# A robust optimization technique for analysis of multi-tracer experiments

Mehdi Gharasoo[1,2,*], Luzie M. Wietzke[3], Bastian Knorr[2], Rani Bakkour[4], Martin Elsner[4], and Christine Stumpp[5]

[1]University of Waterloo, Department of Earth and Environmental Sciences, Ecohydrology, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada
[2]Helmholtz Zentrum München, Institute of Groundwater Ecology, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany
[3]German Research Centre for Geoscience - GFZ, Hydrology, Telegrafenberg, 14473 Potsdam, Germany
[4]Technical University of Munich, Chair of Analytical Chemistry and Water Chemistry, Marchioninistr. 17, 81377 Munich, Germany
[5]University of Natural Resources and Life Sciences, Institute of Hydraulics and Rural Water Management, Muthgasse 18, 1190 Vienna, Austria
[*]Corresponding author, E-mail: mehdi.gharasoo@uwaterloo.ca

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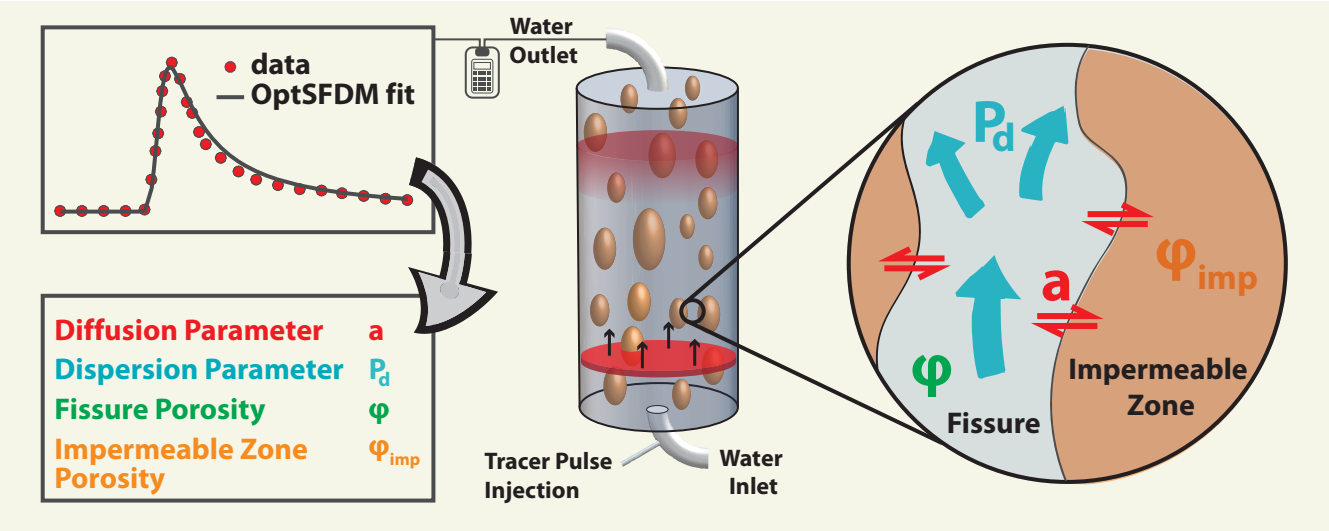
**Abstract**

Fate and transport of solutes in heterogeneous porous media is largely affected by diffusive mass exchange between mobile and immobile water zones. Since it is difficult to directly measure and determine the effect in the aquifers, multi-tracer experiments in combination with mathematical modeling are used to obtain quantitative information about unknown system parameters such as the effective mobile and immobile porosity, and the diffusive mass exchange between mobile and immobile water zones. The Single Fissure Dispersion Model (SFDM) describing nonreactive transport of solutes in saturated dual-porosity media, has been employed as a modeling approach to explain dual-porosity experiments in the field and laboratory (column experiments). SFDM optimization with conventional methods of minimization was immensely difficult due to its complex analytical form. Thus, previous studies used a trial and error procedure to fit it to the experimental observations. In this study, a rigorous optimization technique based on the newly developed scatter search method is presented that automatically minimizes the SFDM to find the optimal values of the hydrogeologically related parameters. The new program (OptSFDM) is accompanied with an easy-to-use graphical user interface (GUI) that is flexible and fully integrated. The program usability is showcased by a few, previously presented experimental case studies, and compared against the currently available, trial-and-error based, command-line executable, SFDM code.

**Keywords**: *Single Fissure Dispersion Model (SFDM); Nonlinear Minimization; Scatter Search; Tracer Experiments; Nonreactive Transport*

## Graphical Abstract




## 1 Introduction

Fate and transport of contaminants in groundwater depends on physical and chemical properties of contaminants as well as aquifer characteristics. Since subsurface transport processes are closely linked to aquifer characteristics, their effect on contaminant movement can be used as a measure to gain knowledge about aquifer. This is particularly beneficial, as it is difficult to quantify aquifer characteristics directly and to determine the value of relevant parameters in-situ. Needless to mention that structural heterogeneities as indigenous features of sedimentary basins and aquifers often add more complexity to direct quantification of those characteristics, resulting in increased measurement uncertainty.

A common way to identify dominating transport processes in an aquifer is to use tracer tests (Flury and Wai, 2003; Knorr et al., 2016a). A tracer is a chemically inactive substance with properties such as low biodegradability, good detectability, and existing at low or constant concentration levels in nature. Measured tracer breakthrough curves form a specific shape according to method of injection which is either continuous, instantaneous or pulsed. The shape of a tracer breakthrough curve is closely related to so called process of matrix diffusion in aquifer (Chapman and Parker, 2005; Parker et al., 2008). Matrix diffusion is the passive exchange of solute between the water in highly permeable zones (mobile water) and the water in impermeable zones (stagnant or immobile water). Solute transport is dominated by advection and hydraulic dispersion in mobile water zones, whereas in stagnant or immobile water zones active flow of water

is considered negligible. In dual-porosity aquifers, the concentration gradients between the two zones allow solutes transported by water in fissures (or mobile water zones) to diffuse into the less-porous stagnant-water zones and to persist there much longer than some other areas of the aquifer. As a consequence, immobile water zones act as storage of contaminants (Lipson et al., 2005) and proceed as source of contaminant when concentration gradients switch (due to back diffusion, see e.g., Carrera et al., 1998; Chapman et al., 2012; Parker et al., 2008). The reverse diffusion of contaminant from already polluted immobile water into mobile water is commonly referred to as contaminant rebound (Geyer et al., 2007; McGuire et al., 2006). This process has been considered as the main control factor of remediation time (Seyedabbasi et al., 2012; West and Kueper, 2010). Since the process strongly depends on the diffusion coefficient of the solutes, often experiments with two or more tracers (with different diffusion coefficients) are conducted (Knorr et al., 2016b; Reimus et al., 2003). The multi-tracer data are then used to quantify the matrix diffusion through the optimization of relevant mathematical models.

Various deterministic(e.g., Cirpka and Kitanidis, 2000) and stochastic-based models (e.g., Lanoiselée et al., 2018; Chechkin et al., 2017), either numerical or analytical have been developed to describe solute migration in heterogeneous systems, and to simulate and thus quantify the observations. While the majority of efforts have concentrated on Fickian-based advection-dispersion models for defining the patterns of transport and dispersion in porous and fractured media, non-Brownian and particle-tracking based models such as continuous-time random walk (CRTW) or the time-fractional advection-dispersion equation (FADE) have equally attracted attention (e.g., Berkowitz et al., 2006; Edery et al., 2014; Metzler and Klafter, 2000; Scher et al., 2002). In this study, we focus on the deterministic-based approaches that solve Fickian-based advection-dispersion models which consist of a set of partial differential equations (PDEs) describing the transport of a reactive or conservative solute in porous media (Cirpka et al., 1999; Gharasoo et al., 2012, 2015; Maloszewski and Zuber, 1985, 1990). To make the calculations easier, many contributions have provided analytical form of solutions for these PDEs for specific cases of fixed initial and boundary conditions. Although the suggested analytical models are limited to the specified conditions, they are preferred in hydrological applications over the numerical models since their optimization is easier due to the existence of a closed-form solution. Two types of modeling approaches have been suggested for dual-porosity systems depending on how the term for the exchange rate between the immobile and mobile water is defined (Carrera et al., 1998). In the first approach, the exchange term is described by a first-order mass transfer coefficient (Bond and Wierenga, 1990; Gaudet et al., 1977; Geyer et al., 2007; van Genuchten and

Wierenga, 1976) while in the second approach it is described by Fick's first law (van Genuchten et al., 1984; Young and Ball, 1998). Depending on the shape of experimental setup, the second approach solves the Fickian law for different geometries. For instance, it solves radial outward diffusion to the surroundings in a cylindrical core for the dual-porosity column setups where the permeable sediments at center are encircled by aquitard layers. These analytical models when describing the non-reactive transport of a tracer in fissured aquifers are divided in two major groups according to the boundary conditions assumed: continuous injection (Neretnieks, 1980; Sudicky and Frind, 1982; Tang et al., 1981) and instantaneous pulse injection (Maloszewski and Zuber, 1985, 1990). The latter approach is called the Single-Fissure Dispersion Model (SFDM) and has been used in combination with multi-tracer tests to inversely estimate the parameters describing the tracer's effective diffusion coefficient, the fracture aperture, and the porosities of both mobile and immobile water zones in dual-porosity aquifers (Einsiedl and Maloszewski, 2005; Knorr et al., 2016a; Maloszewski and Zuber, 1993; Witthüser et al., 2003).

Optimization of the SFDM with conventional methods of minimization (Coleman and Li, 1996; Ehrl et al., 2018; Gharasoo et al., 2019) was highly infeasible due to the complex form of the analytical solution. Therefore, a trial and error approach was used in the previous applications of SFDM optimization (e.g., Knorr et al., 2016a,b, 2017), which was time-consuming and highly subject to the computer skills of the user, requiring knowledge of how the values of fitting parameters affect the final form of the breakthrough curve. Previously used programs were only executable in a command-line environment and their practicality was an issue similar to many early programs in the MS-DOS environment. For instance, the user had no access to the previously obtained fitting schemes which could easily lead to a cycle of repetition. Preparation of input files and the export of graphical illustrations were tedious and a visual comparison between the ensembles was not possible. Moreover, the user could not assess whether the obtained goodness of fit was sufficient since it was not possible to explore the entire space of parameters.

Here, we present a program (OptSFDM) that automatically optimizes the SFDM using a scatter search optimization technique (Glover, 1998; Ugray et al., 2007) in which the entire space of parameters can be scanned. The ultimate aim was to introduce a comprehensive tool for optimizing the complex analytical formula of the SFDM suggested by Maloszewski and Zuber (1985, 1990), enabling hydrologists and hydrogeologists to more easily estimate and quantify the hydrogeological parameters of their heterogeneous dual-porosity environments. The presented approach is not limited to the SFDM and in principle can be used for optimization of other dual-porosity models. The potential of the presented tool is demonstrated and verified through

several case studies that were previously presented in Knorr et al. (2016a).

## 2 Materials and Methods

In natural aquifers, it is difficult to quantify sedimentological heterogeneities which are responsible for geostatistical arrangement of high- and low-permeable zones. The SFDM was originally developed to describe the flow and the transport of a conservative solute in coupled fracture-rock matrix systems. It was also proven to be applicable in porous aquifers (Knorr et al., 2016b). The use of the SFDM in combination with multi tracer tests allows quantifying the effect of solute diffusion into and from immobile water zones as well as estimating hydrological properties of dual-porosity systems such as heterogeneous aquifers. It also helps to better envisage the impact of immobile water regions on the risk of contaminant rebound.

### 2.1 The SFDM background

The dual-porosity medium is considered as a semi-infinite system where identical and parallel fissures are equally spaced in the rock matrix. Fissures are considered as the regions within which the mobile water flows while the immobile water is assumed to be present only in the rock matrix. Non-reactive transport of a tracer in fissures is therefore described by advection, dispersion, and a diffusive mass exchange with the rock matrix. Advection is presumed negligible in the rock matrix, thus, the transport of the tracer in the rock matrix is governed only by diffusion in a direction perpendicular to the fissures. In addition, adsorption effects are assumed negligible and the tracers are considered kinetically non-reactive. It is also assumed that the distance between fractures is sufficiently high, resulting in unlimited penetration depths of solute diffusion into the immobile water zone and thus, the interactions between fractures are excluded. Considering the above assumptions, the following equations describe the mass balance in the fissures and in the matrix (Maloszewski and Zuber, 1985, 1990):

$$\frac{\partial C_f}{\partial t} + v\frac{\partial C_f}{\partial x} - D\frac{\partial^2 C_f}{\partial x^2} - \frac{\phi_p D_p}{2b}\frac{\partial C_p}{\partial y}\Big|_{y=b} = 0 \quad \text{for} \quad 0 \le y < b \tag{1a}$$

$$\frac{\partial C_p}{\partial t} - D_p\frac{\partial^2 C_p}{\partial y^2} = 0 \quad \text{for} \quad b \le y < \infty \tag{1b}$$

where $C_f[ML^{-3}]$ and $C_p[ML^{-3}]$ are the tracer concentrations in water in the mobile (fissures) and immobile zones (rock/silt/clay matrix) respectively, $v[LT^{-1}]$ is the mean water velocity in fissures, $x[L]$ is the coordinate in the direction of flow in fissures (along the axis of cylinder), $y[L]$ is the coordinate perpendicular to $x$, $t[T]$ is the time variable, $\phi_p[-]$ is the porosity of

matrix, $D_p[L^2T^{-1}]$ is the effective molecular diffusion coefficient in the matrix, $D[L^2T^{-1}]$ is the dispersion coefficient in the fissures, $b[L]$ is a geometrical parameter characterizing the mobile water zone. The analytical solution of Eq. (1) with initial and boundary conditions stated in Maloszewski and Zuber (1990) for a Dirac injection of a tracer is given by:

$$C_f(t) = \frac{aM\sqrt{t_0/P_d}}{2\pi Q} \int_0^t \exp\Big( - \frac{(t_0-u)^2}{4ut_0P_d} - \frac{a^2u^2}{t-u}\Big) \frac{du}{\sqrt{u(t-u)^3}} \tag{2}$$

where $Q[L^3T^{-1}]$ is the volumetric flow rate, $u$ is the integration variable, $t_0[T] = V_f/Q$ is the mean transit time of water in fissures, $V_f[L^3]$ is the volume of water in fissures (mobile water), $M[M]$ is the total mass of the injected tracer, $a[T^{-0.5}] = 0.5\phi_p\sqrt{D_p}/b$ is the diffusion parameter, and $P_d[-] = D/vx$ is the dispersion parameter, or the multiplicative inverse of the dimensionless Péclet number. Although the SFDM was originally developed for describing transport in fissured aquifers, it was shown to be also applicable in describing transport in dual-porosity sediments (Knorr et al., 2016b). Of special interest to the SFDM and related analytical solutions is the geometrical parameter $b$. The definition of this parameter varies throughout studies, depending on the geometry of the experimental designs. In the presented analytical solution Eq. (2), $b$ is defined as the half-aperture of the single fracture so that $y = b$ reaches the interface between mobile and immobile water zone (Maloszewski and Zuber, 1985, 1990; Nolte et al., 1991). For column experiments following the design of Young and Ball (1998), the parameter $b$ is described as the radius of the mobile water zone (the cylindrical and permeable inner zone) which is drained by water (Knorr et al., 2016a). A more general approach describes $b$ as the ratio of an aquifer unit column to matrix surface area (Carrera et al., 1998; Reimus and Callahan, 2007). The careful assessment of $b$ is of great importance for the derivation of the porosity of the immobile water zones and for the validation of the model results (as shown in Knorr et al. (2016a)).

The unknown parameters $a$, $P_d$, and $t_0$ are estimated through the fitting of analytical solution Eq. (2) to the measured concentrations of tracer in mobile water $C_f$. This has been done so far through a trial and error procedure (e.g., Knorr et al., 2016a,b, 2017), and the goodness of fit was evaluated by calculating the R-squared values,

$$R^2 = 1 - \frac{\sum_i (C_{exp,i} - C_{f,i})^2}{\sum_i (C_{exp,i} - \bar{C}_{exp})^2} \tag{3}$$

where $C_{exp,i}$ denote the experimental observations, $C_{f,i}$ denotes the corresponding fit of Eq. (2) at data points, and $\bar{C}_{exp}$ is the mean of the observed data. Once the values of these parameters

($a$, $P_d$, and $t_0$) are determined, the values of parameters describing characteristics of the aquifer, such as $b$, $D$, and $\phi_p$ can be derived from them.

## 2.2 Optimization technique

Due to the presence of multiple local minima and high non-linearity of Eq. (2), the optimization was difficult using standard minimization techniques, such as Levenberg and Marquardt (Levenberg, 1944; Marquardt, 1963) or interior-reflective Newton methods (Coleman and Li, 1996; Gharasoo et al., 2017). Here, a new minimization technique based on the scatter search algorithm is employed for fitting. Scatter search described in Glover (1998) and Ugray et al. (2007) is a population-based global approach that has recently been shown highly effective in solving nonlinear optimization problems. The mechanism is based on maintaining a group of diverse and high-quality candidate solutions. For this purpose, the algorithm first generates a set of trial points within the space of parameters and uses them as potential start points. Every trial point is evaluated by the minimization function and obtains a score. The best scored points are then selected as high-quality candidate solutions. Using an iterative procedure, the basins of solution that attract high number of candidate solutions are recombined and weighted. The results of recombination are refined and further evaluated using an embedded heuristic until the global optima is found. Traditional optimization techniques execute iteratively by comparing various solutions till an optimum or a satisfactory solution is found. The success of such methods for minimizing complicated functions with multitude of local minima highly depends on the choice of parameters' initial guess. Since the presented scatter search algorithm fully scans the parameter space (that is the combination of all parameter values within their lower and upper bounds), it is independent to the choice of initial values and as a result less prone to fall into a local optima and thus highly capable of finding the global optimum.

Previous studies (e.g., Knorr et al., 2016a,b, 2017) have calculated and used relative recovery rates $R(t) = Q\int_0^t C_f(t)dt/M$ to improve the trial and error procedure of fitting. This is a redundant exercise using the presented fitting approach as the new procedure directly minimizes Eq. (2).

## 2.3 Case studies

We used the new tool to estimate the value of parameters $a$, $P_d$, and $t_0$ from the data for dual-porosity column experiments presented in Knorr et al. (2016a) which were performed using three different tracers (Uranin, Bromide, and Deuterium) at three different injection/pore velocities.

The estimated values are then compared with the reported values that were obtained through a trial and error fitting procedure.

## 3 Results and Discussion

As shown in supporting information (Fig. S1), the new program (OptSFDM) facilitates the user interactions with the system via a graphical interface. In average, it takes about two minutes to optimize each case study presented in Knorr et al. (2016a) on a quad-cores Intel Core i5-4590 CPU at 3.30GHz with 16GB RAM. The program also provides the opportunity for the user to do a trial and error fitting procedure by solving Eq. (2) with the parameter values provided by the user. R-squared values (Eq. (3)) for every fit are also calculated and shown as a measure for the goodness of fits.

We, unfortunately, do not have access to the the old SFDM source-code, or know the details of how the fits were done by Piotr Malozewski in Knorr et al. (2016a). However, there are small differences between the solution of Eq. (2) obtained in this study with those illustrated in Knorr et al. (2016a). We suspect that due to higher numerical tolerances of solving integrals in older programming environments, the obtained solutions were not as accurate as nowadays. Therefore, the current solution of Eq. (2) with the previously reported parameter values looks slightly different (when comparing the dashed lines in Fig. 1 with the fits in Fig. 2 of Knorr et al. (2016a)). For completeness, we included our MATLAB solution for Eq. (2) in supporting information (Listing S1).

### 3.1 Comparison with previously presented results

The new algorithm was proven remarkably efficient in solving the SFDM optimization. The goodness of fits were found more accurate than the conventional results which were done by a hydrogeological expert through a trial and error procedure. Fig. 1 shows the comparison between the results obtain in this study and those in Knorr et al. (2016a). Furthermore, Table 1 lists the parameter values obtained in this study and compares them to the previously reported values. As shown in Fig. 1, the fits to the data from experiments A and B (performed with pore velocities of 7.1 $m.d^{-1}$ and 1.5 $m.d^{-1}$, respectively) are conveniently good and slightly improved in comparison to the previously presented fits. The estimated parameter values for the fits are also in a good agreement with those reported. However, the fits to the data of experiment C with the lowest flow velocities of 0.55 $m.d^{-1}$ (except for the case of Uranine) do not match the experimental results well, reflected also by the R-squared values calculated according to Eq. (3).

Since further refinement of the fitting scheme did not improve the goodness of fit, the observed differences are speculated to be related to the uncertainties in tracer mass recovery (which is assumed to be 100% in Eq. (2)).

Logarithmic plots (log of concentrations vs. linear time) are occasionally supplied as this type of plots provides a better measure for the goodness of fit at the tailing section (Edery et al., 2014) and thus gives a better perspective on sorption processes. Since sorption was considered negligible here, we avoided this sort of details in general. So in the current setup, root-mean-square errors (RMSE) are minimized with no data scaling (weighting). As a result, the fits preferably pass through the peak of the breakthrough curves (to minimize the error at high concentrations) in which the methodology is identical to the strategy was employed by (Knorr et al., 2016a). If a fit to the tailing or to the starting points is more important, then RMSE at those points can be scaled up (weighted higher). Such adjustments are easily possible within the current potentials of the tool and shown here for specific case of Bromide data (Fig. 2). As illustrated in logarithmic plots of Fig. 2, weighting gave a better fit to the tailing section for experiments A and B. However, this was achieved in cost of a less desirable fit at the breakthrough peak as shown in linear plots. Estimated parameter values for weighted fits ($a = 0.089\ hr^{-0.5}$, $P_d = 0.0068$, $t_0 = 1.77\ hr$ for the experiment A, and $a = 0.08\ hr^{-0.5}$, $P_d = 0.0025$, $t_0 = 8.2\ hr$ for the experiment B) were, however, not significantly different from those listed in Table 1 for non-weighted fits. For the case of experiment C, the weighted fit was nearly identical to the non-weighted fit and so were the estimated parameter values. As it is discussed in the next section, the uncertainty related to the tracer mass recovery was found majorly influential in this case. Hence, without the consideration of correcting mass recovery by taking it as another fitting parameter, the fits could have not been further improved independent to the technique of optimization and data weighting. It is also worth mentioning that the data scaling (or weighting) only changes the final shape of the objective function and has no effect on the ability of the model in fully scanning the parameter space.

### 3.2 Four parameters fit including a mass correction factor

Previous SFDM-based studies has mentioned that additional fitting of recovery rates is useful in order to improve reliability of fitting parameters for experimental results where the tracer recovery is low to moderate (Maloszewski and Zuber, 1990). Since model calibration is embedded in the trial-and-error procedure of Maloszewski and Zuber (1990), the exact procedure remains unknown. To tackle this in the new program OptSFDM, a fourth fitting parameter $M_{cor}$ (or the

mass-recovery correction factor) is introduced to minimize calibration difficulties that arise from low tracer recoveries. This parameter acts as a scaling parameter and expresses the relationship between the injected mass of tracer and the actual mass recovered. Inclusion of this extra fitting parameter changes the form of Eq. (2) to the following with four fitting parameters $a$, $P_d$, $t_0$, and $M_{cor}$:

$$C_f(t) = \frac{aM_{cor}M\sqrt{t_0/P_d}}{2\pi Q}\int_0^t \exp\Big(-\frac{(t_0-u)^2}{4ut_0P_d}-\frac{a^2u^2}{t-u}\Big)\frac{du}{\sqrt{u(t-u)^3}} \tag{4}$$

The value of $M_{cor}$ was set to vary between 0.5 and 2. As shown in Fig. 3, the introduction of $M_{cor}$ led to a more realistic set of parameter values and a better fit to the data of experiment C. It is worth noting that the optimization algorithm was slightly refined by decreasing the radius of basins of attraction (Glover, 1998; Ugray et al., 2007) to handle the four-parameters fitting procedure more efficiently. As shown in Table 2, $M_{cor}$ did not change drastically for Uranine case confirming that the fit with three parameters is already sufficiently perfect. For Bromide, a good fit was obtained with $M_{cor} = 0.8$ meaning that the mass recovery was approximately 20% less than it was assumed. For Deuterium, $M_{cor} = 0.55$ suggests that the mass recovery was estimated even lower (about 45% less than expected). It is also clear from the fits (compare the results of experiment C in Fig. 3 with those in Fig. 1) that the inclusion of mass-recovery correction factor helped obtaining much better fits. The quality of fits were also improved for the previously reported parameter values in Knorr et al. (2016a) when $M_{cor}$ was taken into account.

### 3.3 Further notes in using the SFDM

It is essential to validate the results obtained from the SFDM as there is a chance of over-fitting with four or even three fitting parameters. The obtained parameter values should not thus be regarded as absolutely correct without further considerations. As previously done in Knorr et al. (2016a,b), system parameters need to be verified for reliability, for instance by comparing with literature, direct measurements, or theoretical approximations (e.g., porosity can be roughly estimated from particle size distribution in a system). Another way to verify the estimated parameter values is to repeat the experiments with multiple tracers and at different flow velocities. All multi-tracer tests should result in more and less similar values for medium-related parameters. The estimated parameter values from a decent fit can still be questionable due to several possibilities such as describing the experimental setup with an invalid model and assumptions, or the existence of processes that are not yet addressed in the model.

Furthermore, it should be noted that the use of multiple tracers with different diffusion coef-

ficients is highly crucial in order to unambiguously determine whether the interactions between mobile and immobile water and thus diffusion of solutes between them play an important role in an aquifer. The SFDM was employed for parameter estimation of Knorr et al. (2016a) only when it was evident that immobile water drastically influenced solute transport and as the result all the three tracers formed different breakthrough curves. Note that the tracer with the lowest diffusion coefficient must produce the highest peak and the lowest tailing, and vise-versa.

### 3.4 Potentials of the presented optimization approach

The presented tool only optimizes the analytical SFDM solution provided by Maloszewski and Zuber (1990) for conservative transport of a solute in form of a pulsed input (Dirac injection) through a dual-porosity medium. Since all previously introduced analytical solutions for fissured aquifers have a comparably complicated form (Neretnieks, 1980; Sudicky and Frind, 1982; Tang et al., 1981), a similar optimization technique can be used to effectively minimize them. Furthermore, a similar application of the scatter search algorithm can serve as a reliable optimization procedure for all suggested analytical models for dual-porosity porous environments (e.g., Bond and Wierenga, 1990; Geyer et al., 2007; Leij et al., 1993; van Genuchten and Wierenga, 1976; van Genuchten et al., 1984; van Genuchten, 1985; Young and Ball, 1998).

Although the presented technique was shown highly effective for optimizing deterministic-based Fickian advectiion-dispersion models that have a closed-form solution, it is not currently clear if the method can be equally functional for analytical forms of non-Fickian (or anomalous) transport models (see e.g., Neuman and Tartakovsky, 2009). It is however evident that this method cannot be employed for optimizing the stochastic-based models (e.g., Berkowitz et al., 2006; Lanoiselée et al., 2018; Scher et al., 2002) due to the different nature of their setup and simulations.

## 4 Summary and Conclusions

The new program OptSFDM, presented in this contribution, allows automatic optimization of the complex analytical model suggested by Maloszewski and Zuber (1985, 1990) for dual-porosity media. User interactions with OptSFDM are guided through a graphical user interface (GUI) that provides a platform for importing/exporting data from/to Excel. The simple but effective design of the interface helps users to focus more on the experimental and applied aspects of the research, and less on the mathematical and computational details. The new program further allows the user to practice a trial and error fitting method similar to the old SFDM program. OptSFDM

is easy to operate and flexible, allowing users to concentrate better on data interpretation than on rather elaborate and complicated procedures of manual data fitting by trial and error. It thus offers an invaluable platform to investigate the exchange of solute between immobile and mobile water in heterogeneous media, efficiently quantify the multi-tracer experimental data, and estimate the hydrogeologically related parameters of a system such as the porosity of mobile and immobile water zones and the mean transient time. The results can be employed to evaluate the risk of contaminant rebound in a system. The presented approach of using scatter search algorithm can be further extended to optimize similarly complex analytical solutions in field of hydrology and hydrogeology.

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# Tables

Table 1: Summary of fitting parameters both from this study and from Knorr et al. (2016a) (values in parenthesis). The fits associated with this values are shown in Fig. 1.

| | Uranine | Bromide | Deuterium | Mean±Stdv |
|---|---|---|---|---|
| | Experiment A | | | |
| $a(hr^{-0.5}) \times 10^2$ | 4.8(4.3) | 8.8(7.5) | 11.6(9.4) | |
| $P_d \times 10^3$ | 8.7(7) | 5(6) | 4.8(6) | 6.2±2.2 |
| $t_0(hr)$ | 1.72(1.69) | 1.73(1.73) | 1.7(1.71) | 1.72±0.01 |
| $R^2(\%)$ | 97.8(94.6) | 98.7(97.6) | 99.1(97.4) | |
| | Experiment B | | | |
| $a(hr^{-0.5}) \times 10^2$ | 5.5(4.5) | 10.2(8) | 13(10) | |
| $P_d \times 10^3$ | 4.4(4) | 2(3) | 1.6(2) | 2.6±1.5 |
| $t_0(hr)$ | 8.3(8.1) | 7.9(8.1) | 7.7(8) | 7.9±0.3 |
| $R^2(\%)$ | 98.7(89.7) | 99.8(96.5) | 98.9(92.9) | |
| | Experiment C | | | |
| $a(hr^{-0.5}) \times 10^2$ | 6.1(4.5) | 11.4(8.5) | 18.6(10.5) | |
| $P_d \times 10^3$ | 2.8(4) | 0.7(3) | 0.8(2) | 1.2±1 |
| $t_0(hr)$ | 22.4(23) | 20.9(22) | 17.8(21) | 20.4±2.3 |
| $R^2(\%)$ | 99.4(94.6) | 98.3(83.3) | 87.5(-11) | |

Table 2: Summary of fitting parameters both from this study and from Knorr et al. (2016a) (values in parenthesis) using Eq. (4). Here the mass recovery rate is corrected by the parameter $M_{cor}$ of which the estimated values are shown for each tracer. The fits associated with this values are shown in Fig. 3.

| | Experiment C | | | |
|---|---|---|---|---|
| | Uranine | Bromide | Deuterium | Mean±Stdv |
| $a(hr^{-0.5}) \times 10^2$ | 6.3(4.5) | 9(8.5) | 10.1(10.5) | |
| $P_d \times 10^3$ | 2.6(4) | 1.4(3) | 1.4(2) | 1.8±0.7 |
| $t_0(hr)$ | 22.3(23) | 21.9(22) | 21(21) | 21.7±0.6 |
| $M_{cor}$ | 1.02 | 0.8 | 0.55 | |
| $R^2(\%)$ | 99.5(93.1) | 99.6(97.7) | 98.3(97) | |

## Figures

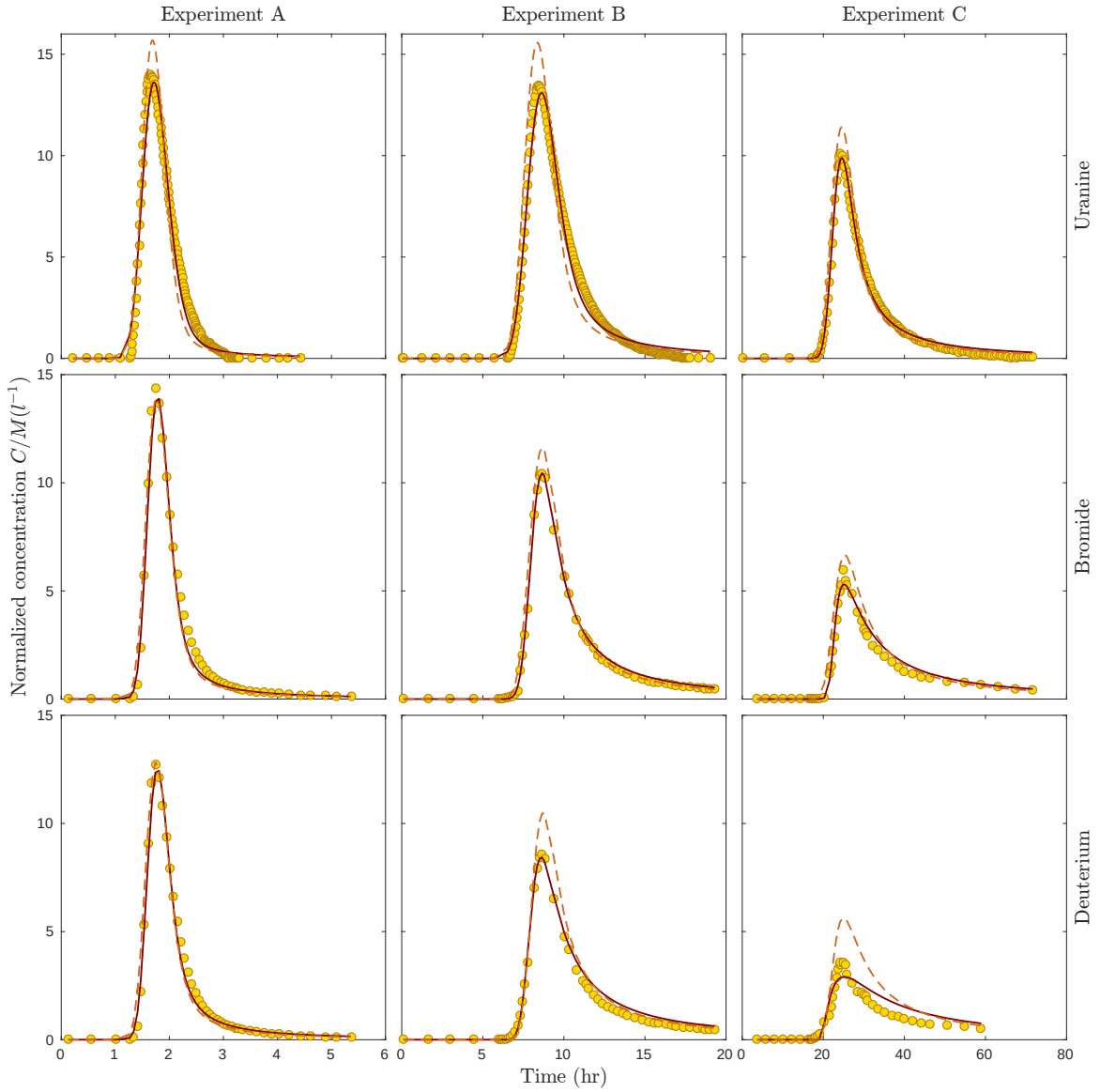


Figure 1: Fits to the data of Knorr et al. (2016a). Estimating the hydrogeological parameters ($a$, $P_d$ and $t_0$) by fitting analytical solution Eq. (2) to the data. Solid lines shows the fits from this study while the dashed lines illustrate the fits obtained by trial and error method in Knorr et al. (2016a).

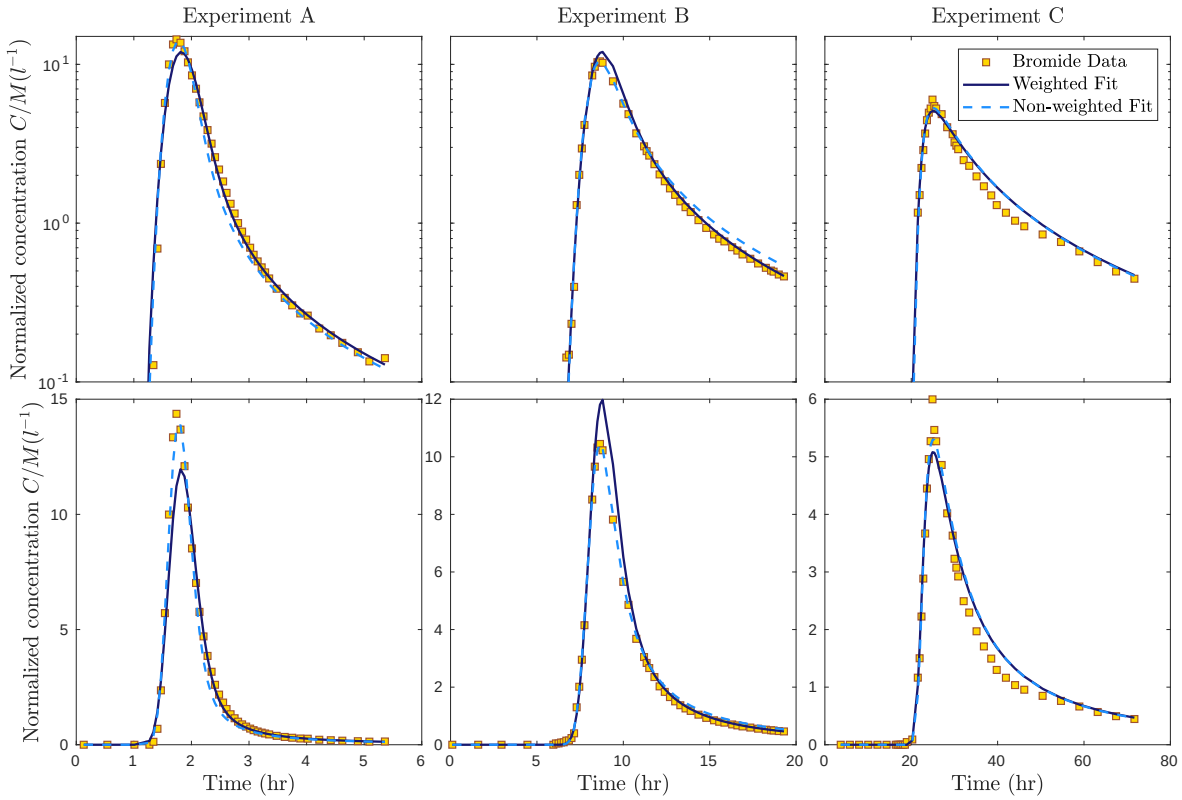


Figure 2: Non-weighted fit (dashed lines, shown also in Fig. 1) vs. weighted fit to the tailing of breakthrough curve (solid lines). Top row shows the fits in logarithmic scale while the bottom row shows them in linear scale. Only Bromide data as an example was used for weighted fitting.

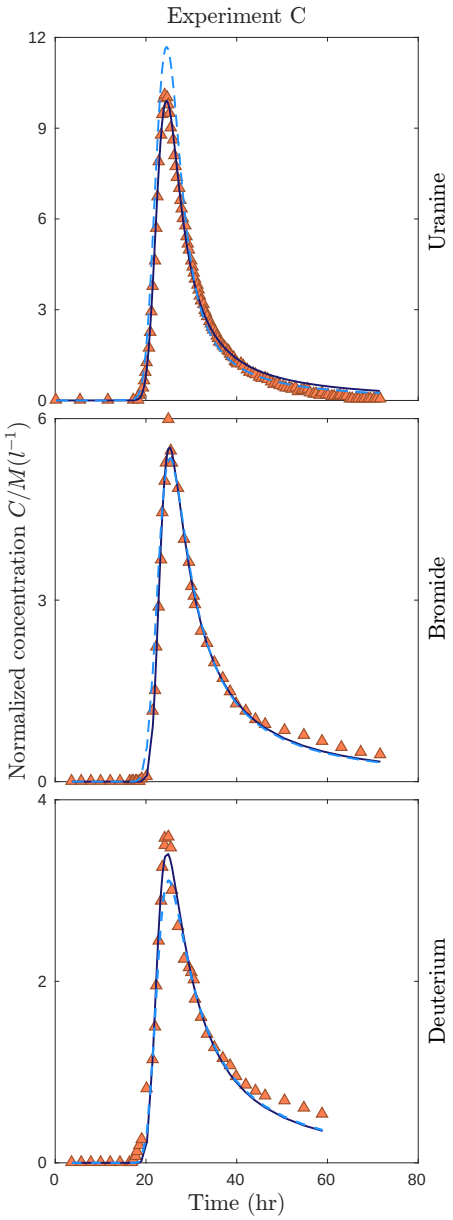


Figure 3: Four parameters fit using Eq. (4). Correction of the mass recovery rate by including another fitting parameter $M_{cor}$ resulted in a better fit and more reasonable parameter values for $a$ and $P_d$ in experiment C. Solid lines shows the fits from this study while the dashed lines illustrate the fits obtained by trial and error procedure in Knorr et al. (2016a). Table 2 lists the obtained parameter values for the fits.