Analysis of the parameter identifiability of the *in situ* diffusion and retention (DR) experiments

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Abstract. *In situ* diffusion experiments have been performed at underground research laboratories to overcome the limitations of laboratory diffusion experiments. The diffusion and retention (DR) experiments are long-term, natural-scale, *in situ* experiments performed in the anisotropic Opalinus Clay Formation at Mont Terri, Switzerland. Dilution data are monitored at the injection interval and overcoring data will be measured at samples around the injection interval at the end of the experiment during overcoring. Interpretation of DR experiments is complicated by the non-ideal effects caused by the sintered filter, the gap between the filter and the borehole wall and the excavation disturbed zone (EdZ). Their impact on parameter estimates has been evaluated with numerical sensitivity analyses and synthetic experiments having the same geometry and parameters as the real DR experiments. Dimensionless sensitivities of tracer concentrations in the injection interval and along the overcoring profiles have been computed numerically. They have been used to identify the tracer parameters that can be best estimated from tracer dilution and overcoring data. Sensitivities of tracer dilution data change with time and those of overcoring concentrations along the bedding are different than those along profiles normal to the bedding. Concentrations along overcoring profiles are sensitive to the effective diffusion coefficient normal to the bedding. Synthetic experiments generated with prescribed known parameters have been interpreted automatically with INVERSE-CORE^{2D} and used to evaluate the relevance of non-ideal effects and ascertain parameter identifiability in the presence of random errors for HTO and $^{22}Na^{+}$. Model results show that it is difficult to estimate the parameters of the undisturbed clay when tracer dilution data contain noise. The convergence of the estimation algorithm improves when the starting values are smaller than the true parameters. Although the parameters of the undisturbed clay and the EdZ cannot be estimated using tracer dilution data, their joint estimation from overcoring noisy data is possible for standard deviations up to 0.05. Large estimation errors in the parameters of the undisturbed clay and poor fits are obtained when the assumption about the existence of EdZ is incorrect. The effective diffusion coefficient of the filter is a key parameter for the interpretation of the experiments. Small errors in the volume of the circulation system do not affect the estimates of the component of the effective diffusion of undisturbed clay parallel to bedding. The proper interpretation of *in situ* DR experiments requires accounting for the filter and the EdZ. Overcoring data allow a more accurate estimation of the parameters of the undisturbed clay than the tracer dilution data.

Key words: diffusion, sorption, numerical model, dimensionless sensitivity, identifiability analysis, tritium, sodium, DR experiment, CORE

1. Introduction

In situ diffusion experiments have been performed at underground research laboratories (URL) in clay formations to overcome the limitations of laboratory diffusion experiments and to investigate possible scale effects. Such experiments have been performed in Opalinus Clay in Switzerland (Palut *et al*., 2003; Tevissen *et al*., 2004; Wersin *et al*., 2004; van Loon *et al*., 2004; Yllera *et al*., 2004; Samper *et al*., 2006a; Soler *et al*., 2008) and Callovo-Oxfordian clay, C-Ox, at Bure in France (Dewonck, 2007; Samper *et al*., 2008a).

The experimental program that is being carried out in the Mont Terri URL (Switzerland) aims at investigating the hydrogeological, geochemical and rock mechanical properties of the Opalinus Clay. The ongoing *in situ* diffusion and retention (DR) experiment is designed to study the transport and retention properties of the Opalinus Clay Formation. Opalinus Clay exhibits significant diffusion anisotropy due to stratification. The interpretation of *in situ* diffusion experiments is complicated by several non-ideal effects caused by the presence of the sintered filter, the gap between the filter and the borehole wall and the excavation disturbed zone, EdZ (Samper *et al.*, 2008a). Samper et al. (2008a) evaluated the relevance of such non-ideal effects and their impact on estimated clay parameters with numerical sensitivity analyses and synthetic experiments for DIR diffusion experiments at the Bure URL on C–Ox clay. They found that DIR experiments can be interpreted with a simple 1D axisymmetric model because tracer dilution curves are not sensitive to diffusion anisotropy. They computed numerical normalized sensitivities of tracer concentrations at the injection interval for several tracers using a time average sensitivity. They found tracer concentrations to be sensitive to all key parameters. Sensitivities were tracer dependent. They analyzed the identifiability of the parameters for HTO and ^{36}Cl from tracer dilution data. They found that data noise makes difficult the estimation of clay parameters. Parameters of clay and EdZ cannot be estimated simultaneously when the data contain noise. Models without an EdZ fail to reproduce synthetic data. The proper interpretation of *in situ* diffusion experiments requires accounting for filter, gap and EdZ. Estimates of the effective diffusion coefficient and of the porosity of clay are highly correlated, indicating that these parameters cannot be estimated simultaneously. Accurate estimation of D_e values and porosities of clay and EdZ is only possible when the standard deviation of random noise is less than 0.01. Small errors in volume of the circulation system do not affect clay parameter estimates.

Here we present a thorough full sensitivity analysis for the DR diffusion experiments performed on Opalinus clay which exhibits a diffusion anisotropy larger than that of C-Ox clay. Our analysis covers not only the sensitivities of tracer dilution data but also the sensitivities of tracer concentrations along overcoring profiles. We extend the analysis of Samper et al. (2008a) by performing the identifiability analysis for HTO and $^{22}Na^+$ by using tracer dilution and overcoring data. We also address the estimation of the two main components of the effective diffusion parallel and normal to the bedding.

The paper starts by describing the DR experiments. Then, numerical methods for their interpretation are presented. A systematic sensitivity analysis performed in terms of dimensionless sensitivities is also presented. Then, the identifiability analysis of HTO and $^{22}Na^{+}$ diffusion and sorption parameters from synthetic diffusion experiments is described. Finally, the main conclusions and their relevance for the interpretation of real DR experiments are presented.

2. DR experiments at Mont Terri

The idea for the DR experiment is similar to that of previous *in situ* diffusion experiments such as the DI-A (Wersin *et al*., 2004; van Loon *et al*., 2004) and DI-B (Yllera et al., 2004; Samper *et al*., 2006a; Soler et al., 2008) in the Opalinus clay and DIR experiments in Callovo-Oxfordian clay (Dewonck, 2007; Samper *et al*., 2008a). The concept, however, has been optimized to determine *in situ* the diffusion anisotropy. The length of the injection intervals is shorter than that of previous experiments. The experimental time is as long as that needed to achieve transport distances larger than the injection interval for conservative tracers, so that diffusion anisotropy can be determined.

The experiment is located in a borehole of the DR niche at the Mont Terri URL. The borehole was drilled at an angle of 45° with respect to the tunnel bottom so that it is normal to the bedding. Three test intervals were isolated by packers. The interval at the bottom serves as an auxiliary interval for the observation of the hydraulic pressure during the experiment. Tracer cocktails were injected into the upper two intervals. Each injection interval is connected to the surface equipment which includes a reservoir tank of 20 L. The fluid circulates continuously to ensure that the tank water and the downhole water are always well mixed.

The tracers added at the upper interval include: $^{60}Co^{+2}$, $^{137}Cs^{+}$, $^{133}Ba^{+2}$, $^{152}Eu^{+3}$, Eu^{+3} and HDO. In the lower interval the following tracers were injected: HTO, $^{22}Na^{+}$, $^{85}Sr^{+2}$, I^{-} (stable), Br^{-} (stable), $^{75}Se^{+6}$, Cs^{+} and ^{18}O. Tracer concentrations and activities in the water of the circulation system are monitored by taking water samples at regular intervals in sampling vials. In addition, γ-emitter tracers (all radioactive tracers but HTO) are monitored on line in both circuits with an online γ-counting technique which was successfully tested in the DI-A experiment. At the end of the experiment the rock around the injection intervals will be overcored and tracer distribution profiles will be measured. The time evolution of the tracer concentrations in the two injection systems denoted here as "tracer dilution data" and the tracer profiles in the rock after overcoring ("overcoring data") will be used to derive tracer diffusion and retention parameters.

3. Numerical interpretation

3.1. Solute transport equation

The transport equation for a tracer which diffuses through a low permeability medium is given by (Bear, 1972):

$$\nabla \cdot (\bar{D}_e \cdot \nabla c) = \alpha \frac{\partial c}{\partial t} \tag{1}$$

where c is the tracer concentration, t is time, α is the the capacity factor which is given by:

$$\alpha = \phi_{acc} + \rho K_d$$

(2)

ϕ_{acc} is the accessible porosity which is equal to the total porosity if the tracer is not affected by anion exclusion, K_d is the distribution coefficient, and ρ is the bulk density. $\bar{D}_e$ is the effective diffusion tensor which in a coordinate system defined along the bedding planes is given by

$$\bar{D}_e = \begin{pmatrix} D_{e//} & 0 & 0 \\ 0 & D_{e//} & 0 \\ 0 & 0 & D_{e\perp} \end{pmatrix} \qquad (3)$$

where $D_{e//}$ and $D_{e\perp}$ are the components of the effective diffusion tensor parallel and normal to the bedding, respectively.

3.2. Numerical models

Numerical interpretation of DR experiments requires the use of 3D models due to the diffusion anisotropy. However, symmetry with respect to the borehole axis allows the use of 2D axi-symmetric models. The left-hand-side boundary of the domain corresponds to the borehole axis. All outer boundaries of the model domain are no-flux boundaries. The following five material zones were considered in the DR model: the injection interval, the 3 mm thick Teflon filter, the 2 mm gap, the EdZ which has a thickness of 20 mm and the undisturbed Opalinus Clay.

Prior estimates of the effective diffusion coefficient, distribution coefficient and accessible porosity for undisturbed Opalinus Clay were derived from available laboratory experiments results or field experiments (Table 1). An anisotropy ratio of 4.0 was considered (van Loon *et al*., 2004). The effective diffusion coefficient and the capacity factor, *α,* of different tracers in porous teflon filters were measured by van Loon and Glaus (2008) using a through-diffusion method. They found that the effective diffusion coefficient in the filter is approximately equal to 10% of the diffusion coefficient in free water. Effective diffusion coefficients for other materials were derived from those of undisturbed clay by using Archie's law with an exponent equal to 4/3. The filter porosity is 0.3 (Fierz, 2006; Dewonck, 2007). On the other hand, porosities of EdZ and gap are unknown. As an educated guess, the porosity of the EdZ was assumed to be twice that of the undisturbed clay while the porosity of the gap was assumed to be 0.6. The undisturbed clay and the EdZ are assumed to have the same distribution coefficient. No sorption takes place in the filter and the gap.

The Gauss-Newton-Levenberg-Marquardt method has been used to minimize the objective function in using the inverse code INVERSE-CORE^{2D} (Dai and Samper, 2004). This code can estimate flow and transport parameters and provides statistical measures of goodness-of-fit as well as parameter uncertainties by computing the covariance and correlation matrices, the eigenvalues and approximate confidence intervals (García-Gutiérrez *et al.,* 2001; Dai and Samper, 2004; Dai and Samper, 2006; Dai *et al*., 2006; Samper *et al*., 2006b). Details of the application of INVERSE-CORE^{2D} to the estimation of parameters in diffusion experiments can be found in Samper *et al*. (2008a; 2008b).

4. Sensitivity analysis

4.1. Sensitivity runs

A model always entails simplifications of the real system. Model results depend on parameters that may contain uncertainties. Since parameter estimation errors are related to sensitivities of the computed concentrations to changes in the parameter, a detailed sensitivity analysis was performed to identify the key parameters. Sensitivities for a given tracer were computed for the dilution data at the injection interval and overcoring data in 2 profiles parallel to the bedding and 4 profiles normal to the bedding (Figure 1). Sensitivity runs were performed by changing one-at-a-time the following parameters within prescribed ranges: 1) The effective diffusion coefficients of the filter and the gap; 2) The main components of the effective diffusion parallel and perpendicular to the bedding, $D_{e//}$ and $D_{e\perp}$, for the EdZ and the undisturbed clay formation; 3) The accessible porosity of the gap, the EdZ and the undisturbed clay; 4) The distribution coefficient, 5) The thickness of the EdZ and 6) The volume of water in the circulation system.

4.2. Definition of relative sensitivities

Tracer concentrations, c, are normalized to their initial values, c_0. Relative concentrations, C, are defined as $C = c/c_0$.

Since model parameters have different units and vary over different ranges of values, their sensitivities cannot be compared directly. In order to compare sensitivities of concentrations to changes in different parameters, relative sensitivities, *RS*, have been computed according to:

$$RS = \frac{\Delta C}{\Delta P} \tag{4}$$

where ΔC is the average change in computed concentrations produced by the change in the parameters, and ΔP is the relative change in the parameters,

$$\Delta P(\%) = \frac{|P_S - P_b|}{P_b} \times 100 \tag{5}$$

where P_b is the value of the parameter in the base run and P_s is the value in the sensitivity run.

Relative sensitivities change with time in the injection interval and vary over space for the overcoring data. Average values of the relative sensitivity, $\overline{RS}$, have been computed from the average changes in concentrations $\overline{\Delta C}$ according to

$$\overline{RS} = \frac{\overline{\Delta C}}{\Delta P} \tag{6}$$

Average changes in computed concentrations at the injection interval, $\overline{\Delta C}_d$, are calculated from:

$$\overline{\Delta C}_d = \frac{1}{T}\int_0^T |C_b - C_s| dt \tag{7}$$

where T is the time period over which sensitivities are calculated, C_b and C_s are computed concentrations in the base and sensitivity runs, respectively and | | denotes the absolute value. This method to compute sensitivities is more systematic than that used by Samper et al. (2008a) for the sensitivities of the DIR experiments who simply computed the arithmetic average of sensitivities at arbitrary times.

Average changes in computed concentrations of overcoring data along profiles normal and parallel to the bedding, $\overline{\Delta C}_n$ and $\overline{\Delta C}_p$ are calculated according to:

$$\overline{\Delta C}_n = \frac{1}{V_n}\int_0^{V_n} \left|C_b - C_s\right| dV = \frac{1}{L}\int_0^{L} \left|C_b - C_s\right| dz \tag{8}$$

$$\overline{\Delta C}_p = \frac{1}{V_p}\int_0^{V_p} \left|C_b - C_s\right| dV = \frac{2}{(R_o^2 - R_i^2)}\int_{R_i}^{R_o} \left|C_b - C_s\right| r\, dr \tag{9}$$

For the profile normal to the bedding, z is the coordinate along the profile, L is the total length of the profile which is defined as the interval in which computed concentrations are above a threshold of 0.01% of the maximum concentration in such profile. For the profile parallel to the bedding, r is the coordinate along the profile, R_i and R_o are the inner and outer radii. The outer radius, R_o, is the radial distance at which the concentration is above a prescribed threshold of 0.01% the maximum concentration along such profile.

It should be noticed that the average relative sensitivities are dimensionless. Therefore, the relative sensitivities of different parameters can be compared directly for dilution and overcoring data.

4.3. Results

Relative sensitivities for dilution data at the injection interval after 3.6 years are listed in Table 2. Sensitivities for overcoring data along profile II are listed in Table 3 while those of overcoring data along profile III are listed in Table 4.

Changes in the thickness of the EdZ and the volume of the circulation system, V, affect significantly tracer concentrations both at the injection interval and in most of the studied overcoring profiles. Therefore, both parameters are key factors for tracer diffusion and sorption in the DR experiments.

Sensitivities to diffusion and sorption parameters are different for different tracers. Conservative tracers are more sensitive to $D_{e//}$ and Φ_{acc} of the undisturbed clay and the EdZ. Weakly-sorbing tracers, however, are more sensitive to the $D_{e//}$ of the filter and the EdZ, the K_d and the $D_{e//}$ of the undisturbed clay. Stongly-sorbing tracers are most sensitive to the D_e of the filter, the K_d and the $D_{e//}$ of the EdZ. Strongly-sorbing tracers lack sensitivities to changes in the parameters of the undisturbed clay.

Changes in the parameters of the gap do not affect tracer concentrations neither at the injection interval nor in overcoring profiles for all of the tracers. Therefore, uncertainties in the parameters of the gap do not affect significantly the interpretation of the DR experiment.

Relative sensitivities for Br^- and I^- of dilution data are generally smaller than those of other tracers, indicating that the parameters of Br^- and I^- are the most difficult to estimate from dilution data. Something similar happens for the relative sensitivities of strongly-sorbing tracers along overcoring profiles. Therefore, it can be concluded that it may be difficult to estimate the parameters of strongly-sorbing tracers from overcoring data.

Figure 2 shows that the concentrations of $^{22}Na^+$ at the injection interval are very sensitive to changes in the D_e of the filter. They are less sensitive to the $D_{e//}$ of the EdZ and the undisturbed clay for the early times while are opposite for the late times. The times at which curves are sensitive to changes in D_e are firstly for the filter, then for the EdZ and finally for the undisturbed clay. This conclusion is similar to the sensitivities found by Samper *et al*. (2008a) for the DIR experiments.

Sensitivities of the tracer concentrations to changes in parameters vary with time. Figure 3 shows the time evolution of the relative sensitivities for HTO. It can be seen that HTO concentrations are most sensitive to changes in the D_e of the filter, the $D_{e//}$ and the Φ_{acc} of the EdZ during the first 100 days. After 100 days, concentrations are most sensitive to changes in $D_{e//}$ of undisturbed clay and EdZ. $^{22}Na^+$ concentrations, however, are most sensitive to changes in the D_e of the filter and the D_{eh} of EdZ during the first 100 days. Between 100 to 400 days, sensitivities to changes in the K_d and the D_{eh} of undisturbed clay become relevant and concentrations are most sensitive to the D_{eh} of the undisturbed clay after 400 days (Figure 4). The time evolution of the relative sensitivities for strongly-sorbing tracers is shown in Figure 5. It can be seen that the concentrations of Cs^+ are most sensitive to changes in the D_e of the filter and the volume of the circulation system. Relative sensitivities to changes in the K_d and the D_{eh} of the EdZ increase before 700 days and then decrease slightly with time.

The sensitivities of overcoring data along profiles contain information which is complementary to that provided by dilution data at the injection interval. For instance, overcoring data are sensitive to changes in the $D_{e\perp}$ of the undisturbed clay for HTO and Br in all the profiles (Figure 6 and 7). The concentrations of the sorbing tracers along profiles I are slightly sensitive to changes in the $D_{e\perp}$ of the EdZ. However, tracer dilution data lack sensitivity to the $D_{e\perp}$ of the undisturbed clay.

Relative sensitivities along overcoring profiles are also tracer dependent and vary between different profiles (see Tables 3 and 4). The largest sensitivities are obtained along radial profiles (profiles I and II) and the vertical profiles located closer to the injection interval (profiles III and IV). Sensitivities for conservative tracers are larger than those of sorbing tracers because the latter penetrate less into the clay formation.

5. Identifiability analysis

5.1 Methodology

Synthetic experiments are often used to study parameter identifiability and parameter uncertainties. Synthetic diffusion experiments having the same geometric properties as real experiments have been simulated numerically for reference values of diffusion and sorption parameters. Synthetic concentration data have then been used to estimate parameters. Since true values are known, one can clearly identify which parameters can be estimated and how reliable these estimates really are.

The procedure for performing the identifiably study with synthetic data involves the following steps: 1) Generating synthetic data from a forward run of the numerical model; 2) Adding multiplicative random noise to synthetic data with increasing standard deviations, σ, ranging from 0 to 0.1, a range includes the values of σ of the measured data in DR experiments; 3) Estimating key diffusion parameters from noisy synthetic data in several stages, starting first with the estimation of $D_{e//}$, accessible porosity or the K_d of the undisturbed clay, followed by the estimation of the EdZ parameters and ending with the joint estimation of all parameters; 4) Evaluating the effect of the uncertainties in the existence and thickness of the EdZ, the volume of water in the injection system, V, and the D_e of the filter. There is no need to evaluate the uncertainties in the parameters of the gap because the sensitivity analysis indicates that gap parameters do not play a major role on the DR experiments.

Parameter identifiabily analyses have been performed with synthetic dilution and overcoring data. Nineteen synthetic dilution data are generated at the same times as the real experiments. Synthetic overcoring data are generated under two assumptions: 1) Ten data along profile II (one datum per cm) and 2) Fourty-two data along profiles I and II.

5.2 Results for HTO

Table 5 summarizes the results of the identifiability analysis for HTO. Estimation runs have been performed considering different initial starting values of the parameters and increasing values of σ.

When only clay $D_{e//}$ is estimated, estimated values are close to the true value ($5.0\cdot10^{-11}$ m^2/s) even for σ = 0.05. It can be seen that noise in the HTO data introduces biases in $D_{e//}$ estimates which for σ = 0.05 is 17.8% for the inverse run performed with dilution data and 6.4% for that performed with overcoring data in profile II.

On the other hand, poor estimates of $D_{e//}$ and Φ_{acc} of the undisturbed clay are obtained for noisy dilution data when they are estimated simultaneously because $D_{e//}$ and Φ_{acc} are highly correlated (ρ = -0.99). However, acceptable estimates of $D_{e//}$ and Φ_{acc} are obtained simultaneously from noisy overcoring data along profile II even for σ = 0.05. Since tracer concentrations along overcoring profiles are more sensitive to changes in Φ_{acc} than to dilution data, Φ_{acc} of HTO can be estimated with overcoring data better than with dilution data. Similar conclusions can be drawn when the $D_{e//}$ and $D_{e\perp}$ of the undisturbed clay are estimated simultaneously. These parameters cannot be estimated simultaneously with noisy dilution data. However, their estimation errors are small when they are estimated from noisy overcoring data along profile II even for σ = 0.05.

$D_{e//}$, $D_{e\perp}$ and Φ_{acc} of the undisturbed clay and the $D_{e//}$ of the EdZ can be estimated simultaneously from noisy overcoring data along profile II even for σ = 0.05. However, parameter estimates depend on the initial starting values. The joint estimation of these parameters from dilution data is only possible with noise-free data.

Several runs were performed by assuming no EdZ (see Table 6). No acceptable estimates were obtained in this case. Since the $D_{e//}$ of the EdZ is larger than that of the undisturbed clay, the estimated values of the $D_{e//}$ of the clay are larger than the reference values when the thickness of the EdZ is 0. Clearly, synthetic data cannot be fit with a model which disregards the EdZ for inverse runs with either dilution or overcoring data (Figure 8).

Uncertainties caused by possible errors in the volume of water in the injection system, V, have been evaluated by estimating clay diffusion parameter with a volume 10% smaller than the true value of V. The error in V does not have a large effect on the estimate of the $D_{e//}$

of the undisturbed clay but introduces a marked bias in the estimate of the clay porosity, especially in the inverse runs performed with dilution data (see Table 6). Clearly, the effect of the uncertainties in V on parameter estimates from dilution data is larger than from overcoring data.

If the D_e of the filter is taken to be twice its reference value, an optimum fit is achieved with a clay porosity slightly smaller than the true value and a $D_{e//}$ of the undisturbed clay slightly larger than the reference value when these parameters are estimated from dilution data. Acceptable estimates of the parameters of the undisturbed clay are obtained from overcoring data even for σ = 0.05. The best fit in this case is shown in Figure 8.

The number of synthetic data has a significant effect on the estimates of the parameters of the undisturbed clay. Such an effect has been evaluated by estimating the parameters of the undisturbed clay for the following 3 cases: 1) 10 data along profile II, 2) 10 data along profiles I and II, respectively and 3) 20 data along profiles I and II, respectively. Model results indicate that the estimation errors are smallest for case 3. Figure 9 shows the comparison of the estimation errors of clay porosity for the three cases. It can be seen that for σ = 0.1, the estimation errors of Φ_{acc} in cases 1 and case 2 are 12.3 and 5.1 times larger than that in case 3.

5.3 Results for $^{22}Na^+$

The identifiability analysis for $^{22}Na^+$ has been performed in a manner similar to that of HTO. Parameter estimation results are summarized in Table 7. The $D_{e//}$ and K_d of $^{22}Na^+$ in the undisturbed clay can be estimated properly even for σ = 0.1 when the rest parameters are perfectly known. Parameter estimation errors from overcoring synthetic data are smaller than those from dilution synthetic data (Figure 10). The estimates of the $D_{e//}$ and the K_d of the undisturbed clay from dilution data depend on the initial values. They can be estimated only for σ < 0.02 because they are strongly correlated (ρ = -0.95). The $D_{e//}$ and K_d of the undisturbed clay can be estimated from noisy overcoring data even for σ = 0.05. In this case their correlation coefficient is equal to 0.57.

The joint estimation of the $D_{e//}$, $D_{e}\perp$ and K_d of the undisturbed clay is only possible when dilution data are free of noise. However, they can be estimated simultaneously with from noisy overcoring data even for σ = 0.1. Data noise affects the estimate of the $D_{e}\perp$ more strongly than to the estimates of $D_{e//}$ and K_d of the undisturbed clay.

When the $D_{e//}$ of undisturbed clay, the $D_{e//}$ of the EdZ and the K_d are estimated simultaneously from dilution data, parameter estimates are poor and depend on the initial values. Acceptable estimates are obtained for σ ≤ 0.01 with initial values smaller than the true values even though the $D_{e//}$ of the undisturbed clay and the EdZ are highly correlated (ρ = -0.96). In the inverse runs performed with overcoring data, however, the $D_{e//}$ and the $D_{e}\perp$ of the undisturbed clay, the $D_{e//}$ of the EdZ and the K_d can be estimated simultaneously even for σ = 0.1. Therefore, the effect of data noise on parameter estimates is much stronger on dilution data than on overcoring data.

The parameters of the undisturbed clay ($D_{e//}$, $D_{e}\perp$ and K_d) cannot be estimated simultaneously when the EdZ is disregarded. Poor estimates are obtained (see Table 8). The fit to the data is poor. Figure 12 shows the fit to overcoring data in this case. Therefore, the uncertainty in the existence of the EdZ has a large effect on the estimates of the parameters of the undisturbed clay.

A decrease of 10% in V leads to estimation errors for σ = 0. The best fit in this case is shown in Figure 11 for the dilution data. Uncertainties in V affect the estimate of K_d more strongly than the estimates of the $D_{e//}$ and the $D_{e}\perp$ of the undisturbed clay. Parameter estimates obtained from overcoring data contain less error than those obtained from dilution data. Estimation errors from overcoring data are 13.4% for K_d, 10.4% for $D_{e//}$ of the clay and 4.0% for the $D_{e}\perp$ of the clay.

Identifiability runs performed using a D_e of the filter twice its true value indicate that parameter estimates deviate from their true values in the inverse runs performed with dilution data even though the fit to synthetic data is good. Acceptable estimates and good fits to data (see Figure 12). are obtained in the inverse runs performed with overcoring data (see Table 8). Therefore, it can be concluded that uncertainties in the D_e of the filter affect strongly the estimates of the parameters of the undisturbed clay when they are derived from dilution data. Such effect is negligible when overcoring data are used.

6. Conclusions and relevance for real diffusion experiments

The interpretation of the DR diffusion and retention experiments performed at the Mont Terri on Opalinus clay is complicated by several non-ideal effects caused by the sintered filter, the gap between the filter and the borehole wall and the EdZ. The relevance of such non-ideal effects and their impact on estimated clay parameters have been evaluated with numerical sensitivity analyses and synthetic experiments.

Dimensionless sensitivities of tracer concentrations at the injection interval and 6 profiles in the rock have been computed numerically. Computed concentrations are tracer dependent, vary with time and are different among different profiles. Contrary to the dilution data, concentrations along overcoring profiles are sensitive to the effective diffusion coefficient normal to the bedding. Sensitivities have been used to identify parameters that can be estimated with less uncertainty.

Synthetic experiments generated with known parameters have been interpreted automatically with INVERSE-CORE^{2D} and then used to evaluate the relevance of non-ideal effects and to ascertain parameter identifiability for HTO and $^{22}Na^{+}$ in the presence of random measurement errors. Identifiability analysis of synthetic experiments reveals that data noise makes the estimation of undisturbed clay parameters difficult. The joint estimation of undisturbed clay and EdZ parameters with dilution data is only possible when $\sigma < 0.01$. However, excellent parameter estimates are obtained simultaneously with the inverse runs performed with overcoring data. The diffusion anisotropy can be estimated from overcoring data but cannot be estimated from dilution data. A model which neglects the EdZ fails to reproduce the synthetic data. The proper interpretation of the *in situ* DR experiments requires accounting for filter and EdZ. Small errors in the volume of the circulation system do not affect significantly the estimates of the clay parameters. Parameter estimates derived from overcoring data contain less errors than those obtained from dilution data.

Dimensionless sensitivities for tracer dilution and overcoring data and the conclusions of the identifiability analysis will be most useful for the calibration and interpretation of the real DR experiments.

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7. References

Bear, J., 1972. Dynamics of fluids in porous media. Elsevier, New York.

Dai, Z., Samper, J., 2004. Inverse problem of multicomponent reactive chemical transport in porous media: Formulation and Applications. Water Resour. Res. 40, W07407, doi:10.1029/2004WR003248.

Dai Z., Samper, J., 2006. Inverse modeling of water flow and multicomponent reactive transport in coastal aquifer systems. J. Hydrol. 327(3-4), 447-461.

Dai Z., Samper, J., Ritzi, R., 2006. Identifying geochemical processes by inverse modeling of multicomponent reactive transport in Aquia aquifer. Geosphere, Vol. 4, Nº 4, 210–219.

Dewonck, S. 2007. Expérimentation DIR. Synthese des résultats obtenus au 01/03/07. Laboratoire de recherche souterrain de Meuse/Haute-Marne. ANDRA report D.RP.ALS.07-0044.

Fierz, T., Solexperts A.G. (2006). Diffusion and retention Experiment Field activities phase 11: Instrumentation and tracer injection. Mont Terri Project TN 06-18.

García-Gutiérrez, M., T. Missana, M. Mingarro, J. Samper, Z. Dai & J. Molinero, 2001 Solute transport properties of compacted Ca-bentonite used in FEBEX project, J Cont Hydrol. Vol. 47, nº 2-4, 127-137.

Palut, J.M., Montarnal, P., Gautschi, A., Tevissen, E., Mouche, E., 2003. Characterisation of HTO diffusion properties by an *in situ* tracer experiment in Opalinus clay at Mont Terri. J. Cont Hydrol. 61(1), 203-218.

Samper, J., C. Yang, A. Naves, A Yllera, A. Hernández, J. Molinero, J. M. Soler, P. Hernán, J.C. Mayor and J. Astudillo, 2006a, A fully 3-D anisotropic model of DI-B *in situ* diffusion experiment in the Opalinus clay formation, Phy. and Chem. Earth, 31, 531-540.

Samper, J., Dai, Z., Molinero, J., García-Gutiérrez, M., Missana, T., Mingarro, M., 2006b. Interpretation of solute transport experiments in compacted Ca-bentonites using inverse modelling. Physics and Chemistry of the Earth 31, 640-648.

Samper, J., Dewonck, S., Zheng, L., Yang, Q., Naves, A. (2008a). Normalized sensitivities and parameter identifiability of *in situ* diffusion experiments on Callovo-Oxfordian clay at Bure site. Physics and Chemistry of the Earth, 33, 1000-1008.

Samper, J., Q. Yang, S. Yi, M. García-Gutiérrez, T. Missana, M. Mingarro, Ú. Alonso, J.L. Cormenzana, 2008b, Numerical modelling of large-scale solid-source diffusion experiment in Callovo-Oxfordian clay, Physics and Chemistry of the Earth, Vol. 33. Supplement 1, S208-S215.

Soler J.M, J. Samper, A. Yllera, A. Hernández, A. Quejido, M. Fernández, C. Yang, A. Naves, P. Hernán, and P. Wersin, 2008, The DI-B in-situ diffusion experiment at mont terri: results and modelling, Physics and Chemistry of the Earth, Vol. 33. Supplement 1, 2008, S196-S207.

Tevissen E., Soler, J. M., Montarnal P., Gautschi A. and van Loon L.R., 2004, Comparison between *in situ* and laboratory diffusion studies of HTO and halides in Opalinus clay from the Mont Terri, Radiochim. Acta 92, 781-786.

van Loon, L.R., Wersin , P., Soler J.M., Eikenberg, J., Gimmi, Th., Hernán, P., Dewonck, S., and Savoye, S., 2004 *In-situ* diffusion of HTO, $^{22}Na^{+}$, Cs^{+} and I^{-} in Opalinus clay at the Mont Terri underground rock laboratory, Radiochim. Acta, 92, 757-763.

van Loon, L.R., Glauss, M.A., 2008. Effective diffusion coefficient of several tracers in Teflon filters. PSI Technical note, Switzerland.

Wersin, P., van Loon, L. R., Soler, J., Yllera, A., Eikenberg, J., Gimmi, T., Hernan, P., Boisson, J.-Y, 2004. Long-term Diffusion Experiment at Mont Terri: First Results from Field and Laboratory Data. Appl. Clay Sci. 26, 123-135.

Yllera, A., Hernández, A., Mingarro, M., Quejido, A., Sedano, L.A., Soler, J.M., Samper, J., Molinero, J., Barcala, J.M., Martín, P.L., Fernández, M., Wersin, P., Rivas, P., Hernán, P., 2004. DI-B experiment: planning, design and performance of an *in situ* diffusion experiment in the Opalinus clay formation. Appl. Clay Sci. 26, 181-196.

Table 1. Reference values of diffusion and sorption parameters in different materials for all the tracers. De// is the effective diffusion parallel to the bedding. The component normal to the bedding is 4 times smaller than De//. Φacc is the accessible porosity and Kd is the distribution coefficient.

		HTO, HDO	Br^-, I^-	$^{22}Na^+$	$^{133}Ba^{2+}$, $^{85}Sr^{2+}$	$^{137}Cs^+$, Cs^+, $^{60}Co^{2+}$
Filter	D_e (10^{-11}m^2/s)	6.27	2.00	8.79	8.79	14
	Φ_{acc}			0.30		
Gap	D_e (10^{-11}m^2/s)	31.7	10.1	44.5	44.5	190
	Φ_{acc}			0.60		
EDZ	$D_{e//}$ (10^{-11}m^2/s)	12.6	9.3	17.6	17.6	75.6
	Φ_{acc}			0.30		
	Thickness (cm)			3.0		
	K_d (10^{-4} m^3/kg)	0	0	2.048	13	5500
Undisturbed clay	$D_{e//}$ (10^{-11}m^2/s)	5.0	1.6	7.0	7.0	30
	Φ_{acc}	0.15	0.08	0.15	0.15	0.15
	K_d (10^{-4}m^3/kg)	0	0	2.048	13	5500

Table 2. Average relative sensitivities, $\overline{RS}$, (defined in Eq. 6) of dilution data at the injection interval at 3.6 years to changes in the parameters. $D_{e//}$ and $D_{e}\perp$ are the effective diffusion components parallel and normal to the bedding and Φ_{acc} is the accessible porosity.

		HTO	HDO	Br^-/I^-	$^{22}Na^+$	$^{133}Ba^{2+}$	$^{85}Sr^{2+}$	Cs^+
Clay $D_{e//}$	$\Delta D_e < 0$	***0.0644***	***0.0635***	***0.0235***	***0.0782***	***0.0667***	***0.0596***	<0.0001
	$\Delta D_e > 0$	***0.0422***	***0.0417***	***0.0160***	***0.0465***	***0.0367***	***0.0323***	<0.0001
Clay $D_e\perp$	$\Delta D_e < 0$	0.0070	0.0069	0.0022	0.0050	0.0017	0.0015	<0.0001
	$\Delta D_e > 0$	0.0053	0.0053	0.0017	0.0041	0.0015	0.0013	<0.0001
Clay Φ_{acc}	$\Delta\Phi a < 0$	***0.0140***	***0.0138***	0.0097	0.0048	0.0011	0.0010	<0.0001
	$\Delta\Phi a > 0$	0.0056	0.0056	0.0036	0.0023	0.0005	0.0005	<0.0001
EdZ $D_{e//}$	$\Delta D_e < 0$	***0.0296***	***0.0292***	***0.0152***	***0.0473***	***0.0818***	***0.0743***	***0.0417***
	$\Delta D_e > 0$	0.0092	0.0090	0.0050	***0.0146***	***0.0266***	***0.0240***	***0.0153***
EdZ $D_e\perp$	$\Delta D_e < 0$	***0.0101***	0.0099	0.0044	***0.0118***	0.0105	0.0092	0.0002
	$\Delta D_e > 0$	0.0077	0.0075	0.0033	0.0088	0.0077	0.0067	0.0002
EdZ Φ_{acc}	$\Delta\Phi a < 0$	0.0096	0.0095	***0.0109***	0.0065	0.0039	0.0035	<0.0001
	$\Delta\Phi a > 0$	0.0093	0.0092	***0.0104***	0.0063	0.0038	0.0035	<0.0001
EdZ thickness	Δthick= -1cm	***0.0227***	***0.0224***	***0.0105***	***0.0341***	***0.0515***	***0.0465***	***0.0134***
	Δthick = 1cm	0.0092	0.0091	0.0040	***0.0136***	0.0180	0.0161	<0.0001
Gap D_e	$\Delta D_e < 0$	0.0028	0.0013	0.0016	0.0044	0.0079	0.0072	0.0099
	$\Delta D_e > 0$	0.0008	0.0008	0.0004	0.0013	0.0023	0.0021	0.0014
Gap Φ_{acc}	$\Delta\Phi a < 0$	0.0010	0.0010	0.0012	0.0007	0.0005	0.0005	<0.0001
	$\Delta\Phi a > 0$	0.0005	0.0005	0.0006	0.0004	0.0002	0.0002	<0.0001
Filter D_e	$\Delta D_e < 0$	0.0063	0.0070	0.0020	***0.0325***	***0.0567***	***0.0772***	***0.2069***
	$\Delta D_e > 0$	0.0019	0.0019	0.0005	0.0096	***0.0168***	***0.0242***	***0.0554***
Volume of circulation system	ΔV = -10%	***0.0133***	***0.0131***	0.0064	***0.0186***	***0.0234***	***0.0228***	***0.1642***
K_d	$\Delta K_d < 0$	--	--	--	***0.0354***	***0.0802***	***0.0728***	***0.0652***
	$\Delta K_d > 0$	--	--	--	***0.0253***	***0.0489***	***0.0437***	***0.0144***

Table 3. Average relative sensitivities, $\overline{RS}$, (defined in Eq. 6) of overcoring data along profile II after 3.6 years to changes in the parameters. $D_{e//}$ and $D_{e}\perp$ are the effective diffusion components parallel and normal to the bedding and Φ_{acc} is the accessible porosity.

		HDO	$^{133}Ba^{2+}$	HTO	$^{22}Na^{+}$	$^{85}Sr^{2+}$	Br^{-} / I^{-}	Cs^{+}/Co^{2+}
Clay $D_{e//}$	$\Delta D_e < 0$	***0.1052***	***0.1130***	***0.1056***	***0.1024***	***0.1097***	***0.1017***	0.0004
	$\Delta D_e > 0$	***0.0485***	***0.0388***	***0.0487***	***0.0388***	***0.0374***	***0.0427***	0.0008
Clay $D_e\perp$	$\Delta D_e < 0$	***0.0291***	0.0028	***0.0297***	***0.0198***	0.0022	***0.0179***	<0.0001
	$\Delta D_e > 0$	***0.0157***	0.0036	***0.0159***	***0.0146***	0.0032	***0.0110***	<0.0001
Clay Φ_{acc}	$\Delta\Phi a < 0$	***0.0833***	0.0037	***0.0832***	***0.0139***	0.0037	***0.1129***	<0.0001
	$\Delta\Phi a > 0$	***0.0497***	0.0036	***0.0496***	***0.0168***	0.0036	***0.0558***	<0.0001
EdZ $D_{e//}$	$\Delta D_e < 0$	***0.0176***	***0.0313***	***0.0176***	***0.0251***	***0.0301***	***0.0329***	0.0068
	$\Delta D_e > 0$	0.0056	0.0087	0.0056	0.0069	0.0084	0.0061	0.0073
EdZ $D_e\perp$`	$\Delta D_e < 0$	0.0021	0.0036	0.0017	0.0026	0.0032	0.0011	<0.0001
	$\Delta D_e > 0$	0.0013	0.0029	0.0013	0.0023	0.0027	0.0007	<0.0001
EdZ Φ_{acc}	$\Delta\Phi a < 0$	0.0021	0.0011	0.0022	0.0017	0.0011	0.0026	<0.0001
	$\Delta\Phi a > 0$	0.0021	0.0011	0.0055	0.0010	0.0032	0.0076	<0.0001
EdZ thickness	Δthick= -1cm	***0.0132***	***0.0219***	***0.0131***	***0.0143***	***0.0211***	***0.0125***	0.0066
	Δthick = 1cm	***0.0112***	***0.0206***	***0.0111***	***0.0141***	***0.0198***	***0.0115***	0.0011
Gap D_e	$\Delta D_e < 0$	0.0014	0.0014	0.0012	0.0014	0.0013	0.0014	<0.0001
	$\Delta D_e > 0$	0.0004	0.0003	0.0004	0.0003	0.0003	0.0004	<0.0001
Gap Φ_{acc}	$\Delta\Phi a < 0$	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	<0.0001
	$\Delta\Phi a > 0$	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	<0.0001
Filter D_e	$\Delta D_e < 0$	0.0037	***0.0132***	0.0030	***0.0114***	***0.0195***	0.0017	0.0020
	$\Delta D_e > 0$	0.0009	0.0031	0.0009	0.0033	0.0051	0.0005	0.0014
Volume of circulation system	ΔV = -10%	***0.0211***	***0.0598***	***0.0215***	***0.0436***	***0.0560***	0.0078	***0.0147***
K_d	$\Delta K_d < 0$	--	***0.0796***	--	***0.0355***	***0.0598***	--	***0.0252***
	$\Delta K_d > 0$	--	***0.0491***	--	***0.0405***	***0.0481***	--	0.0086

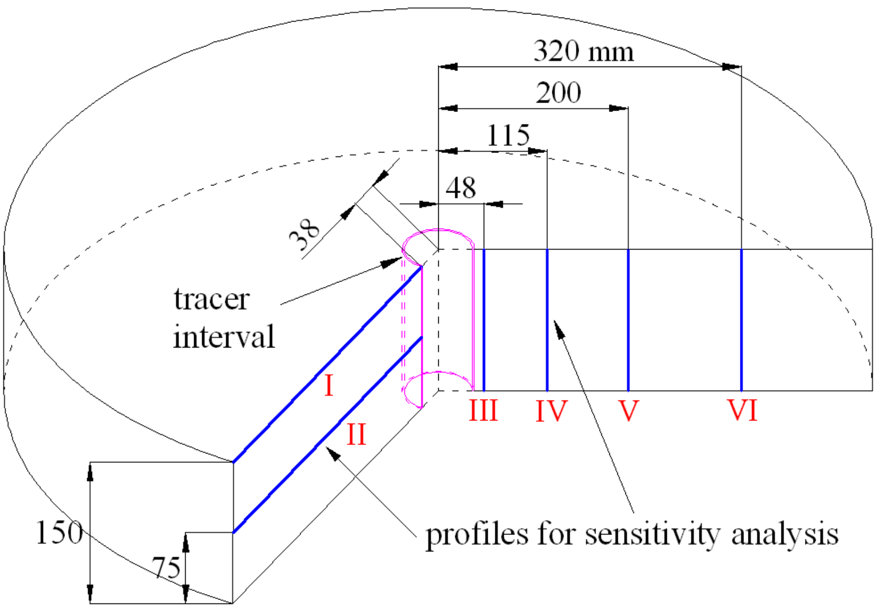

Figure 1. Location of the six types of profiles along which the sensitivities of overcoring data are calculated.

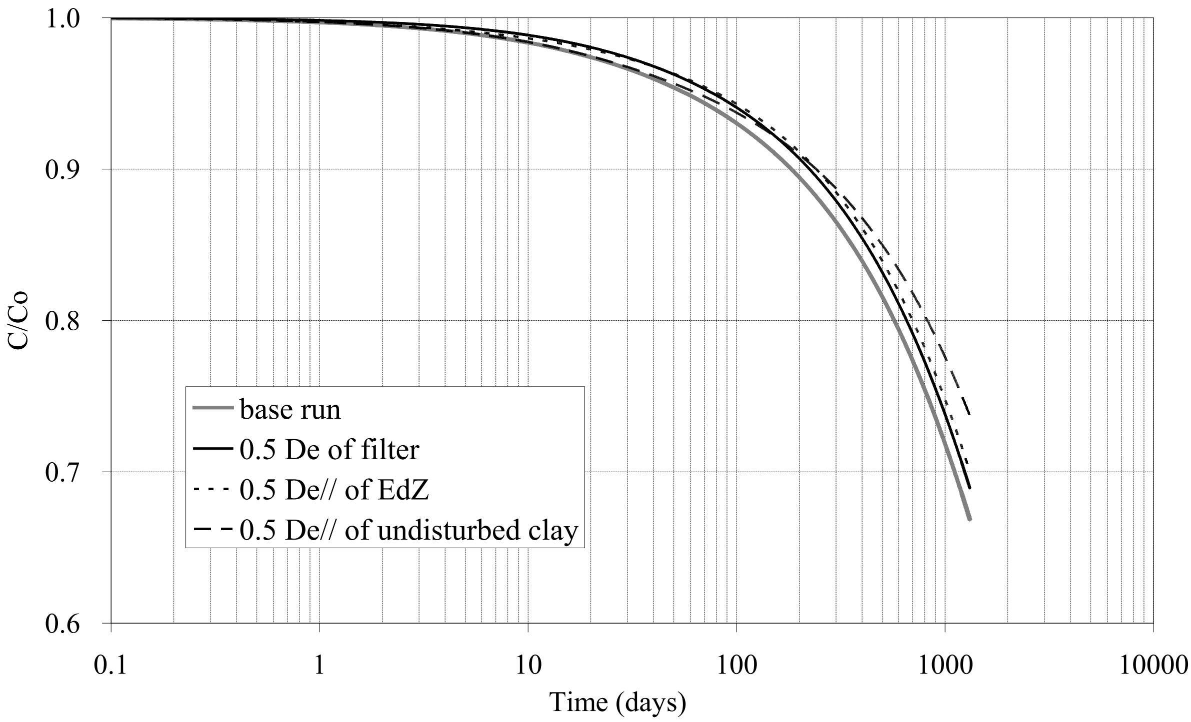

Figure 2. Sensitivity of the concentrations of $^{22}Na^{+}$ at the injection interval to changes in the D_e of the filter, the $D_{e//}$ of the EdZ and the undisturbed clay. The times at which tracer concentrations start to be sensitive are different for each parameter.

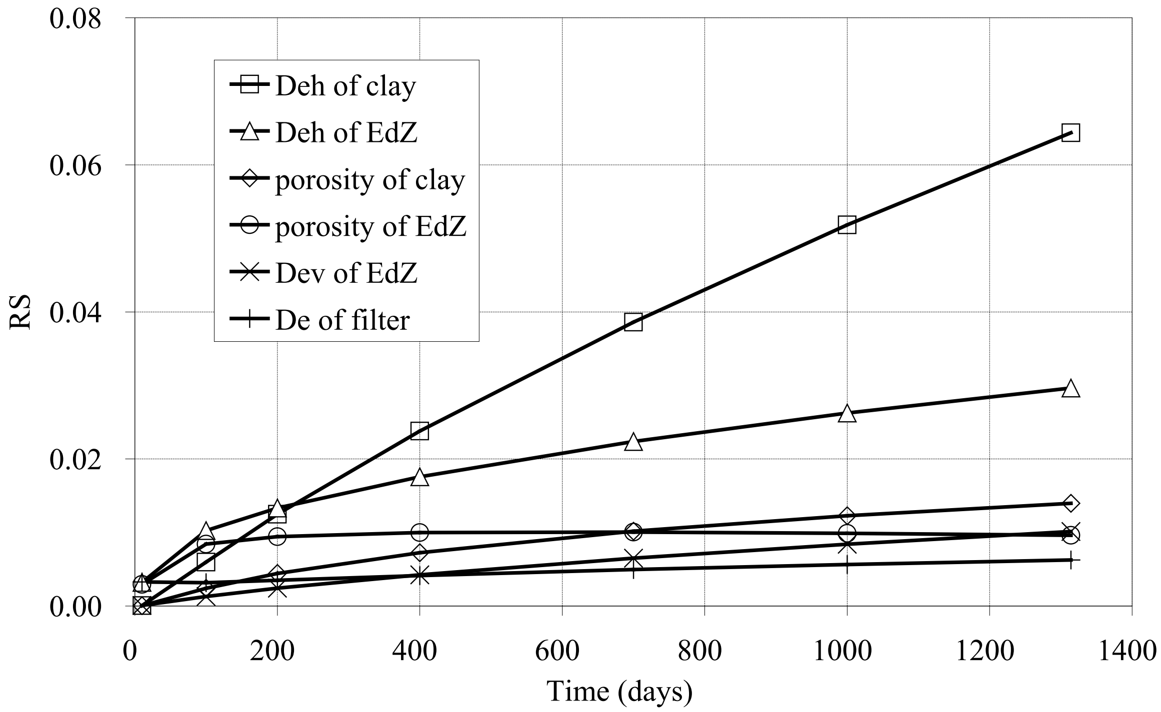

Figure 3. Time evolution of the computed relative sensitivities at the injection interval for HTO. Curves are shown only for the most sensitive parameters.

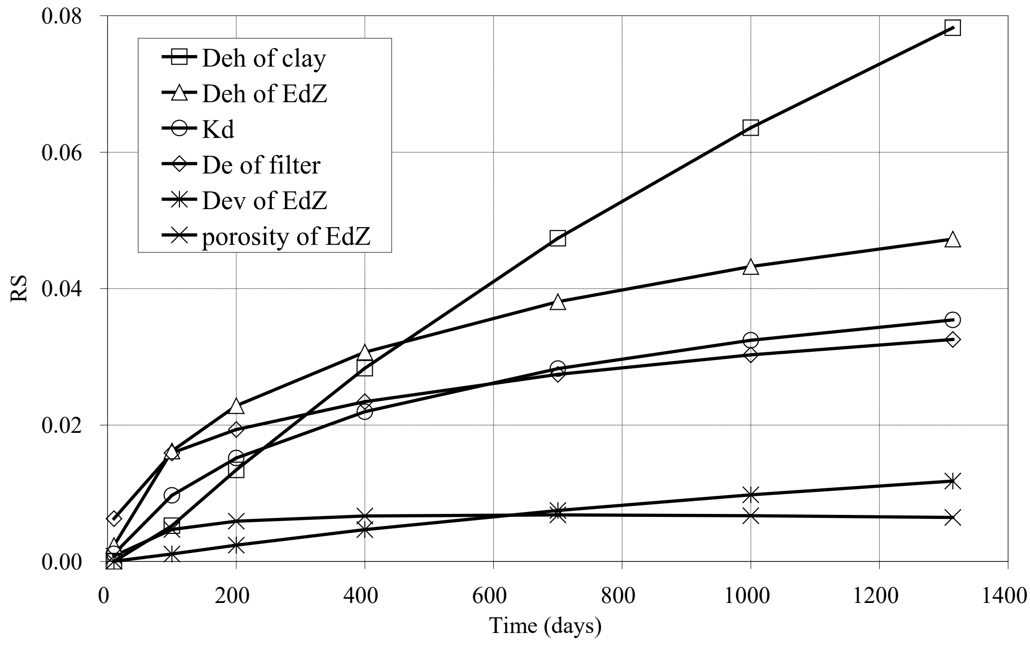

Figure 4. Time evolution of the computed relative sensitivities at the injection interval for $^{22}Na^{+}$. Curves are shown only for the most sensitive parameters.

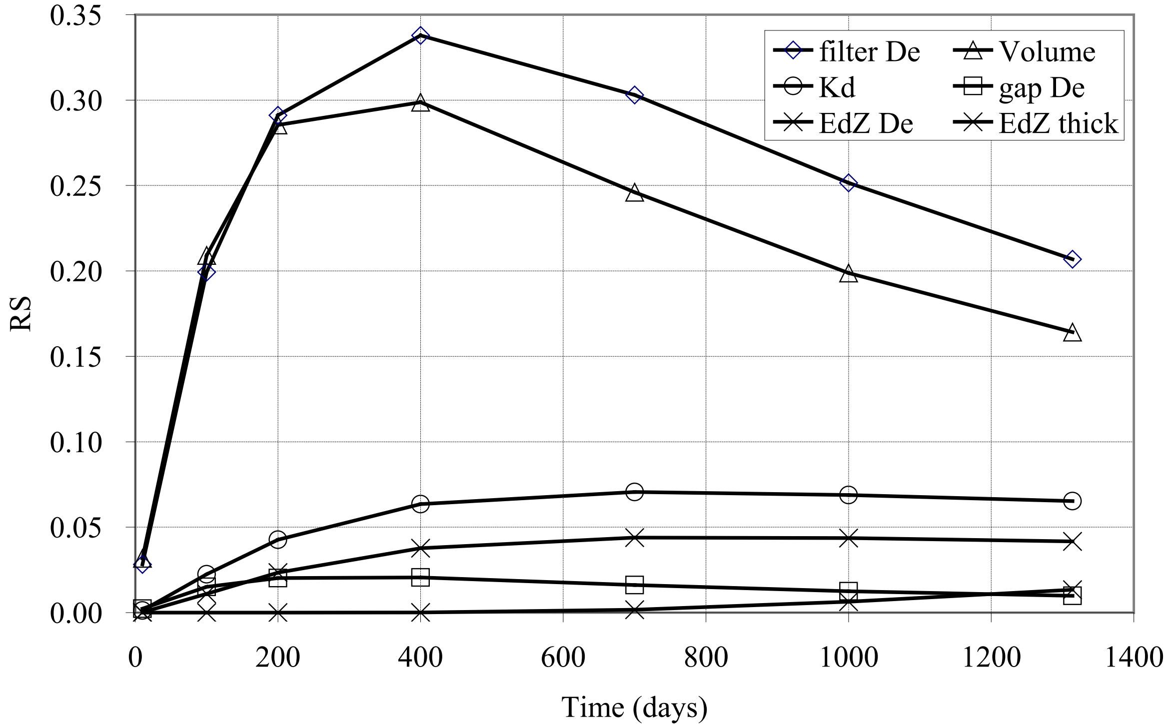

Figure 5. Time evolution of the computed relative sensitivities at the injection interval for Cs^{+}. Curves are shown only for the most sensitive parameters.

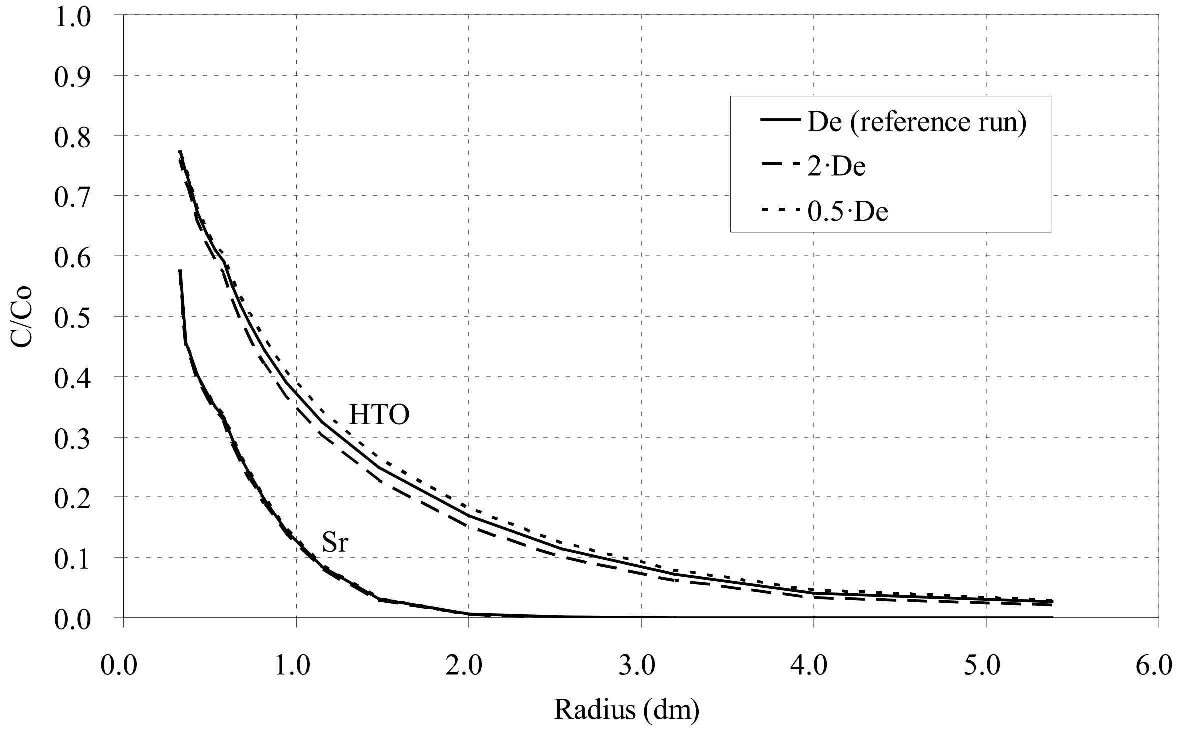

Figure 6. Sensitivity of the concentrations along profile I to changes in the $D_e\perp$ of the undisturbed clay.

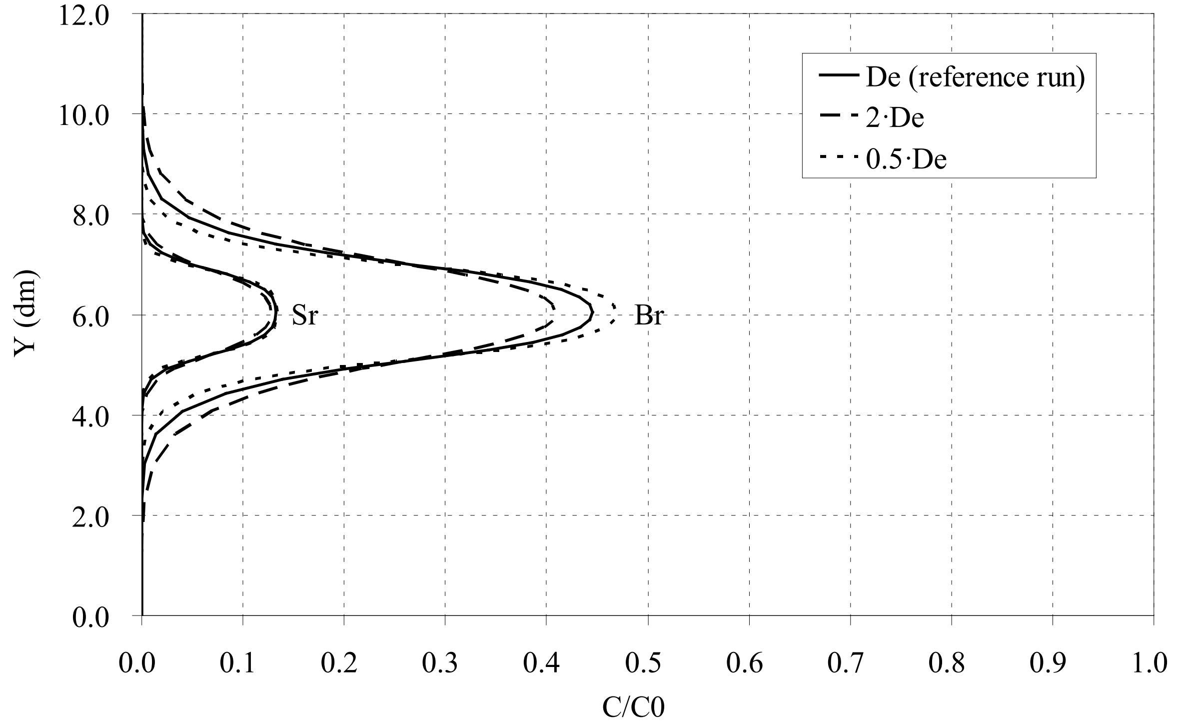

Figure 7. Sensitivity of the concentrations along profile IV to changes in the $D_e\perp$ of the undisturbed clay.

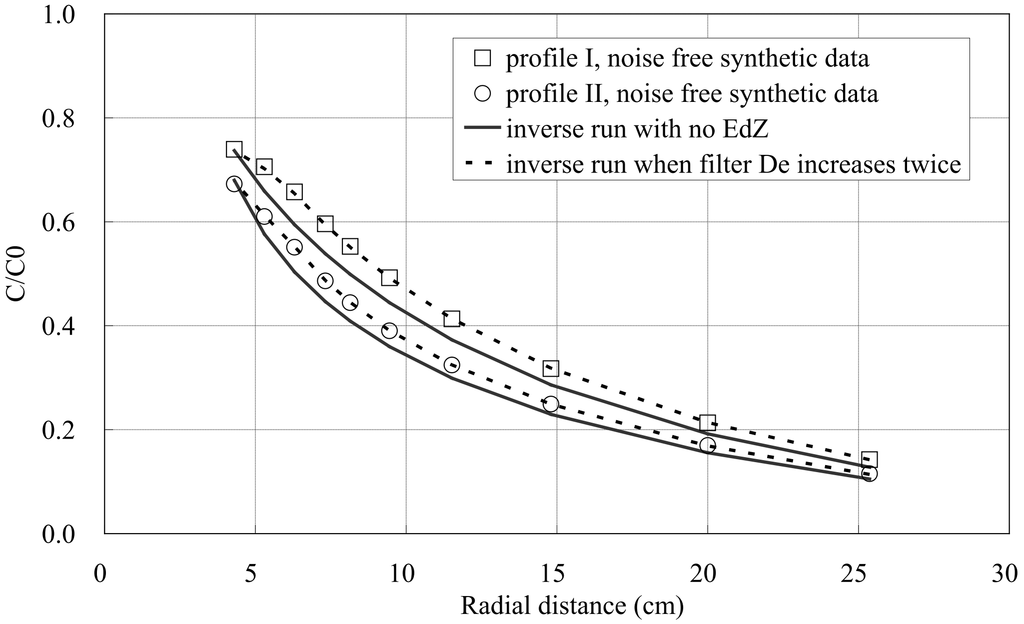

Figure 8. Best fits to HTO noise-free synthetic overcoring data for the inverse runs: 1) with a D_e of the filter twice its true value and 2) No EdZ.

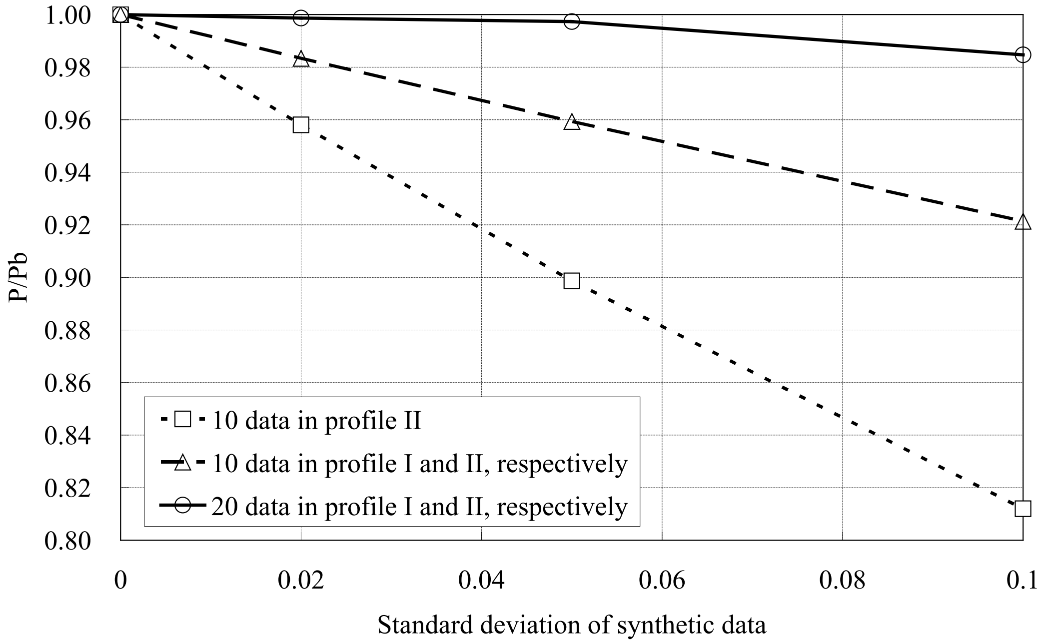

Figure 9. Estimation errors of Φ_{acc} for HTO versus the standard deviation of the synthetic data when the $D_{e//}$ and Φ_{acc} of the undisturbed clay are estimated simultaneously. P is estimated value of the parameter and P_b is the true value of the parameter.

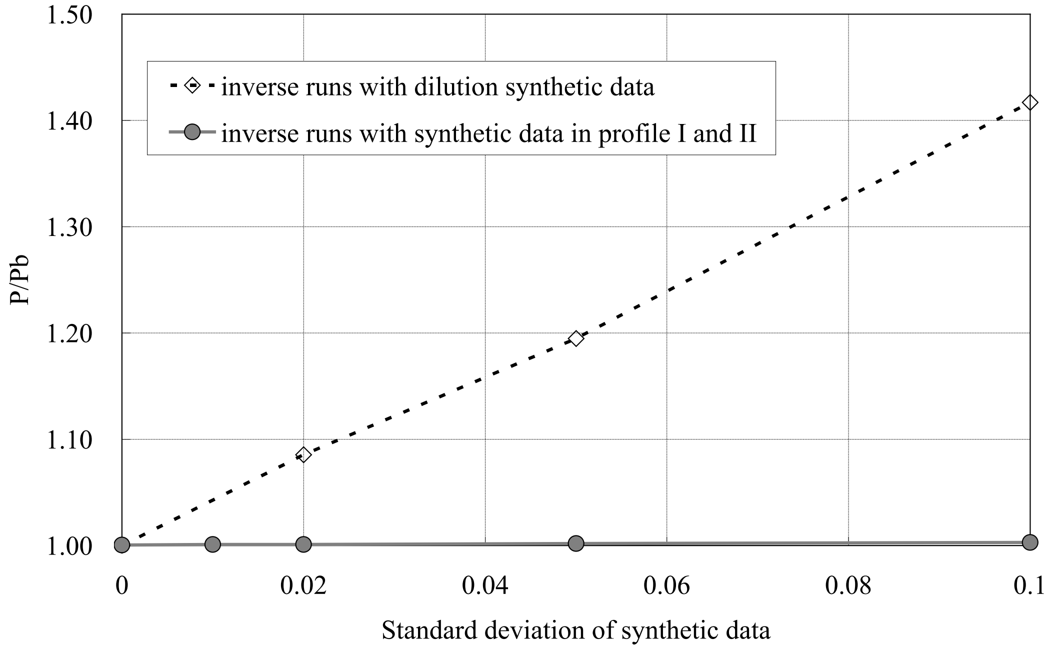

Figure 10. Estimation errors of K_d for $^{22}Na^+$ versus the standard deviation of the synthetic data when only K_d is estimated. P is estimated value of the parameter and P_b is the true value of the parameter. Estimation errors of K_d are much smaller from overcoring data than from dilution data.

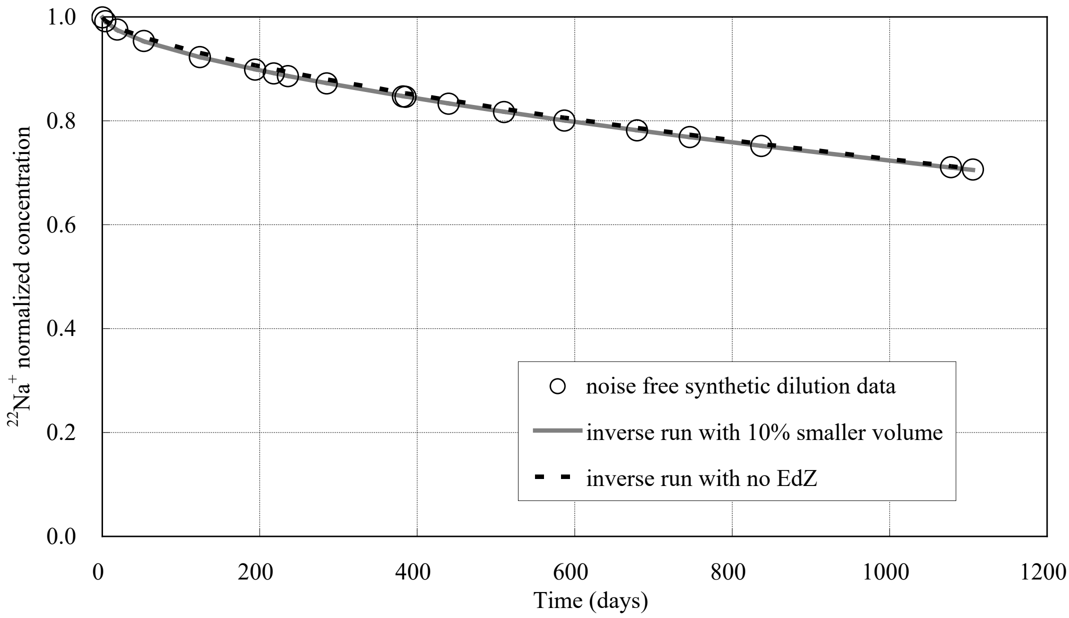

Figure 11. Best fits to $^{22}Na^+$ noise-free synthetic dilution data for the inverse runs: 1) With D_e of the filter twice its true values; and 2) 10% smaller volume of water in the circulation system.

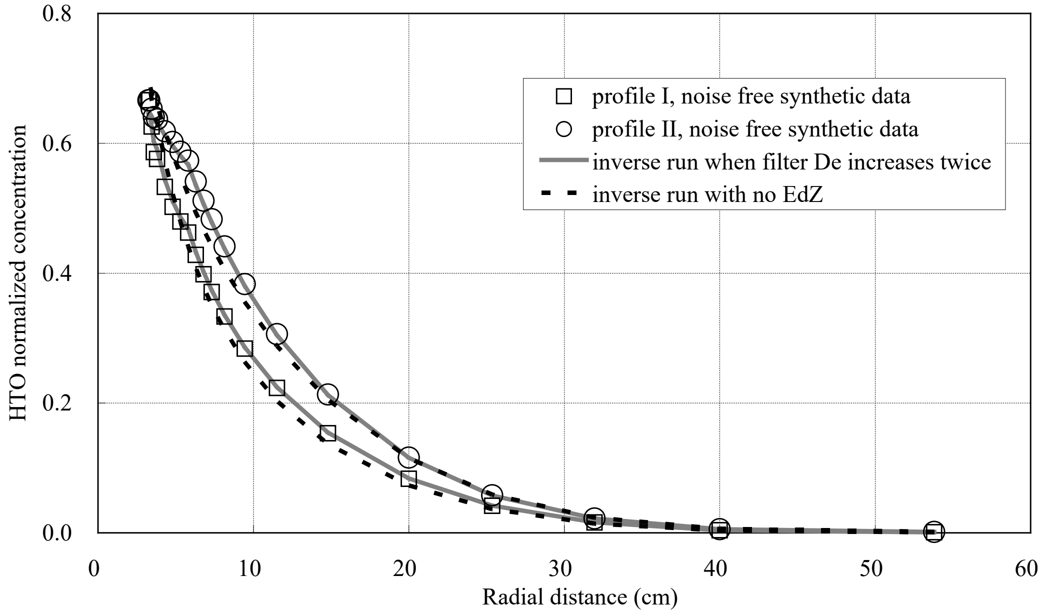

Figure 12. Best fits to $^{22}Na^{+}$ noise-free synthetic overcoring data for the inverse runs: 1) With D_e of the filter twice its true values; and 2) no EdZ.