposed by Rolle et al. (2009). This metric expresses dilution as the “act of distributing
a given solute mass flux over a larger water flux” and was applied to quantify dilution and
reactive mixing in porous media at different scales (e.g., Chiogna et al., 2011b; Chiogna et al.,
2012). In a three-dimensional domain, the flux-related dilution index is defined as:

\[
E_q(x) = \exp \left[ - \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} p_q(x, y, z) \ln p_q(x, y, z) \, dy \, dz \right]
\]

(8)

where \( p_q(x,y,z) \) is defined as:

\[
p_q(x, y, z) = \frac{c(x, y, z)}{F(x)} = \frac{c(x, y, z)}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} c(x, y, z) q_s(x, y, z) \, dy \, dz}
\]

(9)

and \( q_s(x, y, z) \) is the specific discharge [LT\(^{-1}\)].
For the analysis of the results of the flow-through experiments performed in this study, we express the flux-related dilution index in discrete form:

2-D: 
\[ E_Q(x) = \exp \left( -\sum_{k=1}^{N_v} P_{Qk} \ln p_{Qk} q_k \Delta z W \right) \] (10)

3-D: 
\[ E_Q(x) = \exp \left( -\sum_{k=1}^{N_v} \sum_{j=1}^{N_h} P_{Qk,j} \ln p_{Qk,j} q_{k,j} \Delta z \Delta y \right) \] (11)

with

2-D: 
\[ P_{Qk} = \frac{c_k}{\sum_{k=1}^{N_v} c_k q_k} \] (12)

and

3-D: 
\[ P_{Qk,j} = \frac{c_{k,j}}{\sum_{k=1}^{N_v} \sum_{j=1}^{N_h} c_{k,j} q_{k,j}} \] (13)

where \( c_k \) and \( c_{k,j} \) [ML\(^{-3}\)] are the measured concentrations at each sampling port. The ports are located on a vertical array of \( N_v \) elements for the 2-D case and on a \( N_v \times N_h \) array with \( N_v \) rows and \( N_h \) columns, in the 3-D setup. \( q_k \) and \( q_{k,j} \) [L\(^3\)T\(^{-1}\)] are the flow rates at each port. Fig. 3 shows an example of how the solute mass flux is determined at the outlet of the quasi 2-D (upper plots) and the 3-D (lower plots) flow-through setups. The mass flux is calculated from the product of the flow rates and the concentrations measured at each port. Both in the quasi 2-D system, where 7 ports were sampled, and in the 3-D setup, where samples were taken from 49 outlet ports, the measured flow rates show minimal fluctuations. Considering the uniform flow rates, the uniform filling and only negligible effects of vertically asymmetric geometry, we conjecture that uniform flow within the porous media can be assumed for the analysis of the data. The measured concentrations show a regular and symmetric behavior, characteristic of transport in homogeneous isotropic packed beds.
Fig. 3 Experimental determination of flow rates, fluorescein concentrations and mass fluxes in the quasi 2-D and 3-D flow-through systems. The numbers on the abscissae represent the outlet ports in the experimental setups.

For the 2-D and 3-D transport problems considered in this study it is possible to derive semi-analytical solutions describing the spatial evolution of the flux-related dilution index of the solute plumes. Following the approach proposed by Chiogna et al. (2011b) we assume a nested radical form for the value of the flux-related dilution index and obtain the following relations to the inverse dynamic Péclet numbers, \( \varepsilon_z \) and \( \varepsilon_y \), in the transverse vertical and transverse horizontal directions, respectively:

\[
2\text{-D: } E_0(\varepsilon_z) = ZWq_e \left( 1 - \frac{4\pi \varepsilon_z}{4\pi \varepsilon_z + 1 + f(\varepsilon_z)} + \sqrt{4\pi \exp\{1\varepsilon_z\}} \right)
\]
\[ E_0(e_y, e_z) = YZq_x \left( 1 - \frac{4\pi e_y}{\sqrt{4\pi e_y + 1 + f(e_y)}} + \sqrt{4\pi \exp(1)e_y} \right) \]

3-D:

\[ 1 - \frac{4\pi e_z}{\sqrt{4\pi e_z + 1 + f(e_z)}} + \sqrt{4\pi \exp(1)e_z} \]

(15)

where, \( f(e_y) \) and \( f(e_z) \) are functions of the inverse dynamic Péclet numbers in the transverse directions, \( e_y = nxD/(q_yY^2) \) and \( e_z = nxD/(q_zZ^2) \), and \( W [L] \) is the width of the quasi 2-D setup.

The derivation of these expressions is outlined in Appendix A.

As will be illustrated in section 3.3, the predictive capability of Eq. 14 and Eq. 15 was tested with the values of plume dilution measured for the steady-state plumes of fluorescein and oxygen established in the quasi 2-D and in the 3-D laboratory setups.

3. RESULTS AND DISCUSSION

3.1 Concentration Measurements

Normalized concentration profiles where measured twice at the outlet of the quasi two-dimensional and three-dimensional flow-through systems for each experimental run and each tracer solution with a time interval corresponding to half pore volume of the flow-through systems. We obtained a mean absolute difference between the two profiles of 5.7 \times 10^{-3}. In order to investigate the reproducibility of the experimental results, the experiment at 6.5 m/day was repeated repacking the porous medium. The results were in very good agreement (mean absolute difference between the two concentration profiles of 9.9 \times 10^{-3}), thus showing the reliability of the experimental setup. In the following we will refer to the mean value of the two measured concentrations from the two successive samplings in each flow-through experiment. In the following we will refer to the mean value of the two measured concentrations. In each setup, we conducted nine experiments covering flow velocities ranging from 0.5 m/day to 8 m/day. Fig. 4 shows the concentration distribution at the outlet of
the 3-D flow-through system for the experiment with a seepage velocity of 5 m/day. The
measurements are shown as normalized concentrations of fluorescein (plots on the left) and
oxygen (plots on the right). Fig. 4a and Fig. 4d show 2-D maps of normalized concentration at
the outlet. The white crosses indicate the location of the sampling ports, whereas the white
contour lines represent the bicubic interpolation of the measured tracer concentrations at the
outlet ports. The color plot in the background shows the concentration distributions computed
using the analytical solution (Eq. 6) fitted to the experimental data of fluorescein and oxygen.
The comparison between the measured concentrations and the outcome of the 3-D analytical
model with best-fit $D_t$ are also shown as transverse horizontal (Fig. 4b and Fig. 4e) and
vertical profiles (Fig. 4c and Fig. 4f). The approximately Gaussian profiles of the analytical
solution are in good agreement with the measured tracer concentrations. The experimental
concentration distribution shows a slight shift towards the right, but otherwise there is no
significant difference between the horizontal and vertical profiles so that fitting a single
transverse dispersion coefficient appears justified.

The measured peak concentrations of the two tracers differ significantly. The fluorescein
plume has a remarkably higher peak concentration and is less spread in the transverse
direction compared to the one of oxygen, indicating different transverse dispersion
coefficients of the two tracers. Such differences for the two tracers simultaneously transported
in the same porous medium arise from the different diffusivities of the two solutes and cannot
be explained if one would assume the validity of a classical linear parameterization of
transverse dispersion (e.g., Scheidegger, 1961), with the additive contribution of a velocity-
independent pore-diffusion term and a diffusion-independent mechanical dispersion term. In
fact, at the velocity of 5 m/day at which the flow-through experiment was performed the
transport regime is strongly advection-dominated and the contribution of pore diffusion to the
hydrodynamic dispersion coefficient is $< 17\%$ for oxygen and $< 8\%$ for fluorescein, so that
the predicted concentration distributions according to the linear parameterization would be
practically identical for the two compounds. Thus, the observed differences between the two solutes confirm that also the mechanical dispersion term depends on the aqueous diffusion coefficient of the compound, as expressed in Eq. 7. Such compound-specific behavior has already been observed in quasi 2-D multi-tracer experiments (e.g., Chiogna et al., 2010). Pore-scale simulations (e.g., Rolle et al., 2012) allowed explaining the compound-specific behavior by the different extent of incomplete mixing and the development of compound-specific concentration gradients in the pore channels.

Fig. 4 Concentration distributions at the outlet of the 3-D flow-through system for fluorescein (a) and oxygen (d) in a flow-through experiment at 5 m/day. Measured (symbols) and simulated (lines) transverse profiles in the horizontal (b and e) and vertical (c and f) directions.

Fig. 5 shows a comparison between the concentration profiles of fluorescein and oxygen in the quasi 2-D and 3-D setups for three distinct advection-dominated conditions, at flow
velocities of 3, 5, and 8 m/day. Distinct quasi-Gaussian profiles are obtained for the two tracers at the outlet of the quasi 2-D (plots a-c) and 3-D experimental setups (plots d-i). However, the differences in peak concentration among the compounds are significantly more pronounced in the 3-D (37% - 50%) than in the 2-D (13% - 28%) setup for all velocities. This is consistent with the peak concentration scaling with $D_t^{-1/2}$ in 2-D, and with $D_t^{-1}$ in 3-D, if the source is sufficiently small. Thus, the 3-D setup is better suited to appreciate the dependence of transverse mixing on compound-specific diffusivity than the quasi 2-D setup.

Fig. 5 Concentration profiles of fluorescein and oxygen at the outlet of the quasi 2-D setup (a-c) and of the 3-D system in the transverse horizontal (d-f) and vertical (g-i) directions. The experiments were performed at seepage velocities of 3 m/day, 5 m/day and 8 m/day.

3.2 Transverse Dispersion Coefficients

Table 1 lists all fitted transverse dispersion coefficients $D_t$ for fluorescein and oxygen in both setups at all flow velocities. The mean relative difference in the transverse dispersion coefficients estimated using the two concentration profiles measured for each experimental
run is equal to 3%, while the mean relative uncertainty on the estimated $D_t$ values varies between 10% and 15%, for fluorescein and oxygen, respectively. In the following we will refer to the mean value of the transverse dispersion coefficient. We used these values to estimate the parameters $\delta$ and $\beta$ of the compound-specific parameterization according to Eq. 7.

Table 1 Summary of the flow-through experiments and values of transverse dispersion coefficients and flux-related dilution index at the inlet and at the outlet.

<table>
<thead>
<tr>
<th>2-D Setup</th>
<th>3-D Setup</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ [m/day]</td>
<td>$D_{t,fluor}$ [m$^2$/s]</td>
</tr>
<tr>
<td>0.485</td>
<td>5.74x10$^{-10}$</td>
</tr>
<tr>
<td>0.729</td>
<td>7.15x10$^{-10}$</td>
</tr>
<tr>
<td>0.951</td>
<td>9.23x10$^{-10}$</td>
</tr>
<tr>
<td>1.43</td>
<td>1.22x10$^{-9}$</td>
</tr>
<tr>
<td>2.95</td>
<td>2.09x10$^{-9}$</td>
</tr>
<tr>
<td>4.01</td>
<td>2.49x10$^{-9}$</td>
</tr>
<tr>
<td>4.97</td>
<td>3.57x10$^{-9}$</td>
</tr>
<tr>
<td>6.39</td>
<td>3.93x10$^{-9}$</td>
</tr>
<tr>
<td>7.84</td>
<td>4.53x10$^{-9}$</td>
</tr>
<tr>
<td>$v$ [m/day]</td>
<td>$D_{t,fluor}$ [m$^2$/s]</td>
</tr>
<tr>
<td>0.49</td>
<td>6.21x10$^{-10}$</td>
</tr>
<tr>
<td>0.769</td>
<td>8.55x10$^{-10}$</td>
</tr>
<tr>
<td>1.02</td>
<td>9.36x10$^{-10}$</td>
</tr>
<tr>
<td>1.46</td>
<td>1.25x10$^{-9}$</td>
</tr>
<tr>
<td>2.89</td>
<td>1.65x10$^{-9}$</td>
</tr>
<tr>
<td>3.99</td>
<td>2.43x10$^{-9}$</td>
</tr>
<tr>
<td>4.81</td>
<td>2.51x10$^{-9}$</td>
</tr>
<tr>
<td>6.42</td>
<td>3.78x10$^{-9}$</td>
</tr>
<tr>
<td>8.03</td>
<td>3.94x10$^{-9}$</td>
</tr>
<tr>
<td>8.25</td>
<td>8.39x10$^{-9}$</td>
</tr>
</tbody>
</table>

The values for $\delta$ and $\beta$, fitted independently for the two tracers and the two setups, are listed in Table 2 together with their 95% confidence intervals. The two parameters have been computed according to the non-linear least squared method described in Rolle et al., 2012, in which the estimated error is dependent on the measurement error of $D_t$ and on the sensitivity to the parameters. The fitted coefficients are comparable among the quasi 2-D and 3-D experiments and between the two tracers. The $\delta$ values obtained from the fluorescein concentrations are slightly larger than those from oxygen, whereas the $\beta$-values are slightly
smaller for fluorescein. Like in previous quasi 2-D experiments (e.g., Chiogna et al., 2010; Rolle et al., 2012), the exponent $\beta$ is close to 0.5, indicating a dependence of transverse dispersion on the square root of the grain Péclet number $Pe$ at high flow velocities.

Table 2 Fitted parameters $\beta$ and $\delta$ of the compound-specific transverse dispersion parameterization according to Eq. 7. Mean: best-fit solution, CI: confidence interval.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Tank dimension</th>
<th>Mean $\beta$</th>
<th>95% CI $\beta$</th>
<th>Mean $\delta$</th>
<th>95% CI $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>2-D</td>
<td>0.53</td>
<td>0.51 – 0.56</td>
<td>3.6</td>
<td>3.2 – 4.0</td>
</tr>
<tr>
<td></td>
<td>3-D</td>
<td>0.47</td>
<td>0.43 – 0.52</td>
<td>3.3</td>
<td>2.5 – 4.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2-D</td>
<td>0.56</td>
<td>0.48 – 0.64</td>
<td>2.7</td>
<td>2.1 – 3.2</td>
</tr>
<tr>
<td></td>
<td>3-D</td>
<td>0.55</td>
<td>0.30 – 0.80</td>
<td>2.6</td>
<td>1.0 – 4.3</td>
</tr>
</tbody>
</table>

Figure 6 shows the transverse dispersion coefficients obtained in the quasi 2-D and 3-D experiments as a function of the seepage velocity. The continuous lines represent compound-specific parameterization of $D_t$ according to Eq. 7 with $\beta$ and $\delta$ parameters determined by the simultaneous fit of the 2-D and 3-D data ($\beta=0.50$ and $\delta=3.4$ for fluorescein; $\beta=0.55$ and $\delta=2.6$ for oxygen). The results for fluorescein are presented in Fig. 6a while the ones for oxygen are shown in Fig. 6b. The nonlinear relationship consistently explains the dependence of $D_t$ on velocity and the remarkable differences among compounds. The agreement between the experimental data in the 3-D (full symbols) and quasi 2-D (empty symbols) setups and Eq. 7 is satisfactory for both fluorescein and oxygen. For oxygen, the data from the experiments at low flow velocities were not considered in the analysis (and not shown in Table 1 and in Fig. 6b) since, under such low flow conditions, the oxygen concentrations at the outlet are too homogeneously distributed along the transverse profiles to provide a reliable estimation of the transverse dispersion coefficient. The good agreement between the values of $D_t$ determined in the quasi 2-D and 3-D setups for both fluorescein and oxygen shows that although the dimensionality of the system clearly influences the measured concentrations at the outlet (Fig 5), it does not affect the estimation of the parameter controlling transverse mixing. In fact,
consistent values of transverse dispersion coefficients were obtained from the experimental results in the quasi two-dimensional and in the three-dimensional porous media.

![Fig. 6 Relationship between the transverse dispersion coefficient and the seepage velocity: experimental data (symbols) and compound-specific parameterization (lines) for fluorescein (a) and for oxygen (b).](image)

Although it does not affect the estimation of the transverse dispersion coefficient, the dimensionality of the system plays an important role in the interpretation of the experimental results. To illustrate this point in Fig. 7a we report the vertical profiles of a 3-D flow-through experiment at 4.81 m/day, using fluorescein as a tracer. The results show that interpreting such measurements with a purely 2-D approach (Eq. 4) leads to more than 50% overestimation of the $D_t$ value determined with a correct 3-D interpretation using Eq. 6. Such overestimation reduces to 10% in case the tracer is injected from a wider source (i.e., 3 central horizontal ports in the 3-D setup) as shown in Fig. 7b. As shown for example by the modeling study of Liedl et al. (2011), such dimensionality effects have important implications in predicting mixing-controlled reactive transport.
Fig. 7 Steady-state fluorescein plumes and vertical concentration profiles at the center of the 3-D flow-through system for the cases: (a) tracer injection from a single central inlet port and (b) tracer injection from three inlet ports in the central row.

To conclude the discussion on transverse dispersion coefficients, we compare in Figure 8 the experimental results of this study with literature data (e.g., Blackwell, 1962; Chiogna et al., 2010; Grane and Gardner, 1961; Harleman and Rumer, 1964; Olsson and Grathwohl, 2007; Schwille, 1988; Seagren et al., 1999). The results are plotted as inverse dynamic Péclet number ($D_t/v_d$) as function of the grain Péclet number ($Pe$). In the same figure, we present the result of Eq. 7 considering the average values of $\beta$ and $\delta$ (0.5 and 5.37, respectively) from these and previous multi-tracer experiments performed in porous media with different grain sizes (e.g., Chiogna et al., 2010; Rolle et al., 2012). The non-linear model captures the trend of the experimental data in the range of Péclet numbers between $10^1$ and $10^4$. For higher $Pe$ numbers, effects of inertia on flow cannot be neglected anymore, and the assumption of creeping flow in porous media becomes invalid (e.g., Bear, 1972). Fig. 8 also shows the
classical linear parameterization of the transverse dispersion coefficient assuming a diffusion-independent mechanical dispersion term:

$$\frac{D_t}{vd} = \frac{n}{Pe} + C$$  \hspace{1cm} (16)

in which $C$ is a dimensionless constant term, set to 3/16 (e.g., Saffman, 1959). The linear parameterization predicts a constant value for the inverse dynamic Péclet number when $Pe$ is larger than 10 and does not allow reproducing the behavior observed in the flow-through experiments.

Fig. 8 Comparison between literature data on transverse dispersion in porous media (black symbols) and the results of this study in the quasi 2-D (full color symbols) and 3-D (empty color symbols) setups. The lines indicate the classical linear (black) and the non-linear compound-specific $D_t$ parameterizations (green).

3.3 Plume Dilution

Mass-flux measurements were performed at the inlet and at the outlet of the quasi two-dimensional and three-dimensional flow-through systems by measuring flow rates and concentrations at the highly spatially-resolved sampling ports. The mean absolute difference
in the mass fluxes measured with a time interval of half pore volume is $8.7 \times 10^{-6}$ mg/min. Therefore, it was possible to experimentally evaluate the flux-related dilution index of the steady-state plumes at the inlet and at the outlet of the flow-through setup using Eq. 10 and Eq. 11. Thus, for each experiment at a given flow velocity values of the flux-related dilution index in the quasi 2-D and 3-D setups were available for the fluorescein and for the oxygen plumes. As an illustrative example, Fig. 9 shows the results for the flow-through experiments carried out at a seepage velocity of 8 m/day. At the inlet, the flux-related dilution indices of fluorescein and oxygen are identical since the tracers are injected through the same inlet port. At the outlet, the fluorescein plumes are considerably less diluted than the oxygen plumes since the compounds underwent compound-specific transverse mixing in the porous media. The values of flux-related dilution index measured in the quasi 2-D system indicate that the oxygen mass flux is distributed over a volumetric discharge larger than the one carrying fluorescein. The different dilution between the fluorescein and oxygen plumes is even more remarkable in the 3-D setup. The proposed analytical solutions for the 2-D and 3-D transport problems (Eq. 14 and Eq. 15) allow computing the flux-related dilution index inside the porous media. The results (continuous and dash-dot lines in Fig. 9) show that the flux-related dilution index monotonically increases for both tracers and the rate of increase is higher for oxygen, since the dilution of this solute in the porous media is more effective than the one of fluorescein due to its higher transverse dispersion coefficient. The agreement between experimental data and the analytical solutions is very good for the fluorescein plumes in both the quasi 2-D and 3-D systems, whereas the semi-analytical solutions for oxygen slightly underestimate the dilution of the steady-state plumes compared to the measured values. We believe that the latter discrepancy is an experimental artifact that is related to the higher accuracy of fluorescein concentrations, which can be measured over seven orders of magnitude, in comparison to those of oxygen, which can be determined over a considerably smaller range (i.e., three orders of magnitude). Notice that the semi-analytical solutions for $E_Q$
(Eq. 14 and Eq. 15) were applied directly without any additional fitting using the values of the transverse dispersion evaluated from the concentration profiles measured at the outlet of the flow-through systems.

Fig. 9 Flux-related dilution index along the longitudinal direction in the quasi 2-D and 3-D flow-through systems.

The analysis of plume dilution was carried out for every experimental run. Table 1 lists the values of the flux-related dilution index for fluorescein and oxygen in all experiments. These results are also plotted in Fig. 10 as a function of the seepage velocity. The results show increasing dilution of the steady-state plumes with increasing flow velocity. While the dimensionality of the problem does not affect the value of the determined transverse dispersion coefficient that is the same in the quasi 2-D and 3-D setups for any given flow velocity (Fig. 6), dilution is considerably more effective in the three-dimensional domain than in the quasi 2-D system. This finding provides an experimental validation of the theory developed by Kitanidis (1994), for which dilution of a solute plume is a process depending on the dimensionality of the problem. The predictions of the proposed semi-analytical solutions
are in very good agreement with the experimental data of fluorescein in both the quasi 2-D and the 3-D systems (Fig. 10a). The oxygen data show more scattering, in particular in the 3D setup; however, the semi-analytical predictions still capture the distinct dilution trends in both quasi 2-D and 3-D setups (Fig. 10b).

**Fig. 10** Relationship between the flux-related dilution index and the seepage velocity in the quasi 2-D and 3-D setups: experimental data and interpretation with the semi-analytical solution for fluorescein (a) and for oxygen (b).

As observed from the analysis of the concentration profiles at the outlet (Fig. 4 and Fig. 5), also the measured and simulated values of the flux-related dilution index show a clear compound-specific behavior across the whole range of seepage velocities. Such compound-specific differences are more pronounced in the three-dimensional case and have significant implications for mixing-controlled reactive transport processes. For instance, this will influence transport of organic contaminants in groundwater, in particular when the release occurs from a small or point source, since important biodegradation reactions occur in a thin 3-D fringe zone surrounding a three-dimensional contaminant plume.
4. SUMMARY AND CONCLUSIONS

In this study we experimentally investigated transverse mixing in homogeneous, isotropic porous media using quasi two-dimensional and three-dimensional flow-through systems. To this end, we designed a fully 3-D laboratory setup in which we measured the outlet concentration of dissolved compounds and the volumetric flow rate at high spatial resolution (i.e., in 49 outlet ports). The direct comparison between the results of the quasi 2-D and the 3-D systems is illustrative of the influence of transport dimensionality on plume dilution. In fact, the results show a strong enhancement of plume dilution in the fully three-dimensional system in comparison to the quasi 2-D setup where transverse dispersion acts only in one direction. We quantified the degree of plume dilution using the flux-related dilution index, $E_Q$. This quantitative metric of mixing was up to three times larger for the fully 3-D plumes compared to those in the quasi 2-D system. We also presented closed-form approximations of $E_Q$ for steady-state plumes in uniform flow, which were in agreement with the observed data.

Although the transport dimensionality had a strong influence on the concentrations measured at the outlet of the flow-through systems and on the dilution of steady-state plumes, it did not affect the value of the parameter controlling lateral mixing: the transverse dispersion coefficient. In fact, for a specific compound and at any given seepage velocity, a good agreement was found between the values of $D_t$ determined in the quasi 2-D and 3-D systems, confirming that the quasi 2-D and 3-D experiments were fully consistent. The parameterization of $D_t$ is critical to properly describe solute transport under different flow-through conditions. In both the quasi 2-D and 3-D setups a nonlinear compound-specific $D_t$ parameterization, acknowledging the dependence of the mechanical dispersion term on the diffusive properties of the transported solute (e.g., Chiogna et al., 2010; Rolle et al., 2012), was necessary to interpret the experimental observations. The multi-tracer experiments performed in this study showed that the compound-specific description of transverse dispersion is particularly needed in predicting fully three-dimensional plumes. This has also
implications for mixing-controlled reactive transport. For instance, in a theoretical study, Liedl et al. (2011) showed a significant difference of steady-state reactive plume lengths in uniform flow when a fully three-dimensional solution was adopted in contrast to a 2-D representation (e.g., Liedl et al., 2005).

Upscaling to effective transverse mixing in more complex flow fields remains an open question. In a recent study restricted to two-dimensional systems, Rolle et al. (2013a) showed that the effects of compound-specific diffusive processes, occurring at the scale of a pore channel, propagate at larger macroscopic scales and have a significant impact both on transient and steady-state transport of conservative and reactive species. For 2-D porous media, Werth et al. (2006) showed that transverse mixing is enhanced in zones of high velocity, which was experimentally confirmed by Bauer et al. (2009). Chiogna et al. (2011a) and Cirpka et al. (2011) could show by numerical and theoretical studies that the compound-specific effects of transverse dispersion do not vanish in heterogeneous two-dimensional systems, despite mixing enhancement by flow focusing. Truly three-dimensional flow fields in heterogeneous anisotropic media, however, may lead to complex flow topologies involving for example intertwining streamlines (e.g., Bakker and Hemker, 2004). This may facilitate mixing mechanisms that are impossible in homogeneous or two-dimensional heterogeneous domains (e.g., Chiogna et al., 2014). Thus, more research is needed to analyze the importance of compound-specific local-scale transverse dispersion on macroscopic transverse mixing in real geological formations. We are convinced that well designed 3-D bench-scale experiments can contribute to answer these questions.

**Acknowledgments**

This study was supported by the DFG (Deutsche Forschungsgemeinschaft, grants RO 4169/3-1 and CI-26/11-1). M.R. also acknowledges the support of the Marie Curie International Outgoing Fellowship (DILREACT project) within the 7th European Community Framework Programme.
APPENDIX A: Semi-analytical solutions for the flux-related dilution index of steady-state plumes in homogeneous porous media

We consider the dilution of steady-state plumes for the cases of continuous release from (i) a line source in a quasi 2-D homogeneous domain and (ii) a square source in a 3-D homogeneous porous medium. In both cases the semi-analytical expressions for the flux-related dilution index under steady-state flow and transport conditions have to satisfy the two asymptotic limits reported in Table A1.

Table A1 Analytical solutions for the flux-related dilution index at the asymptotic limits.

<table>
<thead>
<tr>
<th>Limit</th>
<th>Interpretation</th>
<th>Line source (quasi 2-D$^a$) theoretical $E_Q$</th>
<th>Square source (3-D) theoretical $E_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_z \to 0, \varepsilon_y \to 0$</td>
<td>Dilution at the source</td>
<td>$ZWq_x$</td>
<td>$YZq_z$</td>
</tr>
<tr>
<td>$\varepsilon_z \to \infty, \varepsilon_y \to \infty$</td>
<td>Dilution at infinite distance from the source</td>
<td>$W\sqrt{4\pi \exp(1)nxDj}q_x$</td>
<td>$4\pi \exp(1)nxDj$</td>
</tr>
</tbody>
</table>

$^a$Uniform concentration is assumed along the width $W$ of the quasi 2-D domain

Considering the constraints given in Table A1, Chiooga et al. (2011a) derived the following semi-analytical expression for the estimation of the flux-related dilution index in a quasi 2-D domain:

$$E_Q(\varepsilon_z) = ZWq_x \left(1 - \sqrt[4\pi \varepsilon_z + 1 + 4\pi \exp(1)\varepsilon_z}$$ (A1)

where $Z$ is the source thickness, $W$ is the width of the quasi 2-D domain, $q_x$ the longitudinal component of the specific discharge and $\varepsilon_z$ represents the inverse dynamic Péclet numbers. The first radical term in Eq. A1 is a function allowing for the transition between the two limiting cases expressed in Table A1.

The direct extension of Eq. A1 to the 3-D case leads to an underestimation of the dilution index, when compared with the numerical integration of Eq. 8. Therefore, in this work we consider a slightly modified version of the first square root term, introducing a correction...
factor \( f(\varepsilon_z) = \sqrt{\alpha \varepsilon_z} \), which allows improving the match with the direct numerical integration of Eq. 8 both for the 2-D and the 3-D cases (see Figure A1). The semi-analytical expressions for the flux-related dilution index in the quasi 2-D and 3-D cases read as:

2-D: \[
E_Q(\varepsilon_z) = ZWq_z \left(1 - \frac{4\pi \varepsilon_z}{\sqrt{4\pi \varepsilon_z + 1 + f(\varepsilon_z)}} \right) + \sqrt{4\pi} \exp(1)\varepsilon_z \] (A2)

3-D: \[
E_Q(\varepsilon_y, \varepsilon_z) = YZq_y \left(1 - \frac{4\pi \varepsilon_y}{\sqrt{4\pi \varepsilon_y + 1 + f(\varepsilon_y)}} \right) + \sqrt{4\pi} \exp(1)\varepsilon_y
\left(1 - \frac{4\pi \varepsilon_z}{\sqrt{4\pi \varepsilon_z + 1 + f(\varepsilon_z)}} \right) + \sqrt{4\pi} \exp(1)\varepsilon_z \] (A3)

in which the best-fit procedure over a wide range of inverse dynamic Péclet numbers yields a value of the parameter \( \alpha = 5 \), thus resulting in the correction terms: \( f(\varepsilon_y) = \sqrt{5\varepsilon_y} \) and \( f(\varepsilon_z) = \sqrt{5\varepsilon_z} \).

Fig. A1 Comparison of the flux-related dilution index computed by numerical integration of Eq. 8 and with the semi-analytical solutions Eq. A2 and Eq. A3.
REFERENCES


