Normalized sensitivities and parameter identifiability of *in situ* diffusion experiments on Callovo-Oxfordian clay at Bure site

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Abstract

DIR (Diffusion of Inert and Reactive tracers) is an experimental program performed by ANDRA at Bure underground research laboratory in Meuse/Haute Marne (France) to characterize diffusion and retention of radionuclides in Callovo-Oxfordian (C-Ox) argillite. *In situ* diffusion experiments were performed in vertical boreholes to determine diffusion and retention parameters of selected radionuclides. C-Ox clay exhibits a mild diffusion anisotropy due to stratification. Interpretation of *in situ* diffusion experiments is complicated by several non-ideal effects caused by the presence of a sintered filter, a gap between the filter and borehole wall and an excavation disturbed zone (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 having similar parameters and geometric characteristics as real DIR experiments. Normalized dimensionless sensitivities of tracer concentrations at the test interval have been computed numerically. Tracer concentrations are found to be sensitive to all key parameters. Sensitivities are tracer dependent and vary with time. Sensitivities are useful to identify which are the parameters that can be estimated with less uncertainty and find the times at which tracer concentrations begin to be sensitive to each parameter. 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 measurement errors. Identifiability analysis of synthetic experiments reveals that data noise makes difficult the estimation of clay parameters. Parameters of clay and EdZ cannot be estimated simultaneously from noisy data. Models without an EdZ fail to reproduce synthetic data. Proper interpretation of *in situ* diffusion experiments requires accounting for filter, gap and EdZ. Estimates of effective diffusion coefficient and porosity of clay are highly correlated, indicating that these parameters cannot be estimated simultaneously. Accurate estimation of D_e and porosities of clay and EdZ is only possible when the standard deviation of random noise is less than 0.01. Small errors in the volume of the circulation system do not affect clay parameter estimates. Interpretation of real DIR *in situ* diffusion experiments greatly benefit from results of the identifiability analysis of synthetic experiments and from normalized sensitivities which have provided insight on inverse estimation of *in situ* diffusion experiments.

Key words: diffusion, retention, numerical model, sensitivity analysis, identifiability analysis, tritium, chloride, CORE

1. Introduction

In situ diffusion experiments have been performed at underground research laboratories in clay formations to overcome the limitations of laboratory diffusion experiments and investigate possible scale effects. These experiments include those performed at Mont Terri 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.*, 2006) and Bure in France (Radwan *et al.*, 2005; Dewonck, 2007; Descostes *et al.*, 2007).

ANDRA has undertaken an extensive characterization program at the Bure site to assess the feasibility of a deep high level radioactive waste (HLW) repository in the Callovo-Oxfordien clay. DIR (Diffusion of Inert and Reactive tracers) is one of such experimental programs which aims at characterizing diffusion and retention of radionuclides in the clay rock. Various *in situ* diffusion experiments were performed in vertical boreholes to determine diffusion and retention parameters of selected radionuclides (Dewonck, 2007; Radwan *et al.*, 2005; Descostes *et al.*, 2007). C-Ox clay exhibits a mild diffusion anisotropy due to stratification. Interpretation of *in situ* diffusion experiments is complicated by several non-ideal effects caused by the presence of a sintered filter, a gap between the filter and borehole wall and an excavation disturbed zone (EdZ) (see Figure 1).

In this paper we evaluate the relevance of such non-ideal effects and their impact on estimated clay parameters by numerical sensitivity analyses and synthetic experiments having similar parameters and geometric characteristics as real DIR *in situ* diffusion experiments. The paper starts by describing DIR *in situ* diffusion experiments. Then, numerical methods for their interpretation are presented. After that we present a systematic sensitivity analysis performed in terms of normalized sensitivities. Then, identifiability analysis of tritium and chloride diffusion parameters based on synthetic diffusion experiments is explained. Finally, main conclusions and their relevance for interpretation of real DIR *in situ* diffusion experiments are described.

2. DIR *in situ* diffusion experiments at Bure site

Several vertical boreholes were drilled in which *in situ* diffusion experiments were performed to determine radionuclide diffusion and retention parameters of radioactive tracers. DIR2001 and DIR2002 experiments were carried out in boreholes drilled from a gallery located at 445 m depth in the Meuse/Haute-Marne underground laboratory. *In situ* diffusion experiments were performed as single point dilution tests by injecting tracers into a 1 m long packed-off section into the boreholes. The required equipment included downhole and surface instrumentation (Palut, 2001). Downhole instrumentation consisted of a pneumatic packer system with a porous screen made of sintered stainless steel mounted just below the packer at the bottom of the borehole. Surface instrumentation included a close stainless steel circuit with a valves system intended to circulate the water containing the tracers and allow for injection and sampling of tracers. Tracer activities at injection section were monitored from 15th March of 2005 to 30th January of 2006. Tritium (HTO), chloride ($^{36}Cl^{-}$) and iode ($^{125}I^{-}$) were employed as tracers in DIR 2001, while tritium (HTO), sodium ($^{22}Na^{+}$) and cesium ($^{134}Cs^{+}$) were used in DIR 2002. Chloride and iodide are subject to anion exclusion while sodium and cesium undergo sorption. The design of EST208 experiment differs from that of DIR 2001 and 2002 experiments because EST208 was performed in a deep borehole drilled from ground surface to a depth of -542.5 m. Downhole instrumentation consists of a 10 m long packed diffusion interval with a steel porous filter and two hydraulic lines for flux recirculation. The test equipment includes two circulation systems. One allows circulation from diffusion chamber to ground surface and the other ensures flow along surface equipment and allows monitoring geochemical parameters and extraction of water samples during the experiment. The following tracers were injected in this borehole: tritium (HTO), chloride ($^{36}Cl^{-}$) and cesium ($^{134}Cs^{+}$).

Diffusion in Bure clay exhibits a mild anisotropy due to stratification. Effective diffusion coefficients along horizontal planes are from 1.5 to 2 times larger than vertical effective diffusion coefficient (Dewonck, 2007).

3. Numerical interpretation of DIR *in situ* diffusion experiments

Attempts were made to interpret diffusion experiments using the analytical solution of Cooper *et al*. (1967) based on the analogy between *in situ* diffusion experiments and pulse tests (Samper *et al.,* 2007). It was not possible to obtain clay parameters because measured tracer data are affected by a number of factors which are not taken into account by the analytical solution such as the presence of a sintered filter, a gap between the casing and the borehole wall and the excavation disturbed zone (Samper *et al.*, 2007). Given the limitations of analytical methods, *in situ* diffusion experiments were interpreted using inverse numerical models.

3.1. Solute transport equation

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

$$\phi_a R \frac{\partial C}{\partial t} = \nabla \cdot (\bar{D}_e \cdot \nabla C) \tag{1}$$

where C is tracer concentration, t is time, ϕ_a is accessible porosity which accounts for anion exclusion and R is retardation coefficient defined as

$$R = 1 + \frac{\rho K_d}{\phi_a} \tag{2}$$

R is equal to 1 and ϕ_a is equal to total porosity if the tracer is not affected by anion exclusion or by adsorption. $\bar{D}_e$ is the effective diffusion tensor given by

$$\bar{D}_e = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \tag{3}$$

which can be diagonalized as

$$\bar{D}_e' = \begin{pmatrix} D_{\xi\xi} & 0 & 0 \\ 0 & D_{\eta\eta} & 0 \\ 0 & 0 & D_{\varsigma\varsigma} \end{pmatrix} \tag{4}$$

where $D_{\xi\xi}$, $D_{\eta\eta}$ and $D_{\zeta\zeta}$ are principal components of the tensor. Components of the effective diffusion tensor in (3) can be calculated from main components in (4) using equations similar to those of the permeability tensor. Here $D_{\xi\xi}$ and $D_{\eta\eta}$ are horizontal diffusion coefficients parallel to bedding while $D_{\zeta\zeta}$ is vertical the diffusion coefficient.

2.2. Inverse problem of solute transport and sorption

The essence of the inverse problem lies on deriving optimum parameter estimates from known concentration data. Optimum parameters are those which minimize an objective function measuring the difference between measured and computed concentrations. Our formulation of the inverse problem is based on generalized least squares criterion (Sun, 1994; Dai and Samper, 2004). Let $\boldsymbol{p} = (p_1, p_2, p_3, \ldots, p_M)$ be the vector of M unknown parameters. The objective function, $E(\boldsymbol{p})$, can be expressed as:

$$E(p) = \sum_{i=1}^{NE} W_i E_i(p) \tag{5}$$

where $i = 1, \ldots, N_E$ denotes different types of data, $i = 1$ for water head; $i = 2$ for dissolved concentrations; $i = 3$ for total concentration; $i = 4$ for water fluxes; $i = 5$ for water contents in unsaturated media; i = 6 for temperature; and $i = 7$ for prior information on model parameters. W_i is the weighting coefficient of the i^th^ generalized least-squares criterion, E_i(p), which is defined as

$$E_i(p) = \sum_{l=1}^{L_i} w_{li}{}^2 r_{li}{}^2(p) \tag{6}$$

$$r_{li} = u^i{}_l(p) - F^i{}_l \tag{7}$$

Where $u^i{}_l(p)$ is the computed value of the i^{th} variable at the observation point; $F^i{}_l$ are measured values; L_i is the number of observations, either in space or in time for the i^{th} type data; and r_{li} is the residual or difference weighting coefficient for l^{th} measurement of the i^{th} type of data. Its value depends on the accuracy of observations. If some data are judged to be unreliable, they should be assigned very small weights w_{li} in order to prevent their pernicious effect on the optimization process. Weights for different types of data W_i in (5) are updated automatically during the iterative optimization process as indicated by Dai and Samper (2004). The Gauss-Newton-Levenberg-Marquardt method has been used to minimize the objective function in (5) using the inverse code INVERSE-CORE^{2D} (Dai and Samper, 1999; 2004). This code can estimate flow and transport parameters and provides statistical measures of goodness-of-fit as well as parameter uncertainty by computing the covariance and correlation matrices, eigenvalues and approximate confidence intervals (Dai and Samper, 2004).

2.3. Numerical models

Numerical interpretation of DIR experiments requires the use of 3D models due to diffusion anisotropy. However, symmetry with respect to borehole axis allows the use of 2D axi-symmetric models. The relevance of diffusion anisotropy on tracer evolution at the test interval depends on the ratio between borehole length and tracer penetration. Anisotropy is especially relevant when the length of the testing interval is not larger than tracer penetration. Since tracer penetration is clearly much smaller than tracer diffusion interval for the EST208 experiment, this experiment can be safely interpreted with an 1D axisymmetric model. Relevance of anisotropy for DIR 2001 and DIR 2002 experiments was unknown *a priori* and had to be ascertained with a 2D axisymmetric anisotropic numerical model. Thus, 2D finite element models were performed. They account for four material zones: 1) borehole with tracer circulation system, 2) excavation disturbed zone (EdZ), 3) undisturbed clay, and 4) steel plate at the bottom of the borehole. Tracer diffusion parameters for undisturbed clay and EdZ were derived from available data from laboratory experiments (Radwan *et al.*, 2005; Dewonck, 2007; Descostes *et al.*, 2007). Results of experiment simulations show that penetration of all tracers is much smaller than the length of tracer interval. Therefore, a simple 1D axisymmetric model without anisotropy was used to simulate DIR *in situ* diffusion experiments. Concentrations at the testing interval computed with 1D and 2D models are completely similar and are not sensitive to the anisotropy of effective diffusion coefficient.

1D axisymmetric models were used to interpret DIR *in situ* diffusion experiments. A 1-D radial domain of unit thickness was used which was discretized with 1D grid of finite elements.

The injection section is composed of an empty central steel cylinder and a 3 mm thick steel filter between which the fluid containing the tracer cocktail circulates. There is a gap of 3 mm between filter and borehole wall. This gap is initially filled with artificial water injected during the hydraulic equilibration period. Later, water in contact with argillite forms possibly a viscous mud. Both this gap and the filter and were taken into account in the model. Therefore five material zones were considered: injection zone, filter, gap, a 2 cm thick EdZ and undisturbed C-Ox clay.

Models of *in situ* diffusion experiments usually consider borehole, geological formation and, sometimes, an EdZ. They rarely take into account filter and gap. Previous studies indicate that tracer dilution curves of in situ DIR experiments cannot be reproduced unless an EdZ is considered (Radwan *et al*., 2005; Descostes *et al*., 2007; Samper *et al*., 2007). The effect of a sintered filter and a gap has been analyzed here by comparing concentrations computed with a detailed model which accounts for filter and gap with those computed with a simplified model which has only three material zones: borehole, EdZ and undisturbed clay. Although patterns of time evolution of tracer concentration in tracer interval, EdZ and undisturbed clay are similar for both models, there are some differences which are small for HTO and noticeable for tracers that are subject to anion exclusion or sorption (see Figure 2). The simplified model overestimates chloride and iodide concentrations in the tracer interval. However, for cesium, tracer concentrations in the tracer intervals are underestimated during the first 4 days and then are overestimated (see Figure 2). In summary, failing to account for the filter and gap may result in significant errors in tracer concentrations.

Values of effective diffusion coefficient, accessible porosity and distribution coefficient of each tracer in Callovo-Oxfordian Clay were derived from available through-diffusion laboratory experiments (see Table 1). An anisotropy ratio of 1.56 was considered. Distribution coefficient, K_d, for $^{22}Na^+$ in C-Ox clay is assumed to be equal to 0.74 ml/g (Radwan *et al.*, 2005). For $^{134}Cs^+$ a K_d of 50 ml/g was used. Effective diffusion coefficients for other materials were derived from those of undisturbed clay by adopting an Archie's law with an exponent equal to 4/3. Filter porosity is 0.3 (Dewonck, 2007). On the other hand, porosities of EdZ and gap are unknown. As an educated guess, porosity of EdZ was assumed equal to twice that of clay while porosity of the gap was assumed equal to 0.6. Undisturbed clay and EdZ were assumed to have the same distribution coefficient.

4. Sensitivity analysis

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 concentrations to changes in parameters, a detailed sensitivity analysis was performed to evaluate parameter uncertainties. For each tracer, its dilution curve was computed first for a set of tracer reference parameters. With these reference parameters, sensitivity runs were performed by changing relevant parameters one-at-a-time within prescribed ranges. Such sensitivities were evaluated for all tracers and the following parameters: 1) Effective diffusion coefficient of the filter, 2) Porosity of the gap, 3) Effective diffusion coefficient and accessible porosity of the EdZ, 4) Effective diffusion coefficient and accessible porosity of undisturbed clay, 5) Distribution coefficient, 6) Thickness of EdZ and 7) Volume of the injection system.

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 used. Such sensitivities are defined as the ratio between relative changes in concentrations and relative changes in parameters, ΔP, which are defined as parameter changes with respect to reference values, P_b:

$$\Delta P(\%) = \frac{|P_S - P_b|}{P_b} \times 100 \tag{8}$$

where | | denotes absolute value and P_s is the parameter value chosen for sensitivity analysis. Relative sensitivity is computed as the ratio between relative change in concentration and relative change in parameter:

$$\Delta C(\%) = \frac{|C_S - C_b|}{C_b} \times 100 \tag{9}$$

where C_b and C_s are computed concentrations for base and sensitivity runs, respectively.

$$RS = \frac{\Delta C}{\Delta P} \tag{10}$$

Calculated *RS* for each tracer are listed in Table 2. It should be noticed that relative sensitivities are dimensionless and therefore relative sensitivities corresponding to different parameters can be compared directly.

Largest relative sensitivities correspond to a decrease in the volume of the circulation system. Such sensitivities range from 0.45 for HTO to 1.09 for $^{134}Cs^+$ in DIR2002 experiment. Therefore, the volume of the circulation system is a key parameter affecting tracer dilution in the testing interval.

Variations in EdZ thickness affect significantly all tracers. It should be noticed that the tracer concentrations are more sensitive to a decrease (from 2 to 0 cm) than to an increase (from 2 to 4 cm) of EdZ thickness. This is especially true for sorbing tracers.

Sensitivities to diffusion and sorption parameters are different for different tracers. HTO is more sensitive to EdZ porosity and D_e of clay and EdZ. Iodide, however, is more sensitive to EdZ parameters. The influence of EdZ parameters is largest for chloride concentrations which are also sensitive to gap porosity.

Relative sensitivities for $^{36}Cl^-$ and $^{125}I^-$ are similar. They are generally smaller than those of other tracers. Therefore, it can concluded that $^{36}Cl^-$ and $^{125}I^-$ parameters are the most difficult to estimate.

Relative sensitivities of $^{22}Na^+$ attain values which are between those of HTO and $^{134}Cs^+$. Sodium is the most sensitive to changes in K_d and D_e of EdZ. This tracer is also sensitive to D_e of clay and filter.

Cesium concentrations are mostly sensitive to changes in D_e of filter, K_d and parameters of EdZ. On the other hand, sodium and cesium lack sensitivity to clay parameters.

Relative sensitivities of a given tracer such as $^{134}Cs^+$ are similar in all experiments in which such tracer is used (see Table 2).

Sensitivities of tracer concentrations to changes in parameters vary with time. Changes in D_e of undisturbed clay affect tracer dilution curves after some time (Figure 3). Early time concentrations are not affected by changes in D_e. Times at which curves are sensitive to changes in D_e depend on the tracer. For instance, HTO data begins to be sensitive to D_e after 20 days while those of sodium are sensitive after 45 days. I concentrations start to be sensitive to D_e after more than 100 days. These times at which tracer concentrations start to be sensitive to D_e are inversely proportional to tracer penetration depths. Such depth is largest for HTO and smallest for Cs. Sorption of Cs is so strong that its concentration in the tracer interval is not sensitive to changes in D_e by a factor of 0.5 and 2 (Figure 3).

Sensitivities of tracer dilution curves to changes in clay accessible porosity are qualitatively similar to those of clay D_e (not shown here). Both early and late time tracer data lack sensitivity to clay porosity. Only tracer data at intermediate times are sensitive to porosity.

The sensitivity of tracer dilution curves to changes in D_e of EdZ also depends on time (Figure 4). Times at which curves are sensitive to changes in D_e of EdZ are smaller than those corresponding to D_e of clay (compare Figures 3 and 4). Concentrations are sensitive to changes in D_e of EdZ after 3 days for HTO and Na and after 20 days for I. These times coincide approximately with the times needed for tracers to diffuse through filter and gap.

All dilution curves are sensitive to changes in D_e of gap and filter. Changes in any of these parameters affect sorbing tracers more strongly than to conservative tracers. Dilution curves are sensitive to such changes from the beginning of the experiment (Figure 5).

Sensitivities of Na and Cs concentrations to changes in K_d by factors of 0.5 and 2 are remarkable (Figure 6). Tracer concentrations at the injection zone begin to be sensitive after approx 1 day. The largest sensitivity is achieved from 20 to 100 days for Na and from 3 to 20 days for Cs. For a reliable estimation of K_d, tracer sampling frequency should be intensified during time periods at which tracer concentrations are most sensitive to K_d.

5. Identifiability analysis

Methodology

Synthetic data have been generated in order to provide insight on inverse estimation of diffusion and sorption experiments and to study parameter identifiably. 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 been then used to estimate parameters. Since true values are known, one can clearly identify which parameter can be estimated and how reliable are parameter estimates by comparing estimated values with true values. The difference between the estimation of real and synthetic experiments is that in real experiments true parameters are unknown while in synthetic experiments they are known.

Synthetic experiments are often used to study parameter identifiability and parameter uncertainties (Carrera *et al.*, 1989). 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 ranging from 0 to 0.05, a value similar to that of noise of actual data from DIR experiments (Samper *et al.,* 2007); 3) Estimating key diffusion parameters from noisy synthetic data in several stages, starting first with estimation of with D_e and accessible porosity, Φ_{acc}, of clay, following with estimation of EdZ parameters and ending with estimation of all four parameters simultaneously; 4) Evaluating uncertainties caused by uncertainties in EdZ existence and thickness, the values of volume of water in the injection system, effective diffusion coefficient of filter and porosity of the gap.

HTO

Table 3 summarizes results of identifiability analysis for HTO. Estimation runs have been performed considering different initial starting values of parameters and standard deviations of synthetic data.

When only the diffusion coefficient of clay is estimated, estimated values are close to the true value ($4.05 \cdot 10^{-11}$ m^2/s) even for a standard deviation of noise of 0.1. It can be seen that noise in HTO data introduces bias in D_e estimates which for a standard deviation of 5% is smaller than 5% and for a standard deviation of 10% is about 10%.

On the other hand, poor estimates of D_e and Φ_{acc} are obtained for noisy data when they are estimated simultaneously. Since clay D_e and Φ_{acc} are highly correlated ($\rho = -0.99$), they cannot be estimated simultaneously when data have noise.

When D_e and Φ_{acc} of EdZ are estimated, it is found that they are strongly correlated (-0.91) and therefore cannot be estimated properly when data have noise.

Joint estimation of effective diffusion coefficients of clay and EdZ as well as porosities of clay and EdZ is only possible when data have no noise. Parameter estimates are strongly correlated. Their correlation coefficients are close to either +1 or -1. Estimates are close to true values when the standard deviation of noise is 0 or 0.01. However, when the standard deviation of noise is 0.05 parameter estimates depend on initial values.

It is well known that prior information on parameters can greatly improve the estimation process (Dai and Samper, 2004). The role of prior information on parameter estimation of DIR experiments has been evaluated with a set on runs in which D_e and Φ_{acc} in clay were estimated. Prior information for each parameter was set equal to its true value. Different weights were tested for prior information. For large weights of prior information, estimates are close to prior information, and consequently, a small value of objective function is obtained. It should be noticed, however, that objective function attains nearly a constant value for weights larger than 1.5 (Figure 7).

Poor estimates are obtained when all four parameters are estimated simultaneously when data have noise even if parameter prior information is available.

A set of runs has been performed assuming no EdZ (see Table 4). Since D_e and Φ_{acc} of EdZ are larger than those of undisturbed clay, estimated values of D_e and Φ_{acc} are larger than reference values when the thickness of EdZ is 0. Acceptable estimates are obtained when D_e and Φ_{acc} are estimated separately by starting with large initial values. However, the inverse algorithm stops at local minima with parameter estimates which differ from true values when initial values are smaller than reference values. Clearly, synthetic data cannot be fit with a model without EdZ.

Uncertainties caused by possible errors in volume of water in the injection system have been evaluated by estimating clay diffusion parameter for volumes from 5 to 10% smaller than true value. Errors of 5 to 10% in the volume of water of the system do not have a large effect on clay D_e, but introduce a marked bias in clay porosity (see Table 4).

An increase in porosity of gap from 0.6 (reference value) to 1 causes a small, but noticeable deviation from synthetic data (Figure 9). In order to compensate for the change in gap porosity, diffusion coefficients and porosities of clay and EdZ have to change. The optimun fit is achieved with porosities slightly larger than reference values and effective diffusion coefficient slightly smaller than reference values. The inverse algorithm converges to local minima when estimation starts at values either larger or smaller than reference values (see Table 4). This means that errors in the porosity of the gap lead to errors in the estimation of tracer diffusion parameters.

If D_e of filter is taken equal to twice its reference value, optimun fit is achieved with porosities slightly larger and effective diffusion coefficients slightly smaller than reference values (Figure 8). The smallest value of the objective function is obtained when estimation starts at reference values. The inverse logarithm converges to local minima when estimation starts at values either larger or smaller than reference values. Therefore, D_e of filter is a key parameter for estimating tracer diffusion parameters too.

Chloride

Identifiability analysis for chloride has been performed similar to that of HTO. Estimates of effective diffusion coefficients and accessible porosities in clay and EdZ are summarized in Table 5. D_e and Φ_{acc} of Cl in clay can be estimated accurately when data are free of noise ($\sigma = 0$). When data include noise, estimated Φ_{acc} reaches either its lower or upper bound no matter the initial guess. Therefore, it can be concluded that these two parameters cannot be estimated at the same time because they are strongly correlated ($\rho = -0.99$). Estimates of EdZ parameters are excellent if $\sigma = 0$ and acceptable for $\sigma = 0.02$ and 0.05. A similar conclusion is reached when D_e of clay and EdZ are estimated simultaneously. These two parameters can be properly estimated simultaneously because their correlation coefficient is not large ($\rho = -0.76$). Results of runs in which accessible porosities of clay and EdZ are estimated show that estimated values coincide with true values for $\sigma = 0$ and are close to true values for noisy data even though the correlation between these two parameters is significant ($\rho = -0.86$).

When four parameters are estimated at the same time, estimates coincide with true values for σ = 0. However, for σ = 0.02 parameter estimates are poor and depend on initial values.

D_e and Φ_{acc} of clay cannot be estimated simultaneously when it is assumed that there is no EdZ (Figure 10). Estimated values are out of parameter range independent of the initial guess (Table 6). Both parameters have been estimated in the case when the volume of water in the circulation system is 5 % smaller than the true value. There are no differences between estimated and true values for σ = 0. However, estimates for data having noise (σ = 0.02) depend on initial values.

Clay diffusion parameters were estimated for a gap porosity of 1. In general, parameter estimates are not close to true values. When initial values are larger than true values, estimated effective diffusion coefficient is acceptable. However, estimated accessible porosity reaches a local minimum. Therefore, uncertainties in porosity of the gap affect strongly the estimation of clay porosity and to a less extent the diffusion coefficient of clay.

Identifiability runs performed with D_e of filter equal to twice its true value show that parameter estimates deviate from true values even though the fit to synthetic data is good. Estimates of D_e are similar in all cases regardless initial parameter values or data noise and estimates of clay porosity reach always lower or upper bounds. Therefore, it can be concluded that uncertainties in D_e of filter affect strongly the estimation of clay porosity and to a less extent the diffusion coefficient of clay.

6. Conclusions and relevance for real diffusion experiments

Interpretation DIR in situ diffusion experiments performed at Bure site on C-Ox argillite is complicated by several non-ideal effects caused by the presence of a sintered filter, a gap between the filter and borehole wall and an excavation disturbed zone (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.

Model results indicate that DIR in situ diffusion experiments can be safely interpreted with a simple 1D axisymmetric model because tracer dilution curves are not sensitive to diffusion anisotropy.

The effect of filter and gap has been analyzed by comparing tracer dilution curves with detailed and simplified computed models. Model results indicate that failing to account for filter and gap may result in significant errors in tracer concentrations.

Normalized dimensionless sensitivities of tracer concentrations at the test interval have been computed numerically. Tracer concentrations are sensitive all key parameters. Their sensitivities are tracer dependent and vary with time. Sensitivities have been used to identify parameters that can be estimated with less uncertainty. Times at which tracer concentrations begin to be sensitive to each parameter have been identified.

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 for HTO and Cl in the presence of random measurement errors. Identifiability analysis of synthetic experiments reveals that data noise makes the estimation of clay parameters difficult. Parameters of clay and EdZ cannot be estimated simultaneously when data contain noise. Models without an EdZ fail to reproduce synthetic data. Proper interpretation of in situ diffusion experiments requires accounting for filter, gap and EdZ. Estimates of effective diffusion coefficient and porosity of clay are highly correlated, indicating that these parameters cannot be estimated simultaneously. Accurate estimation of De 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 circulation system do not affect clay parameter estimates. Interpretation of real DIR in situ diffusion experiments greatly benefit from results of the identifiability analysis of synthetic experiments and normalized sensitivities which have provided insight on inverse estimation of in situ diffusion experiments.

Dimensionless sensitivities, transient tracer sensitivities to parameters as well as conclusions of identifiability analysis are most useful for calibration and interpretation of real diffusion experiments (see Samper *et al.*, 2007).

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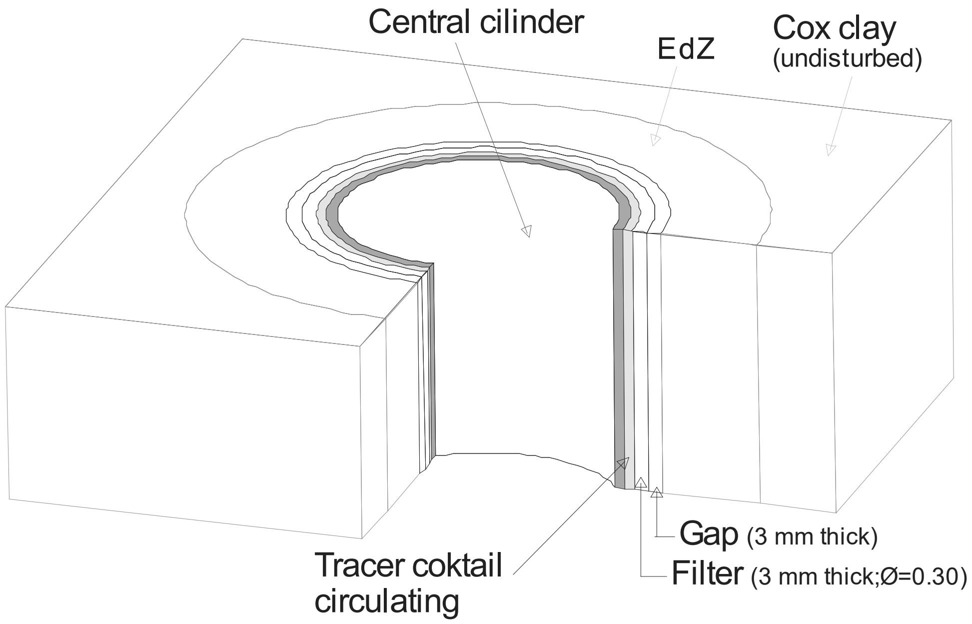
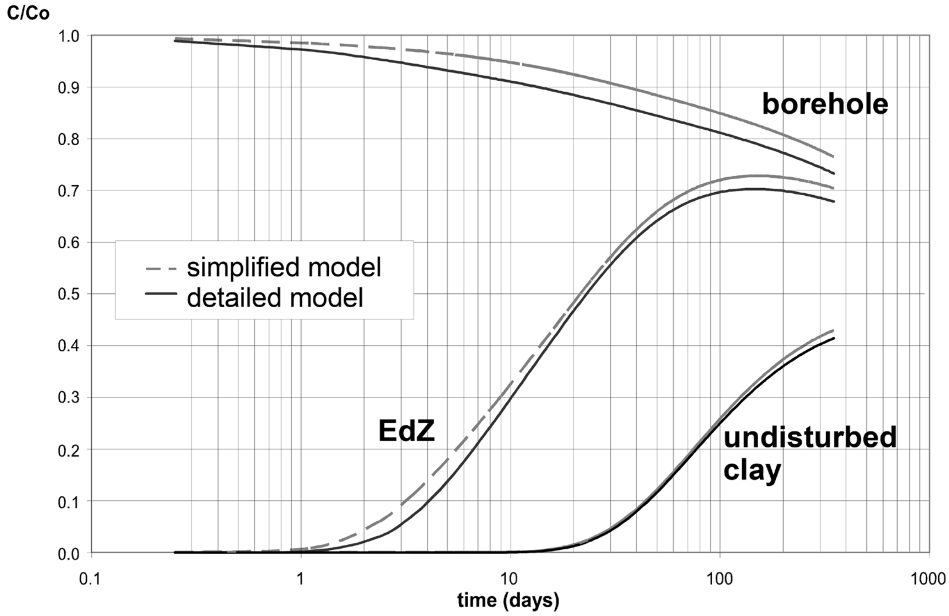


Figure 1. Sketch of borehole geometry for DIR experiments.



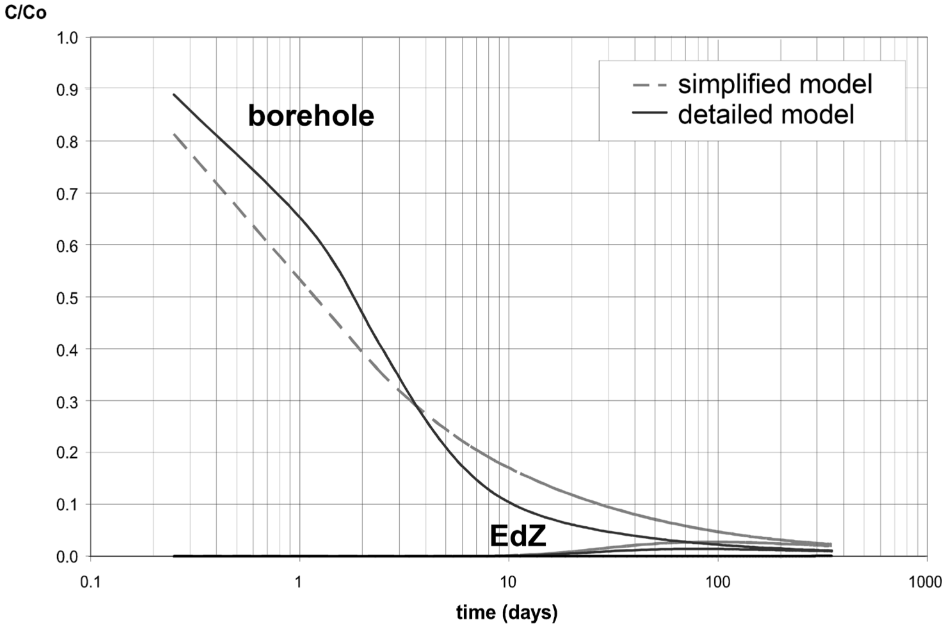


Figure 2. Time evolution of $^{36}Cl^-$ (top) and $^{134}Cs^+$ (bottom) concentrations in borehole, EdZ and undisturbed clay for DIR2001 experiment computed with detailed (solid lines) and simplified (dashed lines) models.

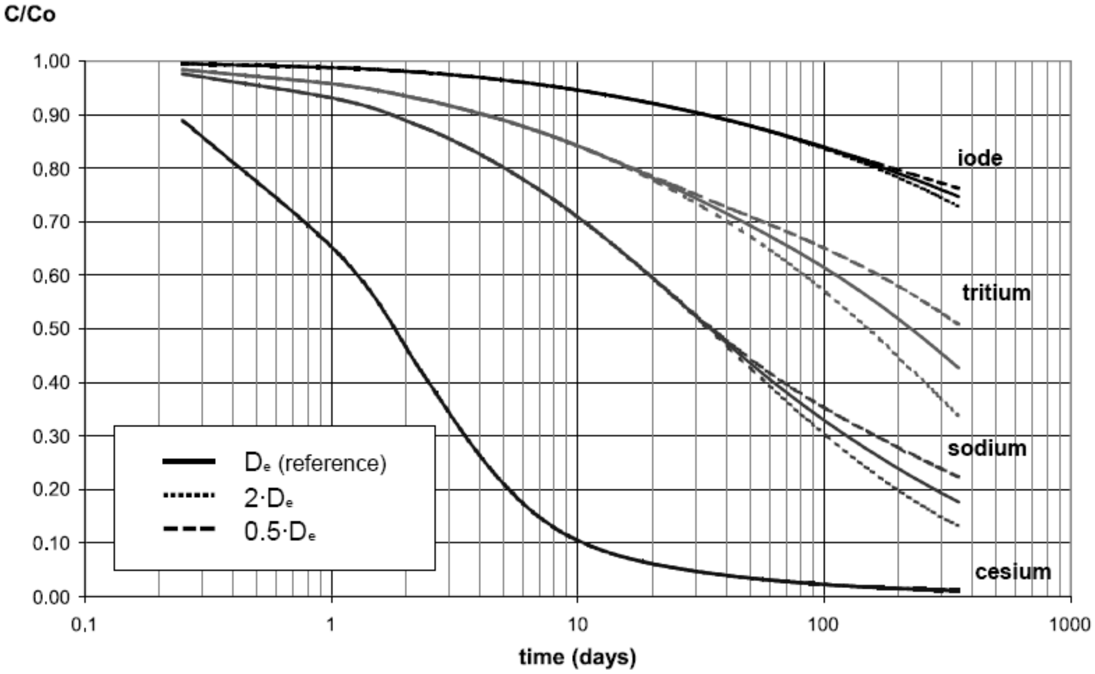


Figure 3. Sensitivity of tracer concentrations in the injection zone to changes in D_e in clay.

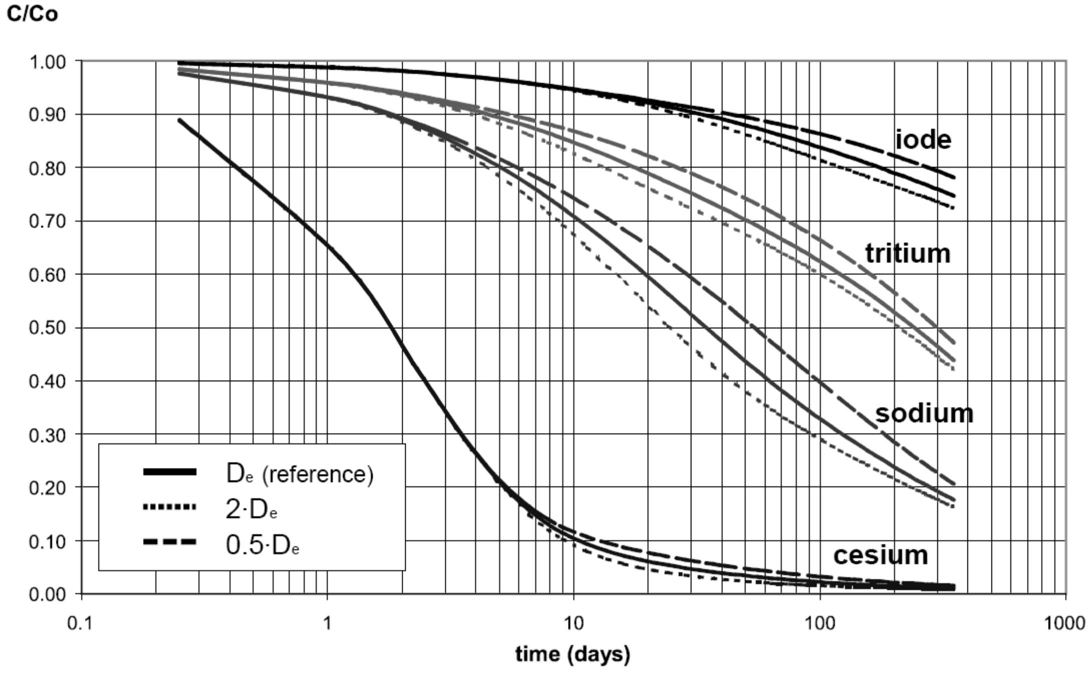


Figure 4. Sensitivity of tracer concentrations in the injection zone to changes in D_e of EdZ.

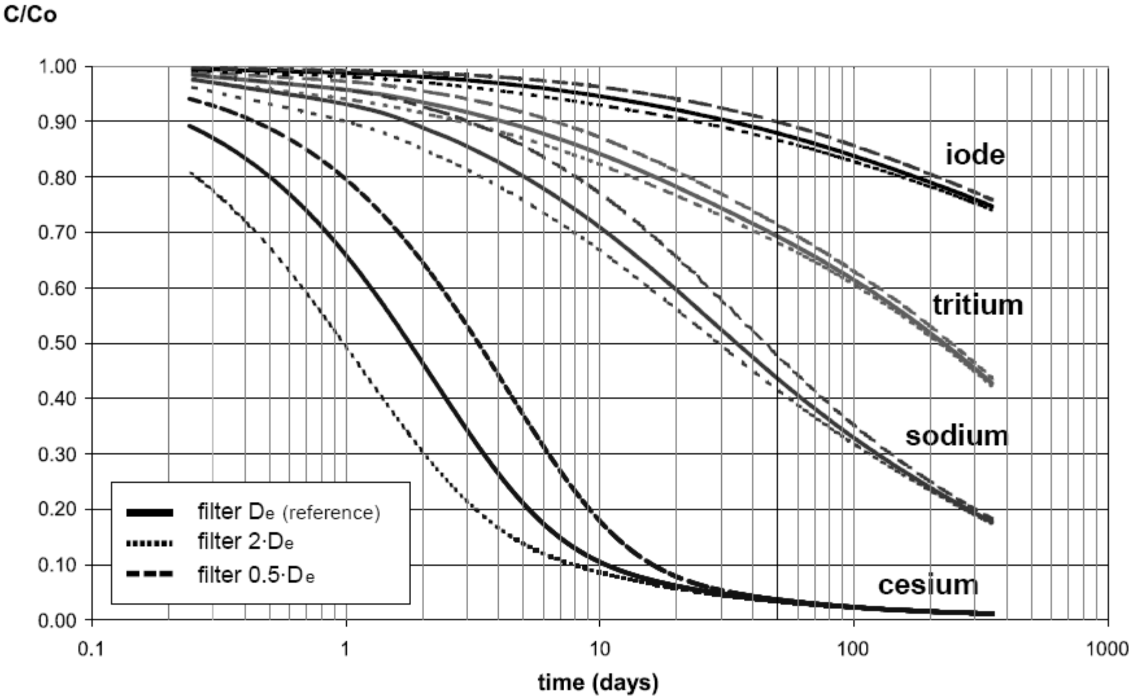


Figure 5. Sensitivity of concentrations in the injection zone to variation in D_e of filter.

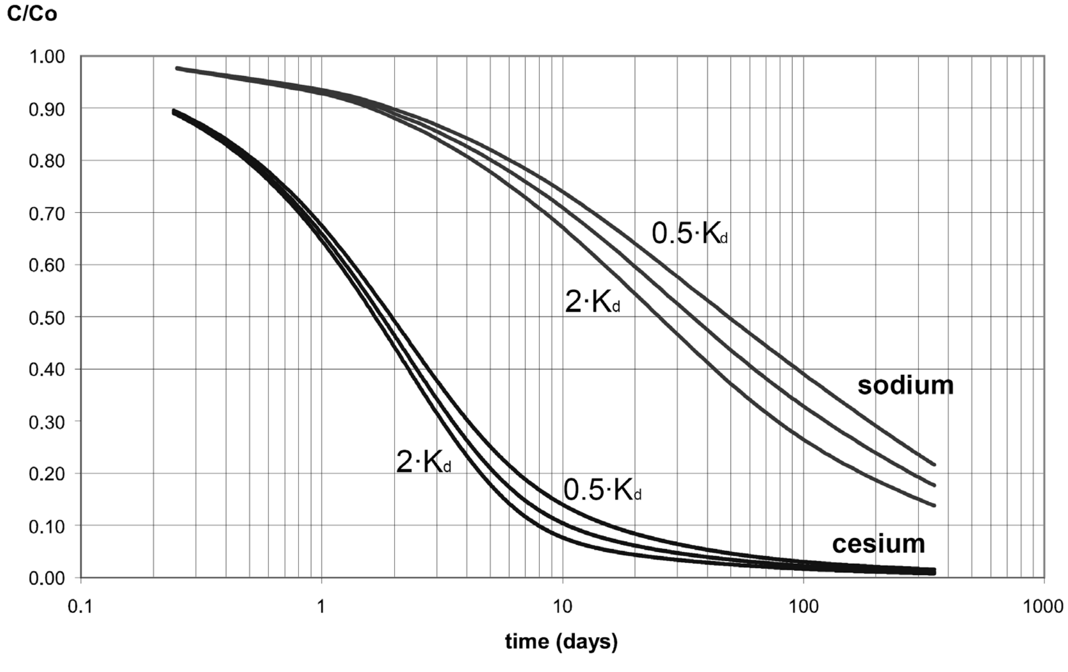


Figure 6. Sensitivity of concentrations in the injection zone to variation in K_d of clay.

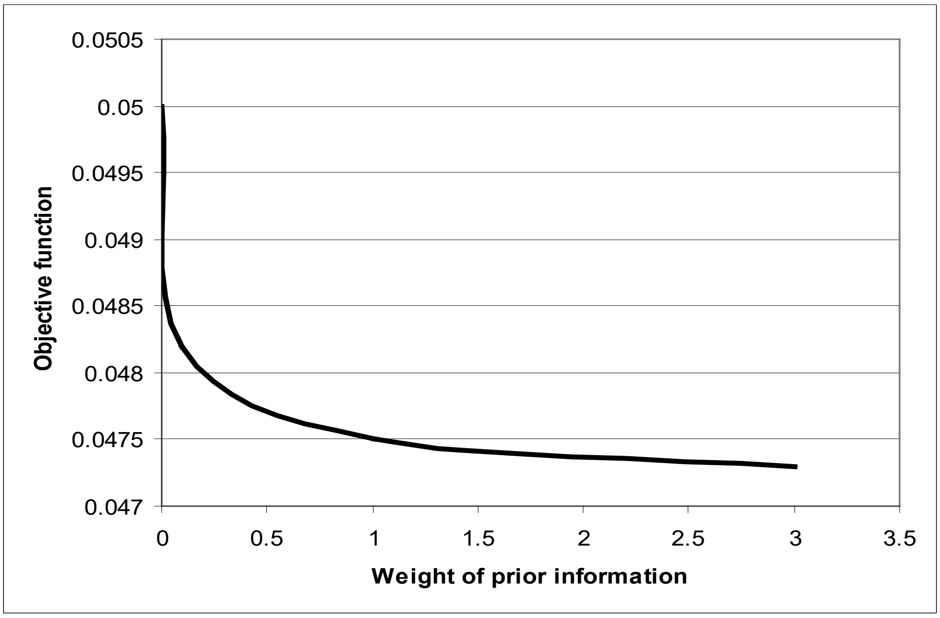


Figure 7. Variation of objective function with the weight given to prior information.

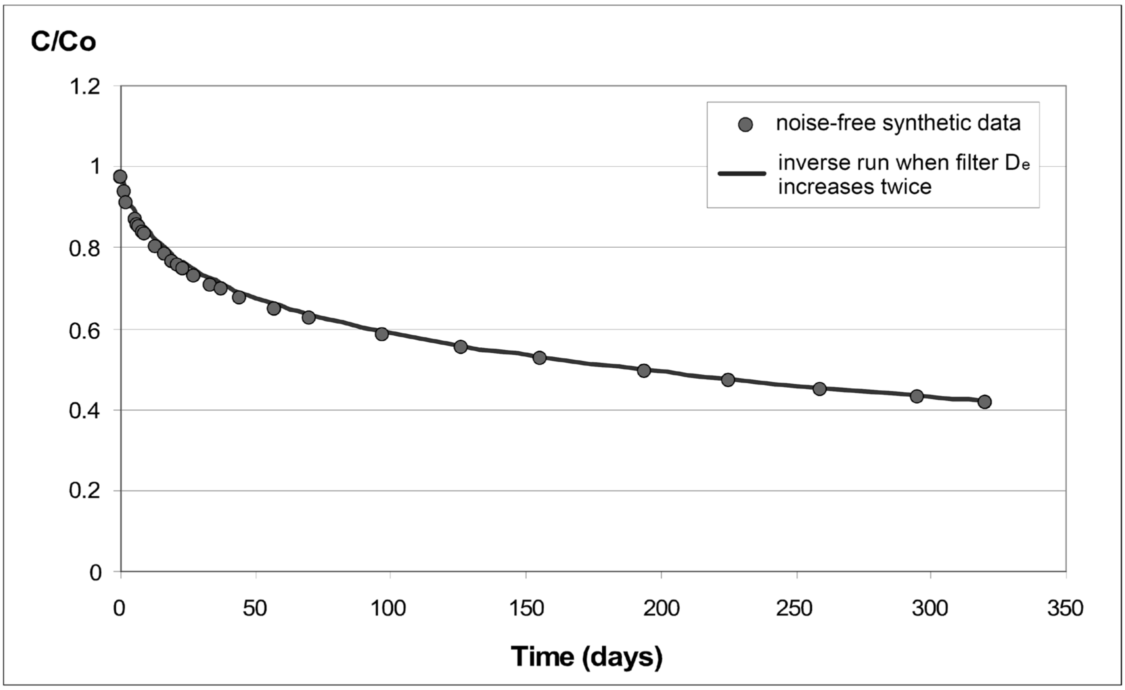


Figure 8. Best fit to HTO noise-free synthetic data when D_e of filter is twice its reference value.

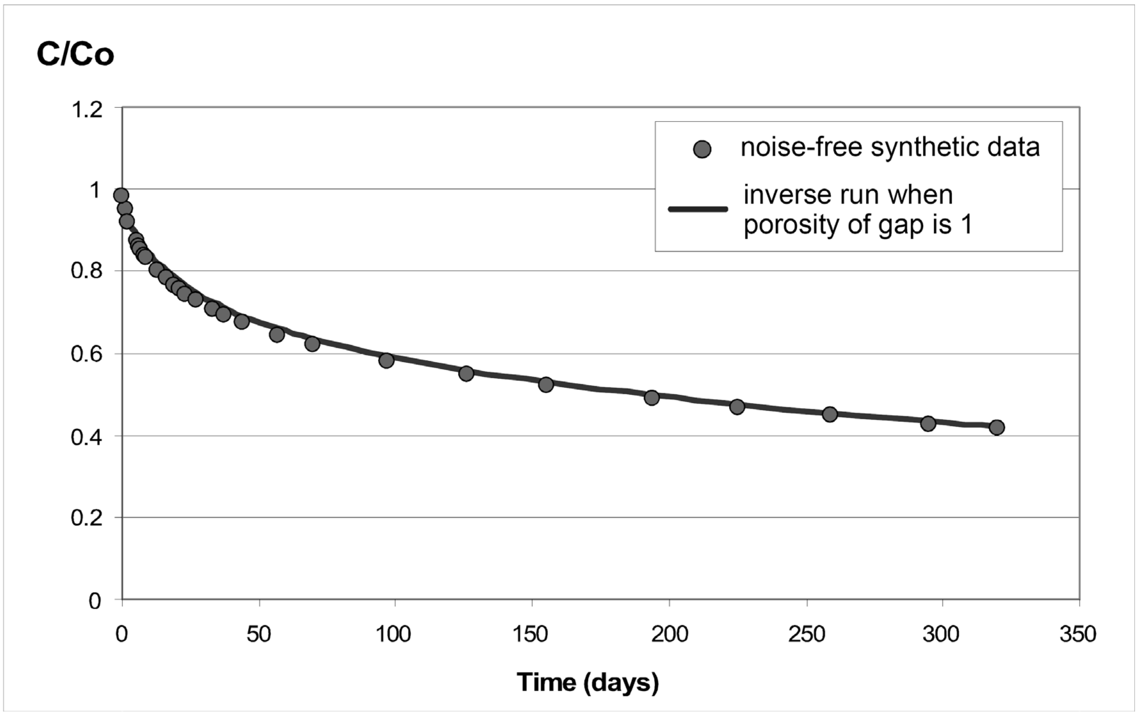


Figure 9. Best fit to HTO noise-free synthetic data when porosity of gap is fixed to a value of 1 which differs from its reference value of 0.6.

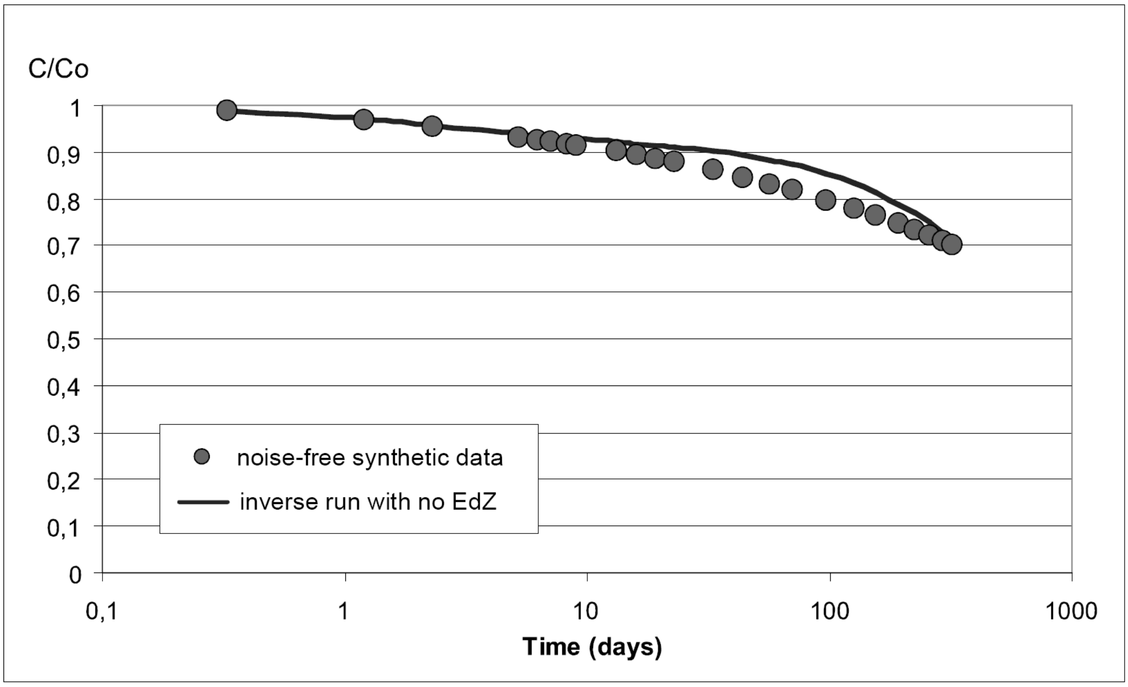


Figure 10. Model fit to $^{36}Cl^{-}$ noise-free synthetic data for EdZ thickness equal to zero.

Table 1. Reference values of diffusion and sorption parameters in different materials for all the tracers. D_e// is horizontal effective diffusion coefficient, Φ_{acc} is accessible porosity and K_d is distribution coefficient.

		HTO	**$^{36}\mathrm{Cl}^-$**	**$^{125}\mathrm{I}^-$**	**$^{22}\mathrm{Na}^+$**	**$^{134}\mathrm{Cs}^+$**
Clay	D_e (m/s^2)	$4.1\cdot10^{-11}$	$9.1\cdot10^{-12}$	$4.4\cdot10^{-12}$	$6.7\cdot10^{-11}$	$3.6\cdot10^{-10}$
	Φ_{acc}	0.18	0.09	0.13	0.18	0.18
	K_d (ml/g)	---	---	---	0.74	50
EdZ	D_e (m/s^2)	10^{-10}	$2.3\cdot10^{-11}$	$1.1\cdot10^{-11}$	$1.7\cdot10^{-10}$	$9\cdot10^{-10}$
	Φ_{acc}	0.36	0.18	0.26	0.36	0.36
	K_d (ml/g)	---	---	---	0.74	50
Gap	D_e (m/s^2)	$2\cdot10^{-10}$	$1.1\cdot10^{-10}$	$3.4\cdot10^{-11}$	$3.3\cdot10^{-10}$	$1.8\cdot10^{-9}$
	Φ_{acc}	0.6	0.6	0.6	0.6	0.6
	K_d (ml/g)	---	---	---	0.74	50
Filter	D_e (m/s^2)	$8\cdot10^{-11}$	$4.5\cdot10^{-11}$	$1.3\cdot10^{-11}$	$1.3\cdot10^{-10}$	$7.1\cdot10^{-11}$
	Φ_{acc}	0.3	0.3	0.3	0.3	0.3

Table 2. Computed relative sensitivities of tracer dilution curves to changes in parameters. Cesium results are shown for two experiments in order to compare variation of *RS* with experiment design.

		HTO	**$^{36}\mathrm{Cl}^-$**	**$^{125}\mathrm{I}^-$**	**$^{22}\mathrm{Na}^+$**	**$^{134}\mathrm{Cs}^+$**	
		DIR2001	DIR2001	DIR2001	DIR2002	DIR2002	EST208
Total volume	$\Delta V = -10\%$	***0.462***	***0.221***	***0.194***	***0.77***	***1.09***	***1.11***
EdZ thickness	$\Delta e = -2$ cm	***0.124***	***0.072***	***0.055***	***0.21***	***0.387***	***0.344***
	$\Delta e = +2$ cm	0.074	0.038	0.012	0.082	0.018	0.016
Filter D_e //	$\Delta D_e > 0$	0.014	0.018	0.012	0.033	0.053	0.049
	$\Delta D_e < 0$	0.051	0.024	0.038	***0.125***	***0.258***	***0.24***
Gap D_e //	$\Delta D_e > 0$	0.014	0.014	0.003	0.011	0.026	0.025
	$\Delta D_e < 0$	0.018	0.022	0.011	0.045	0.11	0.106
Gap Φ_{acc}	$\Delta\Phi_{acc} > 0$	0.061	***0.051***	0.02	0.03	0.063	0.071
	$\Delta\Phi_{acc} < 0$	0.071	***0.062***	0.033	0.031	0.071	0.076
EdZ D_e //	$\Delta D_e > 0$	0.034	0.016	0.022	0.089	***0.22***	***0.334***
	$\Delta D_e < 0$	***0.113***	***0.047***	***0.054***	***0.316***	***0.726***	***1.388***
EdZ Φ_{acc}	$\Delta\Phi_{acc} > 0$	***0.084***	***0.053***	***0.043***	0.039	***0.22***	***1.289***
	$\Delta\Phi_{acc} < 0$	***0.171***	***0.074***	***0.057***	0.033	***0.186***	***0.198***
Clay D_e //	$\Delta D_e > 0$	***0.082***	0.02	0.006	***0.1***	0.018	0.016
	$\Delta D_e < 0$	***0.143***	0.031	0.010	***0.197***	0.033	0.03
Clay Φ_{acc}	$\Delta\Phi_{acc} > 0$	0.06	0.016	0.006	0.012	0.005	0.005
	$\Delta\Phi_{acc} < 0$	0.072	0.022	0.007	0.011	0.005	0.005
K_d	$\Delta K_d > 0$	---	---	---	***0.163***	***0.245***	***0.263***
	$\Delta K_d < 0$	---	---	---	***0.32***	***0.689***	***0.76***

Table 3. Summary of inverse runs in which effective diffusion coefficients and accessible porosities of undisturbed clay and EdZ are estimated for HTO.

(a) With prior information: prior parameter estimates are $4.1\cdot10^{-11}$ m^2/day and 0.18 with a weight of 1.

	Clay D_e (m^2/s)		**Clay Φ_{acc}**		**EdZ D_e (m^2/s)**		**EdZ Φ_{acc}**	
Standard dev σ	**initial**	**estimated**	**initial**	**estimated**	**initial**	**estimated**	**initial**	**estimated**
0.01	$8.2\cdot10^{-11}$	$3.6\cdot10^{-11}$	-	-	-	-	-	-
0.05	$8.2\cdot10^{-11}$	$2.1\cdot10^{-11}$	0.36	0.36	-	-	-	-
0.01	-	-	-	-	$5.1\cdot10^{-11}$	$2\cdot10^{-10}$	0.18	0.18
0.01	$2.1\cdot10^{-11}$	$3\cdot10^{-11}$	0.09	0.28	$5.1\cdot10^{-11}$	$1.4\cdot10^{-10}$	0.54	0.29
0.01	$8.1\cdot10^{-11}$	$4.1\cdot10^{-11}$	0.36	0.13	$2.1\cdot10^{-10}$	$1.1\cdot10^{-10}$	0.54	0.35
0.05	$2.1\cdot10^{-11}$	$2.1\cdot10^{-11}$	0.09	0.36	$5.1\cdot10^{-11}$	$7.9\cdot10^{-10}$	0.54	0.18
0.05	$8.1\cdot10^{-11}$	$3.2\cdot10^{-11}$	0.36	0.15	$2.1\cdot10^{-10}$	$1.7\cdot10^{-10}$	0.54	0.32
0.05	$8.1\cdot10^{-11}$	(a) $3.7\cdot10^{-11}$	0.25	(a) 0.24	-	-	-	-
0.05	$8.1\cdot10^{-11}$	(a) $3.4\cdot10^{-11}$	0.25	(a) 0.21	$2\cdot10^{-10}$	$9.8\cdot10^{-11}$	0.56	0.55
True value		**$4.1\cdot10^{-11}$**		**0.18**		**10^{-10}**		**0.36**

Table 4. Summary of inverse runs in which effective diffusion coefficients and accessible porosities of undisturbed clay and EdZ are estimated for HTO in order to study relevance of uncertainties in thickness of EdZ, volume of water in the injection system, porosity of gap and diffusion coefficient of the filter.

Hypothesis	**Clay D_e (m^2/s)**		**Clay Φ_{acc}**		**EdZ D_e (m^2/s)**		**EdZ Φ_{acc}**		
	initial	**estimated**	**initial**	**estimated**	**Initial**	**estimated**	**initial**	**estimated**	**σ**
No EdZ	$8.1\cdot10^{-11}$	$8.1\cdot10^{-11}$	0.25	0.24	-	-	-	-	0
	$2.1\cdot10^{-11}$	$5\cdot10^{-11}$	0.09	0.1	-	-	-	-	0
Total volume 5% smaller	$8.1\cdot10^{-11}$	$5\cdot10^{-11}$	0.25	0.09	-	-	-	-	0
	$8.1\cdot10^{-11}$	$4.4\cdot10^{-11}$	0.25	0.1	-	-	-	-	0.05
Porosity of gap equal 1	$4.1\cdot10^{-11}$	$3.9\cdot10^{-11}$	0.18	0.23	10^{-10}	$7.4\cdot10^{-11}$	0.36	0.36	0
	$2.1\cdot10^{-11}$	$3.1\cdot10^{-11}$	0.09	0.35	$5.1\cdot10^{-11}$	$1.4\cdot10^{-10}$	0.18	0.18	0
	$8.1\cdot10^{-11}$	$3\cdot10^{-11}$	0.36	0.36	$2.1\cdot10^{-11}$	$1.2\cdot10^{-11}$	0.56	0.25	0
D_e of filter two times reference one	$4.1\cdot10^{-11}$	$3.9\cdot10^{-11}$	0.18	0.23	10^{-10}	$7.4\cdot10^{-11}$	0.36	0.37	0
	$2.1\cdot10^{-11}$	$2.9\cdot10^{-11}$	0.09	0.29	$5.1\cdot10^{-11}$	$1.4\cdot10^{-10}$	0.18	0.18	0
	$8.1\cdot10^{-11}$	$3\cdot10^{-11}$	0.36	0.36	$2.1\cdot10^{-11}$	$1.2\cdot10^{-11}$	0.56	0.25	0
True value		**$4.1\cdot10^{-11}$**		**0.18**		**10^{-10}**		**0.36**	

Table 5. Summary of inverse runs in which effective diffusion coefficients and accessible porosities of undisturbed clay and EdZ are estimated for $^{36}Cl^{-}$.

Standard dev σ	**Clay D_e (m^2/s)**		**Clay Φ_{acc}**		**EdZ D_e (m^2/s)**		**EdZ Φ_{acc}**	
	initial	**estimated**	**initial**	**estimated**	**initial**	**estimated**	**initial**	**estimated**
0.02	$1.9\cdot10^{-11}$	$1.6\cdot10^{-12}$	0.15	0.04	-	-	-	-
0.02	-	-	-	-	$4.5\cdot10^{-11}$	$2.3\cdot10^{-11}$	0.36	0.19
0.02	$1.9\cdot10^{-11}$	$1\cdot10^{-11}$	-	-	$4.5\cdot10^{-11}$	$2.3\cdot10^{-11}$	-	-
0.02	-	-	0.05	0.11	-	-	0.12	0.18
0.02	$4.5\cdot10^{-12}$	$1.3\cdot10^{-10}$	0.05	0.04	$1.1\cdot10^{-11}$	$1.5\cdot10^{-9}$	0.09	0.27
0.02	$1.9\cdot10^{-11}$	$1.3\cdot10^{-10}$	0.12	0.04	$4.5\cdot10^{-11}$	$7.9\cdot10^{-12}$	0.26	0.56
True value		**$9.1\cdot10^{-12}$**		**0.09**		**$2.3\cdot10^{-11}$**		**0.18**

Table 6. Summary of inverse runs in which effective diffusion coefficients and accessible porosities of undisturbed clay and EdZ are estimated for $^{36}Cl^{-}$ in order to study relevance of uncertainties related to thickness of EdZ, volume of water in the injection system, porosity of gap and diffusion coefficient of filter.

Hypothesis	**Clay D_e (m^2/s)**		**Clay Φ_{acc}**		
	initial	**estimated**	**initial**	**estimated**	**σ**
No EdZ	$4.5\cdot10^{-12}$	10^{-10}	0.05	0.36	0
	$1.9\cdot10^{-11}$	10^{-10}	0.18	0.36	0
Total volume 5% smaller	$4.5\cdot10^{-12}$	$9.1\cdot10^{-12}$	0.05	0.089	0
	$4.5\cdot10^{-12}$	$9.8\cdot10^{-12}$	0.05	0.12	0.02
	$1.9\cdot10^{-11}$	$1.3\cdot10^{-11}$	0.15	0.06	0.02
Porosity of gap equal 1	$4.5\cdot10^{-12}$	$3.9\cdot10^{-12}$	0.05	0.17	0
	$1.9\cdot10^{-11}$	$7.9\cdot10^{-12}$	0.18	0.05	0
D_e of filter two times reference one	$4.5\cdot10^{-12}$	$2.8\cdot10^{-12}$	0.05	0.38	0
	$1.9\cdot10^{-11}$	$1.4\cdot10^{-11}$	0.18	0.05	0
True value		**$9.1\cdot10^{-12}$**		**0.09**	