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Upscaling of radionuclide transport and retention in crystalline rocks exhibiting micro-scale heterogeneity of the rock matrix

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Abstract

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In different in-situ diffusion experiments carried out in fractured crystalline rocks, sorbing radionuclides have shown a behaviour that strongly differs from what is predicted by homogeneous-based models. Their breakthrough curves are in fact often characterised by a fast first-arrival and these radionuclides can penetrate surprisingly long distances deep into the matrix. The heterogeneous structure of mineral distribution and porosity geometry had been offered as an explanation for these discrepancies. Here, we use reactive transport simulations to investigate the effect of the sparse distribution of sorption sites on the breakthrough curves of sorbing radionuclides. At small scale, the computed breakthrough curves significantly differ from those predicted using homogeneous models. For instance, the early part of these curves does not show any clear separation with the corresponding part of the curve of a non-sorbing tracer and a long transition zone is observed, with a very smooth slope of the tailing. Two different upscaling strategies, aimed at propagating the signal of heterogeneous retention over larger scales, are proposed and demonstrated against independent solutions computed at intermediate scales. The upscaling strategies are also used to show that at large scales (e.g. the scale of interest in a safety assessment study for a deep geological repository for nuclear waste) the signature of mineralogical heterogeneity is smoothed out and the heterogeneous breakthrough curve is well approximated by a homogeneous solution where the radionuclide distribution coefficient for the pure mineral phase is scaled by the mineral volume fraction. However, the spatial persistence of the heterogeneous signature is significant when the sorbing mineral is present in a low amount.

Keywords: mineralogical heterogeneity, heterogeneous retention, fractured media, upscaling

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64 **1. Introduction**

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66 Since the pioneering work of Fried et al. [1], considerable efforts have been
67 devoted to understanding, characterising and modelling the retention capacity
68 of the rock matrix for radionuclides. In fact, the capacity of the rock matrix
69 to retain potentially harmful radionuclides is a *sine qua non* condition for the
70 consideration of a crystalline rock system as a potential host for the geological
71 disposal of spent nuclear fuel.

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73 Different analytical solutions [e.g. 2, 3, 4] and mathematical formulations
74 [e.g. 5, 6, 7] have been developed to account for the influence of matrix retention
75 on radionuclide transport in fractured media, and particular emphasis has been
76 placed on analysing the effects of matrix diffusion and sorption processes on the
77 radionuclide breakthrough curves observed at a fracture outlet [8].

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79 In all the studies mentioned above, radionuclide retention properties are
80 assumed to be constant in the whole rock matrix. In parallel to the increas-
81 ing availability and reliability of micro-characterisation methods, such as X-
82 ray micro-computed tomography (X- μ CT) or the ^{14}C -PolyMethylMethAcrylate
83 (^{14}C -PMMA) method [9, 10], recently efforts have been placed in understanding
84 the influence of the heterogeneity of the matrix of crystalline rocks on radionu-
85 chloride diffusion and retention. Sardini et al. [11] interpreted data of an out-
86 diffusion experiment performed on a core sample of Palmottu granite (Eastern
87 Finland) using time domain random walk simulations. The calculations were
88 carried out in an inverse fashion on a two-dimensional porosity map obtained
89 using the ^{14}C -PMMA method. The results of this study point out that, at
90 the investigated spatial scale, the considered granite behaves as a composite
91 system, with micro-cracks acting as preferential diffusive pathways and with
92 microporous zones controlling the late-time diffusive discharge. The composite
93 behaviour of the rock matrix of crystalline rocks was also pointed out by other
94 studies based on micro-characterisation data [e.g. 12, 13, 14]. At a larger scale,
95 solutions that partly account for changes in diffusion and retention properties
96 in the rock matrix were provided by Painter et al. [15], who used a time-domain
97 Lagrangian framework to propose a piecewise approximation of changes in dif-
98 fusion and retention properties, and Cvetkovic [16], who included a layer-based
99 parameterisation of the matrix. More recently, Trincherro et al. [17] developed
100 a numerical framework for the dynamic update of the retention properties of
101 the rock matrix based on changes of the background geochemical conditions.
102 However, the upscaling of the afore-mentioned micro-scale results to a larger
103 scale remains a largely unresolved issue [12].

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105 In parallel to the modelling efforts, different in-situ experiments have been
106 carried out to investigate the rock retention capacity; e.g. the TRUE Block Ex-
107 periment [18] and the Long Term Sorption Diffusion Experiment (LTDE-SD)
108 [19] at the Äspö Hard Rock Laboratory (HRL) in Sweden, the Water Phase Dif-
109 fusion Experiment (WPDE) [20] at Onkalo (Finland) and the Grimsel migration
110 experiment [21] (Switzerland). In some, if not all, of these experiments, models
111 based on the assumption of homogeneity of the rock matrix fail to describe field
112 observations, particularly for sorbing radionuclides [e.g. 22]. The heterogeneous

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46 behaviour observed in some of these experiments (e.g. the very long penetration
47 depth observed for strongly sorbing radionuclides) has been attributed, in part,
48 to the heterogeneous and sparse distribution of sorption sites [e.g. 13].

49 In this work we use numerical simulations and two novel upscaling method-
50 ologies to gain insight into the effect that the heterogeneous distribution of active
51 mineral grains of the rock matrix (i.e. mineral grains that have the potential to
52 retain radionuclides) has on radionuclide breakthrough curves in dual porosity
53 systems. The sparse distribution of mineral grains is simulated using Bernoulli
54 distributions that honour the considered bulk mineral volume fraction.

55 2. Problem formulation and research questions

56 The classical models of retention of solutes in fractures build on the work of
57 Carslaw and Jaeger [23] who considered heat transfer in slabs. The mathemat-
58 ical solution of Carslaw and Jaeger was then used by Neretnieks [2] to quantify
59 the effect of retention in crystalline fractures by matrix diffusion and sorption;
60 this was the basis for all subsequent conceptual models of tracer transport in
61 fractures with retention [e.g. 4, 7]. In all these approaches the micro-structure
62 and processes related to sorption are homogenised, in the sense that sorption
63 reactions are expressed by a single equilibrium distribution coefficient (K_d),
64 while mineralogical heterogeneity is neglected. These homogenised models are
65 a practical necessity. Microscopic heterogeneity in the rock matrix of crystalline
66 rocks is clearly present both as mineralogical and structural (in form of micro-
67 fissures) heterogeneity, yet the issue of its effect on radionuclide transport and
68 its possible upscaling to larger scales has not been systematically studied.

69 In this work, we address the implications of physical and mineralogical
70 heterogeneity of the rock matrix on radionuclide transport and retention by
71 considering three scales as illustrated in Figure 1: i) the laboratory scale, ii)
72 the field-scale, and iii) the site-scale. Our main focus is first to better under-
73 stand the potential effect of micro-scale reactions and heterogeneity on tracer
74 transport through fractures in crystalline rocks, and then to explore upscal-
75 ing/homogenisation strategies that can be used in applications. The three spe-
76 cific research questions we address in this work are:

- 77 1. What are the potential effects of micro-scale heterogeneity on reactive
78 tracer transport through fractures in crystalline rocks?
- 79 2. How can we account for the physical and mineralogical heterogeneity of the
80 rock matrix when modelling radionuclide transport in fractured media?
- 81 3. What are the most efficient and reliable upscaling/homogenisation strate-
82 gies?

83 Thus, our work assesses radionuclide transport at different spatial scales and
84 is organised as follows. In the next section we summarise evidence of micro-scale
85 heterogeneity in the crystalline matrix. Next in section 4, we build a detailed
86 process-based model of reactive tracer transport in a single fracture on the
87 laboratory scale, using state-of-art simulation tools. In section 5 we present

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88 and evaluate alternative strategies for upscaling from the laboratory scale to
89 the field scale, while in section 6 we consider upscaling to the site scale. Finally
90 we draw main conclusions in section 8.

91 **3. Evidence of mineralogical heterogeneity**

92 A number of characterisation studies, carried out in the context of safety
93 analyses of deep geological repositories for nuclear waste, points out that the
94 rock matrix of fractured crystalline media is highly heterogeneous [e.g. 24, 25].
95 This heterogeneity is not only related to the pore space available for diffusion
96 (which is typically a complex distribution of inter- and intra-granular pore space
97 [11, 26, 27]) but is also associated with the sparse distribution of chemically
98 active mineral grains; that is, mineral grains that interact with the dissolved
99 solute species.

100 For instance, a mineral phase that is particularly important in this context
101 is biotite, a phyllosilicate mineral within the mica group that contains iron
102 in its reduced form. Biotite (and its alteration product chlorite) is in fact
103 considered as an important buffer against the infiltration of oxidative redox
104 fronts [28, 29, 30]. Moreover, biotite has a high sorption capacity and a high
105 affinity with potentially harmful radionuclides, such as cesium [31].

106 Observations made with microscopy in a granitic rock sample taken at Fors-
107 mark (the site selected for geological disposal of high-level radioactive waste in
108 Sweden) suggest that a typical biotite crystal has an average size of $\sim 400 \times$
109 $200 \mu\text{m}^2$ ($\sim 0.08 \text{ mm}^2$) although aggregates of grains up to 2 mm^2 can also
110 be found [32]. A simple visual inspection of the pothomicrographs shows that
111 biotite grains are indeed sparsely distributed (Figure 2).

112 Besides direct evidence, the existence of a heterogeneous and sparse distri-
113 bution of sorption sites, and its relevance for the diffusion patterns of sorbing
114 radionuclides, has also been inferred from the results of different in-situ exper-
115 iments. One of these experiments is the Long Term Sorption Diffusion Ex-
116 periment (LTDE-SD) carried out at the Äspö Hard Rock Laboratory (HRL)
117 in Sweden. In the experiment, 21 radionuclide trace elements and one stable
118 trace element were injected, circulated and sampled for around 200 days in a
119 closed borehole section [33]. The trace elements included non-sorbing and sorb-
120 ing tracers. Two borehole sections were put in contact with the tracer labelled
121 groundwater: the first section was part of a natural fracture surface whereas
122 the second section was in the unaltered matrix rock, devoid of natural frac-
123 tures. One of the autoradiography analyses carried out on different core sam-
124 ples taken from the investigated rock volume is shown in Figure 3. Although no
125 independent calibration was performed to separate the contributions from the
126 different radionuclides, it is thought that the black areas of the autoradiography
127 are generated mostly by cesium (namely, the isotope Cs-137), although other
128 nuclides such as Ni-63 and Na-22 might also partly contribute to the blacken-
129 ing. These black areas correlate well with the distribution of areas with dark
130 (mafic) minerals (e.g. biotite and chlorite, titanite and amphibole) (see the
131 photography of the core in Figure 3), which points out the evident control of

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232 the sparse distribution of sorbing minerals on the diffusion of strongly sorbing
233 radionuclides.

234 4. Cesium transport in a fracture with a physically and mineralogi- 235 cally heterogeneous matrix

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237 The domain considered is a single fracture-matrix system of dimension 0.25
238 m x 0.1 m x $4.7 \cdot 10^{-3}$ m. The fracture is parallel to the x-z plane and has an half
239 aperture of $2.5 \cdot 10^{-4}$ m. The domain was discretised with 7,600,000 regular grid
240 cells of dimension $\delta = 2.5 \cdot 10^{-4}$ m (i.e. same size of the fracture half-aperture).

241 The heterogeneity of the matrix was simulated using a micro-DFN approach
242 similar to that described in Svensson et al. [27]; i.e. three different fracture
243 sets of length from one to a few millimeters were used to mimic grain-boundary
244 pores as well as micro fractures that transect different mineral grains.

245 The micro-DFN was generated using the finite-volume groundwater flow
246 simulator DarcyTools [34, 35]. In DarcyTools, fracture orientation follows a
247 Fisher distribution (but here a random orientation was used) and spatial centers
248 are statistically independent and follow a Poisson process. The generation of
249 fractures is governed by the following equation:

$$250 \quad n = \frac{I}{a} \left[\left(\frac{l + dl}{l_{ref}} \right)^a - \left(\frac{l}{l_{ref}} \right)^a \right] \quad (1)$$

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252 where n is the number of fractures per unit volume, I [$1/\text{m}^3$] is the intensity,
253 a [-] is the power law exponent, l [m] is the fracture length and l_{ref} [m] is the
254 reference length, which was here set to 1 m. The micro-DFN was constructed
255 using the same fracture recipe used by Svensson et al. [27] to model a through-
256 diffusion experiment carried out in a rock sample taken at Forsmark (Table
257 1). The micro-DFN was then represented onto the underlying continuum grid
258 using the formulation provided by Svensson [36, 37], thus obtaining DFN-derived
259 values of porosity and pore diffusivity (Figure 4).

260 The fracture water volumetric flux was set to 10^{-8} m/s and a first calculation
261 was run where a non-sorbing tracer was injected along the inlet boundary of
262 the fracture for a short period of time. This simulation and all the numerical
263 calculations presented in this section were run on the supercomputer JUQUEEN
264 of the Jülich Supercomputing Centre [38] using the reactive transport code
265 PFLOTRAN [39, 40].

266 Snapshots of tracer concentration computed after 1 yr and 8 yr from the
267 beginning of the injection are shown in Figure 5. The finger-shaped penetration
268 profiles are related to preferential diffusive pathways, which in turn correspond
269 to zones of the matrix with higher intensity of micro-fractures and grain bound-
270 ary pores. The breakthrough curve computed at the fracture outlet was fitted
271 with Sudicky's analytical solution [4] by setting the matrix porosity to the av-
272 erage value of the heterogeneous field ($\phi = 2.2 \cdot 10^{-3}$) and using pore diffusivity
273 as the only calibration parameter. The resulting fit, which was obtained with
274 a value of pore diffusivity $D_p = 3.5 \cdot 10^{-13}$ m^2/s , is shown in Figure 6. The

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172 late-time deviation from the $-3/2$ slope of the breakthrough curve is due to the
173 limited extension of the matrix. The generally good agreement between the
174 heterogeneous model and the homogeneous-based analytical solution indicates
175 that the behaviour of a non-sorbing tracer can be described using a homogeneous
176 model parameterised based on equivalent parameters.

177 In the reactive transport calculations, a typical Littorina-type water (e.g.
178 Trinchero et al. [30] and references therein) was used as resident water. The
179 composition of the groundwater is listed in Table 2. The same water, containing
180 cesium in trace concentration ($1 \cdot 10^{-8}$ mol/L), was injected at the inlet of the
181 fracture for a short period of time.

182 Cesium and the other cations sorb onto the available biotite grains via cation
183 exchange. The sorption model (i.e. cation exchange reactions and related selec-
184 tivity coefficients - see Table 3) is taken from Kyllönen et al. [31], who assumed
185 three different types of ion exchange sites similar to the model of Bradbury
186 and Baeyens [41] for illite: sites on basal planes (95% abundance), interlayer
187 sites on crystal edges (frayed-edge sites, FES) (0.02% abundance) and a third
188 intermediate type site (5% abundance). Considering a mineral density of 3,000
189 $\text{kg}/\text{m}^3_{min}$, the cation exchange capacity of the exchanger is $CEC_{min} = 48.9$
190 $\text{eq}/\text{m}^3_{min}$ (subscript min indicates here *mineral*).

191 Two random uncorrelated realisations of biotite grains were generated. In
192 the first realisation, denoted as Model A (MA) around 8% of the grid cells of
193 the matrix were assumed to contain biotite with a unitary volume fraction (ω
194 $[\text{m}^3_{min}/\text{m}^3_b]$, where b stands for *bulk*) whereas in the second realisation (Model
195 B, MB) a twofold biotite content was considered (Figure 7). The distribution
196 of biotite was used to define the bulk cation exchange capacity of each grid cell
197 ($CEC_b = CEC_{min} \cdot \omega$). No sorption sites are available in the fracture.

198 Snapshots of the distribution of aqueous and sorbed cesium computed with
199 MB after 30 yr from the beginning of the injection are shown in Figure 8.
200 Compared to the non-sorbing tracer (Figure 5), the penetration of cesium is
201 much more limited. The spots with low cesium aqueous concentration and high
202 concentration of cesium in the solid phase correspond to biotite grains.

203 The cesium breakthrough curves computed for MA and MB are shown in
204 Figure 9. From a simple analysis of these curves, the following conclusion can
205 be drawn:

- 206 1. Unlike what was observed for the non-sorbing tracer, both breakthrough
207 curves clearly deviate from the typically expected homogeneous behaviour.
- 208 2. The tailing of the breakthrough curves is characterised by a long transition
209 zone, with the slope of the tailing gradually changing from a value of
210 $\sim -1/2$ to the $-3/2$ slope typically observed in dual porosity systems [8].
- 211 3. When less biotite is available in the matrix (MA), a shorter transition
212 zone and a lower level of the late-time tailing is observed.
- 213 4. Unlike what is expected considering a homogeneous matrix, at early times
214 no clear separation is observed between the cesium breakthrough curves
215 and the breakthrough curve of the non-sorbing tracer.

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216 5. Compared to the non-sorbing tracer, the cesium breakthrough curves have
217 a lower peak, which is observed at slightly earlier time. This evidence is
218 also in contrast with what is expected when assuming a homogeneous
219 distribution of sorption sites, when the peak of the breakthrough curve is
220 clearly displaced to later times.

349 5. Upscaling of heterogeneous retention

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351 The sketch of Figure 1 shows a gross representation of the spatial scales that
352 are typically assessed when studying radionuclide transport in fractured media.

353 Drill cores with isolated fractures are sometimes used to carry out tracer
354 test experiments in the lab [e.g. 42, 43]. This spatial scale is denoted here as
355 *lab-scale* and can be roughly related with a characteristic length of 0.1 to 1 m.

356 In-situ experiments, such as those mentioned and discussed in sections 1
357 and 3, are used to investigate e.g. rock matrix retention properties at depth.
358 This scale, denoted as *field-scale*, spans characteristic lengths from 1 to 10 m,
359 approximately.

360 In safety assessment studies for deep geological disposal of nuclear waste, the
361 scale of interest, denoted here as *site-scale*, has a characteristic length of a few
362 hundred meters to a few kilometers; i.e. the distance travelled by a radionuclide
363 released at repository depth and discharged somewhere in the surface system.

364 In this chapter we assess how laboratory tracer test data for sorbing nuclides
365 can be upscaled to the *field-scale*. In the next chapter, we also evaluate how
366 the signature of mineralogical heterogeneity propagates and affects radionuclide
367 transport and retention at the *site-scale*.

368 5.1. Mineralogically heterogeneous models

369 A single fracture-matrix system of dimension 2.5 m x 0.1 m is discretised
370 using 4,000,000 regular grid cells of size $\delta = 2.5 \cdot 10^{-4}$ m. The fracture is parallel
371 to the x-axis, meaning that its length is 2.5 m. All the parameters describing the
372 system are specified in Table 4. Notice that the models discussed in this section
373 are 2D. A sensitivity analysis to adding the third dimension was carried out
374 and the related results showed no significant change with the results presented
375 hereafter.

376 Sorption properties in the matrix are described by the following Bernoulli
377 distribution

$$378 f(k; p) = p^k(1 - p)^{1-k} \quad \text{for } k \in \{0, 1\} \quad (2)$$

379 where k is the local mineral volume fraction (i.e. volume fraction of the
380 sorbing mineral in the grid cell), which is 1 if the mineral is present and 0
381 otherwise, and p is the bulk mineral volume fraction in the matrix. If the
382 mineral is present, a linear isotherm sorption model is applied with a distribution
383 coefficient $K_d^g=5.3$ L/kg, which corresponds to a retardation factor $R_g=1,600$.
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254 The calculations were carried out in the JURECA booster module [44] of the
255 Jülich Supercomputing Centre using PFLOTRAN. A generic sorbing radionu-
256 clide was injected, as a short pulse, at the inlet of the fracture. Two observation
257 points were included, one at a distance of 0.25 m from the fracture inlet and the
258 second at the fracture outlet (2.5 m). The breakthrough curve computed in the
259 first observation point is representative of *lab-scale* while the second observation
260 point simulates a breakthrough curve observed at *field-scale*.

261 Figure 10 shows the breakthrough curve computed at *lab-scale* for a model
262 with $p = 0.16$. In the same plot, homogeneous breakthrough curves computed
263 using Tang’s solution [3] and different retardation values in the matrix are also
264 shown. The breakthrough curve simulated with the 2D mineralogically hetero-
265 geneous model is characterised by similar features as those already observed
266 and discussed for the 3D physically and mineralogically heterogeneous models
267 (section 4). For instance, at early times there is no clear separation between
268 the breakthrough curve of the heterogeneous model and the homogeneous solu-
269 tion for a non-sorbing radionuclide (while all the homogeneous curves computed
270 with $R > 1$ are shifted to later times). Also, analogously to what was discussed in
271 section 4, the tailing of the heterogeneous breakthrough curve is characterised
272 by a transition zone with the slope (log-log scale) being first very smooth and
273 then approaching gradually the $-3/2$ slope.

274 The results obtained at *field-scale* (Figure 11) point out that the signature of
275 mineralogical heterogeneity propagates and has a significant effect over larger
276 scales. Although the shape of the heterogeneous breakthrough curve is now
277 smoothed out and the transition in the slope is no longer evident, the curve still
278 exhibits a significant early arrival and an anomalous rising limb. Interestingly,
279 the declining limb of the curve is reasonably well described by the homogeneous
280 solution with $K_d = K_d^g \cdot p$. However, as for the *lab-scale*, none of the homo-
281 geneous solutions are able to capture the full shape of the curve. The need to
282 investigate how the heterogeneous signal propagates over larger spatial scales
283 and practical limitations to further extend the heterogeneous mechanistic mod-
284 els motivates the development of upscaling strategies, which are detailed in the
285 next two sub-sections.

286 *5.2. Upscaling strategy I: Direct Sampling (DS) of the Retention Time Distri-*
287 *bution (RTD)*

288 The two upscaling approaches proposed hereafter make use of standard con-
289 cepts used in time domain random walk (TDRW) methods. The calculations
290 presented hereafter were carried out using the computer code MARFA [15, 45].

291 The basic spatial unit used here is defined as a *segment*. A segment is
292 typically associated to a part of a particle pathline that lies in a fracture and
293 is delimited by the intersection with two adjacent fractures. Nevertheless, this
294 definition is not stringent, meaning that different and alternative conceptual
295 representations of a segment can be envisaged. Here, we define a segment as
296 the fracture length sampled by a *lab-scale* tracer test experiment.

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455 The unit response of a *lab-scale* tracer test can be expressed as [15]:
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$$457 \quad f_{tran}(t) = \int_0^\infty \int_0^\infty f_{ret}(t - \tau | \beta) f_{\beta|\tau}(\beta | \tau) f_\tau(\tau) d\tau d\beta \quad (3)$$

459 where τ [y] is the groundwater travel time in the fracture segment, with re-
460 lated probability density function f_τ , $t - \tau = t_{ret} \geq 0$ is the retention time in the
461 matrix and f_{ret} is its corresponding probability density function, denoted here
462 as *retention time distribution* and β [y/m] is a hydrodynamic control parameter
463 denoted as *transport resistance*, defined as [e.g. 7]:
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$$465 \quad \beta(\tau) = \int_0^\tau \frac{d\theta}{b(\theta)} \quad (4)$$

467 where b [m] is the fracture half aperture and θ is the variable of integra-
468 tion. The integration is along the segment. Notice that β and τ are strongly
469 correlated, which explains why the distribution of β is conditional on τ .

470 We consider here a simplified model, denoted with superscript *SM*, charac-
471 terised by $f_\tau = \delta(\tau - \tau_0)$ and $b = b_0$. For this model the following relationship
472 holds:
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$$474 \quad f_{tran}^{SM}(t) = f_{ret}^{SM}(t - \tau_0) \quad (5)$$

475 By equating Equations 5 and 3, we obtain an equivalent retention time dis-
476 tribution, which can be seen as a non-parameteric function that lumps together
477 all the random processes that might affect a particle; i.e. in-plane dispersion,
478 matrix diffusion and retention into either fracture surface or in the rock matrix.
479 f_{ret}^{SM} can be directly inferred from the lab-scale breakthrough curve, this is why
480 the proposed approach is denoted as *Direct Sampling (DS) approach*. f_{ret}^{SM} is
481 then used in TDRW simulations to route particles along pathlines made-up of
482 N segments, under the basic premise that each segment is characterised by the
483 same hydrodynamic processes (i.e. same distribution of τ and β).
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485 The practical implementation of the upscaling exercise is carried out using
486 the following stepwise approach:
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- 488 1. The breakthrough curve of the sorbing radionuclide obtained at 0.25 m
489 distance from the inlet (Figure 10) is used to extract f_{ret}^{SM} .
- 490 2. For the i -th particle, the retention time, $t_{ret} = t_{tran} - \tau_0$ is sampled from
491 f_{ret}^{SM} and the particle clock is set to $t_{clk,i}^j = t_{clk,i}^{j-1} + t_{ret} + \tau_0$. Notice that
492 index j indicates the fracture segment and that $t_{clk,i}^0 = 0$; i.e. the particle
493 clock is set to 0 at the inlet segment.
- 494 3. For the i -th particle, step 2 is repeated ten times until obtaining the par-
495 ticle arrival time, $t_{ar,i}$, at the end of a pathline of length 2.5 m.

496 The cumulative breakthrough curve is computed from all the particle arrival
497 times and the instantaneous breakthrough curve is reconstructed using a kernel-
498 based method [15]. The result of the TDRW simulation are compared with the
499 breakthrough curve obtained using PFLOTRAN at a distance of 2.5 m from
500 the inlet (Figure 11).
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505 The results of the exercise are shown in Figure 12. The small fluctuations
 506 observed in the MARFA solution at late times are related to statistical noise
 507 intrinsic in particle-based Monte Carlo methods. Yet, the agreement between
 508 the breakthrough curve computed with MARFA and the synthetic solution ob-
 509 tained with PFLOTRAN is very good, which indicates that the heterogeneous
 510 signal observed at *lab-scale* and affected by heterogeneous retention can be ex-
 511 tracted and successfully convoluted at larger scale. This evidence motivates the
 512 development of a parameteric upscaling strategy (next sub-section) that has
 513 a broader application and is not only limited to pathlines with fixed fracture
 514 aperture.

5.3. Upscaling strategy II: three parallel pathway model (TPPM)

521 Different analytical solutions were derived for f_{ret} [e.g. 3, 4, 16]. Here we will
 522 use the simplest solution, which is based on the assumption of a homogeneous
 523 infinite matrix [3] and which expresses the retention time distribution as
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$$525 f_{ret} = \frac{\mathcal{H}(t_{ret})\kappa\beta}{2\sqrt{\pi}t_{ret}^{3/2}} \exp\left(\frac{-\kappa^2\beta^2}{4t_{ret}}\right) \quad (6)$$

526 where $\mathcal{H}()$ is the Heaviside function. In Equation 6, κ [(m²/y)^{0.5}] is a ma-
 527 terial parameter group defined as $\kappa = \phi\sqrt{D_e R} = \sqrt{D_p}\phi^3 R$.

528 We assume here that mass discharge at the fracture outlet is the linear
 529 combination of three parallel pathways:

$$530 f_{tran}(t) = \alpha f_{tran}^{ns}(t) + \beta f_{tran}^{ms}(t) + \gamma f_{tran}^{hs}(t) \quad (7)$$

531 where f_{tran} is defined as in Equation 3 and α , β and γ [-] are three coefficients
 532 that provide the relative amount of mass that is routed through each of the three
 533 pathways. Mass conservation is ensured by setting

$$534 \alpha + \beta + \gamma = 1 \quad (8)$$

535 The three pathways are characterised by the same transport resistance, while
 536 κ varies as each pathway is characterised by different retention properties: in the
 537 non-sorbing pathway (superscript *ns*) there is no sorption (R=1), in the mildy
 538 sorbing pathway (superscript *ms*) retardation is equal to half of the retardation
 539 in the mineral grains (R=R_g/2) whereas in the highly sorbing pathway (super-
 540 script *hs*) R=R_g. The corresponding retention time distributions are defined as
 541 f_{ret}^{ns} , f_{ret}^{ms} and f_{ret}^{hs} . No mass exchange is considered between pathways.

542 Before discussing details of the upscaling approach, it is worthwhile noting
 543 that evidence of a similar composite behaviour of the heterogeneous rock ma-
 544 trix has been found in different laboratory and field experiments [46, 47, 19].
 545 Moreover, Iraola et al. [13] recently used a two-parallel pathways model to qual-
 546 itatively interpret results of the LTDE-SD experiment whereas Trincherio et al.
 547 [48] pointed out that the transport of oxygen in a granitic rock is characterised
 548 by a composite behaviour, with the average oxygen penetration profile being

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567 the result of multiple parallel diffusive pathway characterised by different “re-
568 activity”.

569 The three-parallel pathway model (TPPM) was implemented in MARFA
570 using a conditional sampling scheme explained in detail in Appendix A.

571 The models used in this upscaling exercise are analogous to that used in
572 section 5.2 and illustrated in section 5.1, however here different mineral distri-
573 butions are considered, which span from $p = 0.04$ to $p = 0.5$; i.e. respectively
574 4% and 50% of sorbing mineral volume fraction. The exercise is carried out
575 using a stepwise approach:
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- 577 • Step 1 (calibration): the breakthrough curves of the *lab-scale* experiments
578 are best fitted using MARFA and the TPPM. A single segment is used
579 and the best fit is performed by mean squared error minimisation.
- 580 • Step 2 (validation): for each considered mineral distribution, the coeffi-
581 cients estimated in step 1 are used to run a MARFA calculation with the
582 TPPM and 10 equally spaced segments. The results of step 2 are com-
583 pared with the breakthrough curves obtained using PFLOTRAN and the
584 related mineral distribution at a distance of 2.5 m from the inlet.

585 The results of step 1 are shown in Figure 13 and the coefficients estimated
586 for each considered mineral distribution are plotted in Figure 14. The TPPM
587 model describes well the *lab-scale* breakthrough curves, which indicates that,
588 consistently with what was observed in previous studies [e.g. 12, 13, 48], the
589 medium indeed behaves as a composite system. Until a volume fraction of the
590 sorbing mineral of around 15%, the system is fairly well approximated by a
591 dual parallel pathway model built as a linear combination of the non-sorbing
592 and the mildly sorbing pathway. For a higher amount of sorbing mineral, an
593 additional degree of freedom (i.e. the highly sorbing pathway) is needed to
594 properly capture the composite behaviour of the medium.

595 The results of step 2 are shown in Figure 15. Slight differences between the
596 PFLOTRAN and MARFA solutions are observed in the rising limb of the break-
597 through curve computed for a very low amount of sorbing mineral ($p = 0.04$).
598 For all the other breakthrough curves, the agreement between the synthetic ex-
599 periment and the upscaled solution is very good. This suggests that, as already
600 observed in section 5.2, when the signal of a *lab-scale* experiment affected by
601 heterogeneous retention is properly captured, it can then be successfully prop-
602 agated along the pathway to describe the signal over a much larger scale.

603 6. Large-scale modelling

604 6.1. Models with constant transport properties

605 In sections 5.2 and 5.3 we have demonstrated that the signal observed in a
606 tracer test analysed at *lab-scale* and affected by heterogenous retention can be
607 extracted and propagated over larger scales. In this section, we take advantage
608 of this methodological approach to investigate the effect that heterogeneous
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409 retention in the matrix, due to the sparse availability of sorption sites, has
410 on radionuclide transport at *site-scale*; i.e. the scale of interest in a safety
411 assessment study for a deep geological repository for nuclear waste.

412 We consider a pathline of 250 m length constituted by 1000 fracture seg-
413 ments of 0.25 m length. Each fracture segment and the surrounding matrix are
414 described by the parameters in Table 4. It is also assumed that the amount
415 of sorbing mineral is $p = 0.16$. The propagation of the heterogeneous signal is
416 done using TPPM. Notice that analogous results have been obtained using the
417 DS approach (results are not shown here for the sake of brevity).

418 The heterogeneous breakthrough curve is compared with three homogeneous
419 calculations: one, where no sorption is included, a second, where homogeneous
420 retention is set with $R=1,600$, and a third with $R=250$ (i.e. $K_d = K_d^g \cdot p$) in the
421 whole matrix. The comparison of the different breakthrough curves is shown in
422 Figure 16. At large-scale the heterogeneous signature is no longer evident. As
423 already noticed in the previous sections, the breakthrough curve computed with
424 the homogeneous model and with $R=1,600$ (i.e. retardation equal to retardation
425 in the pure mineral phase) strongly overestimates the retardation capacity of
426 the matrix. Interestingly, the heterogeneous breakthrough curve is very well
427 described by a model where the distribution coefficient in the pure mineral
428 phase is scaled by the mineral volume fraction.

6.2. Spatial persistence of the heterogeneous signature

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430 We have discussed earlier that, at small scale, the sparse distribution of
431 mineral grains leads to a heterogeneous signature, which affects the early part
432 (rising limb) of the breakthrough curves of sorbing radionuclides. At large scale
433 the deviation from the homogeneous-based solution is smoothed out. We aim
434 at assessing here the spatial persistence of this heterogeneous signature. To
435 this end, the five different mineral distributions of section 5.3 are considered
436 (i.e. $p = 0.04$ to $p = 0.5$). For each mineral distribution the TPPM model
437 is run with the related coefficients (see Figure 14) along a pathline made up
438 of N equally time spaced segments, each segment being equal to the *lab-scale*
439 model of section 5.1. These models are here denoted as *heterogeneous models*.
440 A corresponding homogeneous calculation (*homogeneous model* from now on)
441 was also run with $K_d = K_d^g \cdot p$ and the relative difference in the first arrival
442 time was computed as $(t_{hom} - t_{het})/t_{het}$ where t_{hom} and t_{het} [T] is the time
443 when 1% of the total injected mass reaches the considered segment outlet for
444 the homogeneous and heterogeneous model, respectively.

445 Figure 17 shows the relative error in the estimate of the first arrival time as
446 a function of cumulative β , for the five considered mineral distributions. It is
447 interesting to notice that, for a high amount of sorbing mineral (e.g. $p = 0.5$),
448 the homogeneous model largely over-predicts the first arrival time at small scales
449 but the solution approaches the homogeneous breakthrough curves at relatively
450 short distances. For a small amount of sorbing mineral, the error at small scales
451 is lower but the spatial persistence of the heterogeneous signature is much longer;
452 e.g. errors above 20% for $\beta \leq 50,000$ y/m.

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453 At large scales the results of all the tested heterogeneous models approach
454 those of the equivalent homogeneous models, although a slightly negative error
455 is observed as the homogeneous model slightly under-predicts the early arrival
456 time; see e.g. the rising limb of the two curves in Figure 16.

457 The significance of biotite for the retention of potentially harmful radionu-
458 clides, particularly cesium (e.g., Cs-137 and Cs-135) and sodium, has been dis-
459 cussed early in this manuscript. At Forsmark biotite is found to be present in a
460 relatively low amount: e.g. from 0.8 to 8 vol% in granitic rock [32]. In the last
461 Swedish safety analysis for a deep geological repository for spent nuclear fuel
462 (SR-Site), typical values of cumulative β associated with failing canisters varied
463 from about $1.5 \cdot 10^4$ y/m to 10^5 y/m [49]. It turns out that the significantly
464 long persistence of the heterogeneous signature pointed out in this work might
465 have implications for calculations of radionuclide transport carried out at the
466 scale of a typical safety assessment study.

693 6.3. Models based on different transport classes

694 Radionuclide transport calculations carried out at the *site-scale* entail the
695 need to account for different rock types [32] that are characterised by specific re-
696 tention properties, which are in turn related to the different mineralogical prop-
697 erties of the considered lithological units [50]. This heterogeneity is typically
698 treated by defining a finite number of transport classes, with related retention
699 properties, that are sampled statistically conditioned on the lithological unit to
700 which the given fracture segment belongs [e.g. 51].

701 Here, the effect of longitudinal heterogeneity is assessed in an idealised way
702 by defining five simplified transport classes characterised by different amount of
703 sorbing mineral: TC1 with $p = 0.04$, TC2 with $p = 0.08$, TC3 with $p = 0.16$,
704 TC4 with $p = 0.32$ and TC5 with $p = 0.5$. The transport calculation is carried
705 along a pathline made up of 1000 equally time spaced segments, each segment
706 being equal to the *lab-scale* model of section 5.1. Furthermore, each segment
707 is related to one of the five transport classes and the TPPM is used, with the
708 coefficients shown in Figure 14.

709 The five different transport classes were distributed along the considered
710 transport pathway using a sequential indicator simulation that was carried out
711 with the computer code SGeMS [52]. Equal fractions of each transport class
712 were considered (i.e. 20% each), which gives an average amount of sorbing
713 mineral equal to $\langle p \rangle = 0.22$. A spherical isotropic semivariogram, with a
714 range equal to 10 m was used. An additional case was also included in the
715 analysis, in which the same proportion of transport classes was distributed in
716 an uncorrelated way along the pathway. The two resulting distributions of
717 transport classes are shown in Figure 18. The two models are here defined as
718 *correlated* and *uncorrelated* models.

719 In Figure 19, the breakthrough curve computed with the *correlated* model is
720 compared with the related breakthrough curves obtained using three different
721 homogeneous models: one where sorption in the matrix is assumed to be equal
722 to sorption in the pure mineral phase ($R = 1,600$), a second where no sorption
723 in the matrix is considered and a third where the distribution coefficient is

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735 scaled by the average mineral volume fraction: $K_d = K_d^g \cdot \langle p \rangle$ (i.e. $R = 352$).
736 Results are very similar to those already discussed in section 6.1: the model with
737 no sorption and the model with sorption equal to sorption in the pure mineral
738 phase, respectively, significantly underestimate and overestimate the retention
739 capacity of crystalline rocks. On the contrary, the equivalent homogeneous
740 model based on the distribution coefficient scaled by the average mineral volume
741 fraction (arithmetic mean) provides a good approximation to the heterogeneous
742 solution, although the rising limb of the curve is displaced to earlier times. A
743 similar slight underestimation of the early arrival was already discussed in the
744 previous section (see also Figure 17).

745 The results of the correlated and the uncorrelated heterogeneous models
746 were almost identical (results not shown here), which indicates that longitudinal
747 correlation in transport classes has a modest effect on radionuclide transport.
748 This finding provides support for the methodology employed in previous safety
749 cases to populate fracture segments with transport classes sampled statistically
750 without considering any spatial correlation [see e.g. 51].

751 7. Discussion

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753 Micro-characterisation studies, based on e.g. micro-computed tomography
754 or digital autoradiography, have pointed out that in granitic rocks sorbing min-
755 erals are sparsely distributed and this heterogeneous distribution leads to diffu-
756 sion patterns that differ from what is typically predicted by homogeneous-based
757 models. This heterogeneous behaviour has been observed in different in-situ dif-
758 fusion experiments.

759 The available experimental evidence has led us to formulate three research
760 questions (see section 2). Based on the results of this work, the following answers
761 can be given: (i) at small scale, the sparse distribution of sorption sites, which is
762 intrinsically related to the underlying micro-scale heterogeneity, has a significant
763 impact on diffusive patterns leading to heterogeneous breakthrough curves for
764 sorbing radionuclides, (ii) these heterogeneous breakthrough curves can be used
765 to infer non-parameteric retention time distribution functions or, alternatively,
766 to calibrate the parameters of a model based on parallel diffusive pathways that
767 account for the underlying micro-scale heterogeneity, and (iii) at large scale,
768 the heterogeneous breakthrough curves are smoothed out and the breakthrough
769 curves of sorbing radionuclides are well described by homogeneous solutions
770 based on equivalent distribution coefficients.

771 The proposed upscaling procedures are based on idealised segmented path-
772 ways characterised by constant hydrodynamic properties (i.e. τ and β). Real
773 fracture systems are obviously much more complex and might show strong con-
774 trasts in velocity and aperture between nearby fractures [e.g. 25]. Moreover,
775 fractures might have experienced different hydrothermal alteration events that
776 could have altered the properties of the rock matrix close the flowing fracture.
777 Therefore, additional work is needed to make the proposed framework applica-
778 ble to study contaminant transport in large-scale fractured media. A possible
779 approach would be to use a piecewise-approximation in which fracture segments

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542 are grouped into transport classes and the related RTD functions are derived
543 from reactive transport models as shown in section 5.1. A similar approach
544 based on transport classes was used in the in last Finnish safety assessment
545 study of Olkiluoto, the designated location for a repository of spent nuclear
546 fuel, to account for different radionuclide retention properties of different types
547 of rock matrices [53]. However, it is worthwhile pointing out here that one of the
548 main outcomes of this work is that at large-scale the heterogeneous and sparse
549 availability of sorption sites can be well described by an equivalent distribution
550 coefficient. This simple yet practical approach is of direct relevance for any
551 existing radionuclide transport model in fractured crystalline rock.

552 Another pending task is to elucidate the mutual interplay between fracture
553 internal aperture heterogeneity and heterogeneous retention which could be done
554 by combing theoretical models [e.g. 54] with direct simulations. The simulations
555 would focus on resolving both the complex topology of a real fracture and the
556 surrounding rock matrix, which in turn should include an explicit description
557 of the sparsely distributed sorption sites.

558 8. Summary and conclusions

559 In the first part of this work we have presented a detailed process-based
560 simulation of a radionuclide tracer test in a synthetic fracture-matrix system
561 to analyse the influence of micro-scale heterogeneity on breakthrough curves of
562 sorbing radionuclides. The results of the reactive transport simulations point
563 out that at small scale (e.g. the scale representative of a laboratory tracer test
564 experiment) the breakthrough curve is characterised by a shape that signifi-
565 cantly differs from homogeneous-based solutions, with a very early arrival and a
566 smooth slope of the tailing at intermediate times. This heterogeneous signature
567 is caused by the sparse distribution of sorption sites.

568 Starting from this evidence and using a formulation based on retention time
569 distributions we have provided two different upscaling strategies. The main
570 general conclusions can be summarised as follows:

- 571 1. The heterogeneous radionuclide breakthrough curve observed at small
572 scale (e.g. *lab-scale*) can be used to extract the radionuclide retention
573 time distribution in the matrix.
- 574 2. Using the retention time distribution extracted from point 1, the hetero-
575 geneous signal can be successfully propagated along larger scale.
- 576 3. At large scales (e.g. *site-scale*) the heterogeneous signature of the smal-
577 scale signal is smoothed out and the breakthrough curve is well approx-
578 imated by a homogeneous model in which the distribution coefficient of
579 the sorbing mineral grains is scaled by the mineral volume fraction.
- 580 4. The heterogeneous signature is shown to persist, particularly when the
581 sorbing mineral is present in low amount.

582 Changes in retention properties along a transport pathway have also been as-
583 sessed by defining simplified transport classes characterised by different amount

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584 of sorbing mineral. The results of these longitudinally heterogeneous models
585 have shown that, at large scale, the resulting radionuclide breakthrough curve
586 can fairly well be described by an equivalent homogeneous model based on the
587 distribution coefficient of the pure mineral phase scaled by the average amount
588 of sorbing mineral along the pathway. The spatial correlation of the different
589 transport classes along the transport pathway was shown to have a negligible
590 effect on the results.

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Parameter	Set 1	Set 2	Set 3
Length interval [mm]	5-20	4-5	1-2
Intensity I [m^{-3}]	0.60	100	500
Aperture [m]	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$
Intrinsic local tortuosity τ_D^l [-]	$\sqrt{5}$	$\sqrt{5}$	$\sqrt{5}$
Power law exponent a [-]	-2.6	-2.6	-2.6
Fracture centre orientation	Poisson	Poisson	Close to 4-5 mm set
Fracture normal vector orientation	Poisson	Poisson	Poisson

Table 1: Input data used to generate the heterogeneous matrix.

Groundwater composition	
pH	7.3
Total concentration (mol/L)	
Na^+	$3.3 \cdot 10^{-2}$
K^+	$6.1 \cdot 10^{-4}$
Ca^{2+}	$9.5 \cdot 10^{-4}$
Cl^-	$3.1 \cdot 10^{-2}$
SO_4^{2-}	$2.1 \cdot 10^{-3}$

Table 2: Chemical composition of the groundwater used in the reactive transport calculations.

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Reaction	Selectivity coefficients ($\log K$)
Planar sites	
$X^- + Na^+ \leftrightarrow NaX$	0.0
$X^- + K^+ \leftrightarrow KX$	2.3
$X^- + Cs^+ \leftrightarrow CsX$	2.0
Intermediate sites	
$X_{int}^- + Na^+ \leftrightarrow NaX_{int}$	0.0
$X_{int}^- + K^+ \leftrightarrow KX_{int}$	2.3
$X_{int}^- + Cs^+ \leftrightarrow CsX_{int}$	4.5
Frayed-edge sites	
$X_{FES}^- + Na^+ \leftrightarrow NaX_{FES}$	0.0
$X_{FES}^- + K^+ \leftrightarrow KX_{FES}$	2.5
$X_{FES}^- + Cs^+ \leftrightarrow CsX_{FES}$	8.0

Table 3: Cation exchange reactions and selectivity coefficients (Gaines-Thomas convention) [31].

Parameter	Value
Half fracture spacing (δ_m)	0.1 m
Half fracture aperture (δ_f)	$0.25 \cdot 10^{-3}$ m
Pore diffusion coefficient (D_p)	$3.5 \cdot 10^{-13}$ m ² /s
Matrix porosity (ϕ)	$1.0 \cdot 10^{-2}$
Rock density (ρ)	$3.0 \cdot 10^3$ kg/m ³
Fracture water volumetric flux ($\ \mathbf{q}_f\ $)	$1.0 \cdot 10^{-8}$ m/s

Table 4: Parameters for the single fracture-matrix system.

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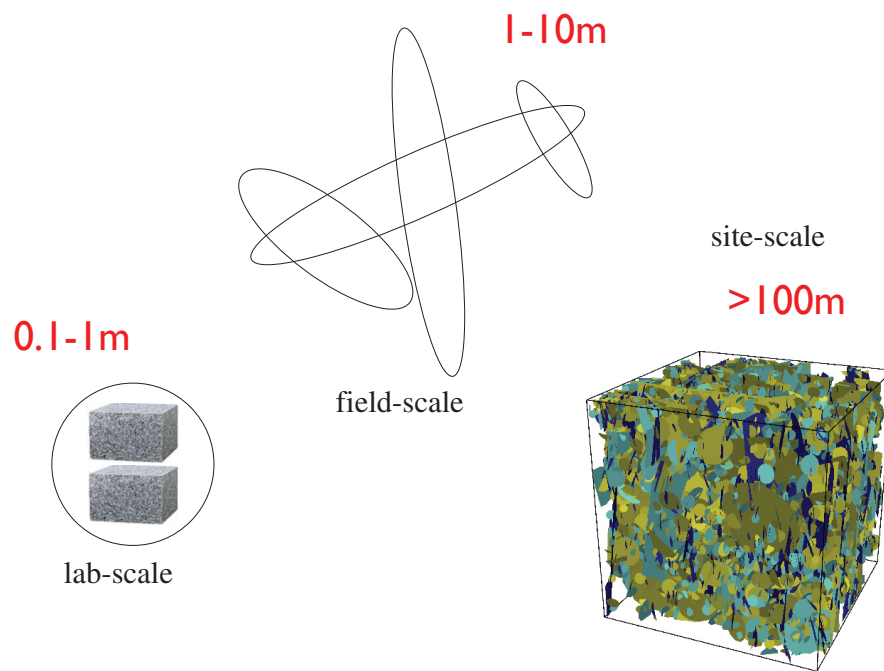


Figure 1: Sketch showing the different spatial scales considered when assessing radionuclide transport in fractured rock.

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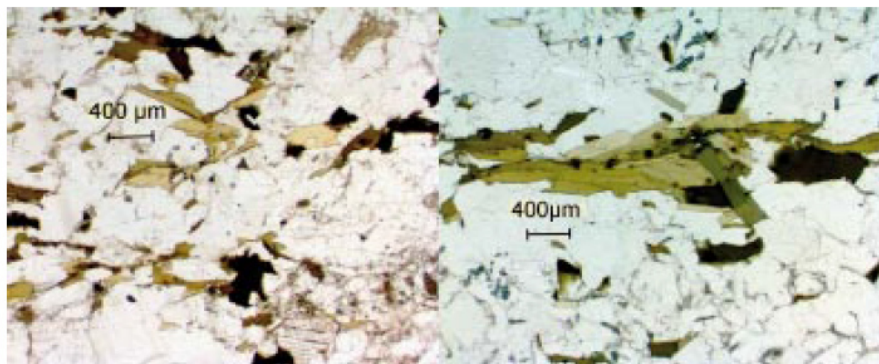


Figure 2: Photomicrograph of biotite crystals of normal size (left) and a larger aggregate of biotite crystals (right) in a rock sample taken from Forsmark (Sweden). All dark green to black minerals in the images are biotite crystals. Image reproduced with permission from Drake et al. [32].



Figure 3: (left) Autoradiography analysis of core D7.1 from borehole KA3065A03 and (right) photograph of the same core. The core was drilled and sampled after the finalisation of the Long Term Sorption Diffusion Experiment (LTDE-SD) at Äspö (Sweden). The basis of the slice is approximately 16 mm. The blackening on the autoradiograph represents radioactivity of primarily cesium ($Cs-137$). Figure reproduced with permission from Nilsson et al. [19].

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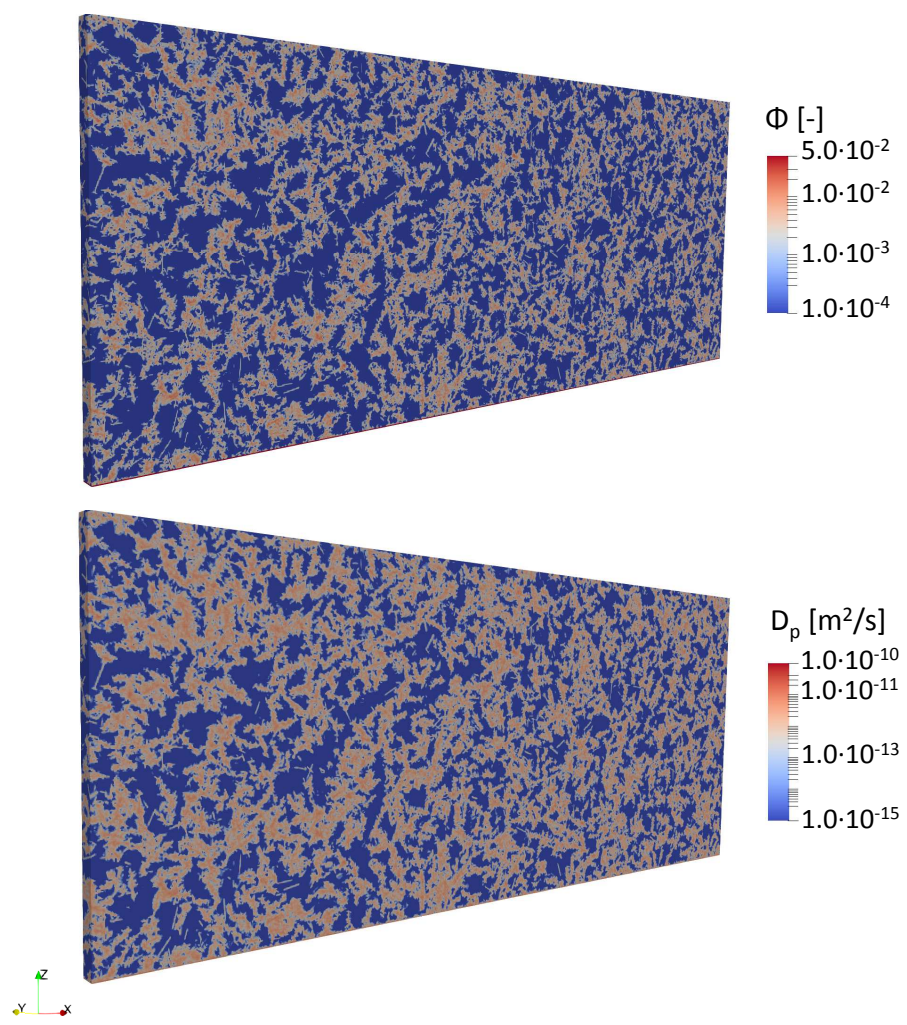


Figure 4: DFN-derived distribution of (top) porosity and (bottom) pore diffusivity as represented in the continuum model.

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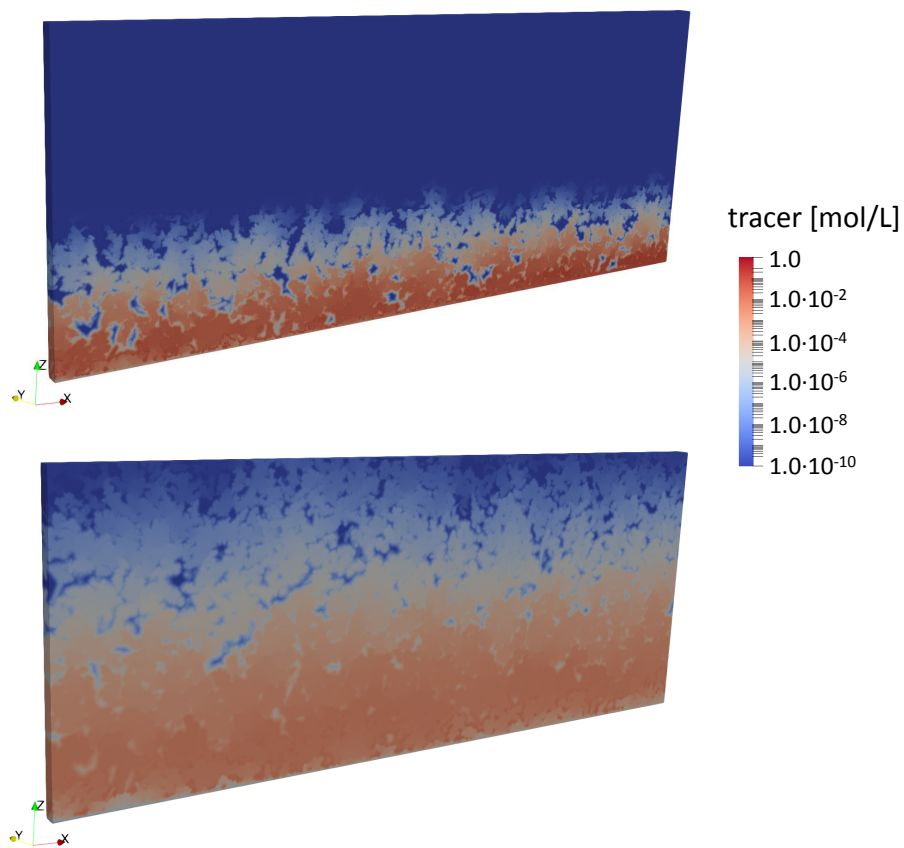


Figure 5: Snapshots of tracer concentration after (top) 1 yr and (bottom) 8 yr from the beginning of the injection.

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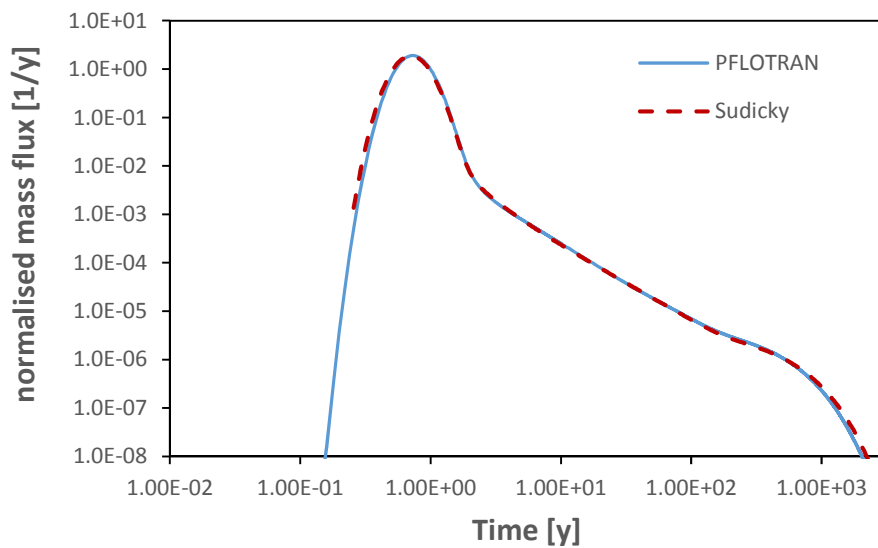


Figure 6: Breakthrough curve of a non-sorbing tracer computed with the “heterogeneous matrix model” (continuous line) and fit computed using equivalent parameters and Sudicky’s analytical solution [4] (dashed line).

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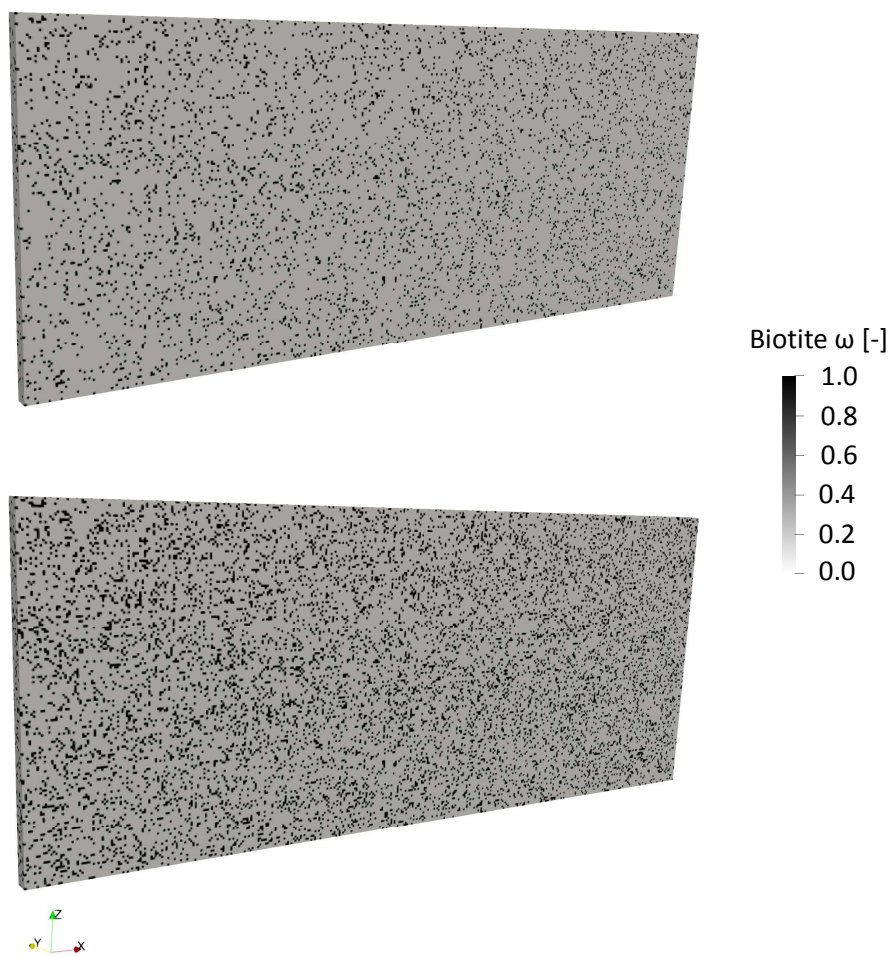


Figure 7: Biotite volume fraction for (top) MA, i.e. the model with 8% biotite and (bottom) MB, i.e. the model with 16% biotite.

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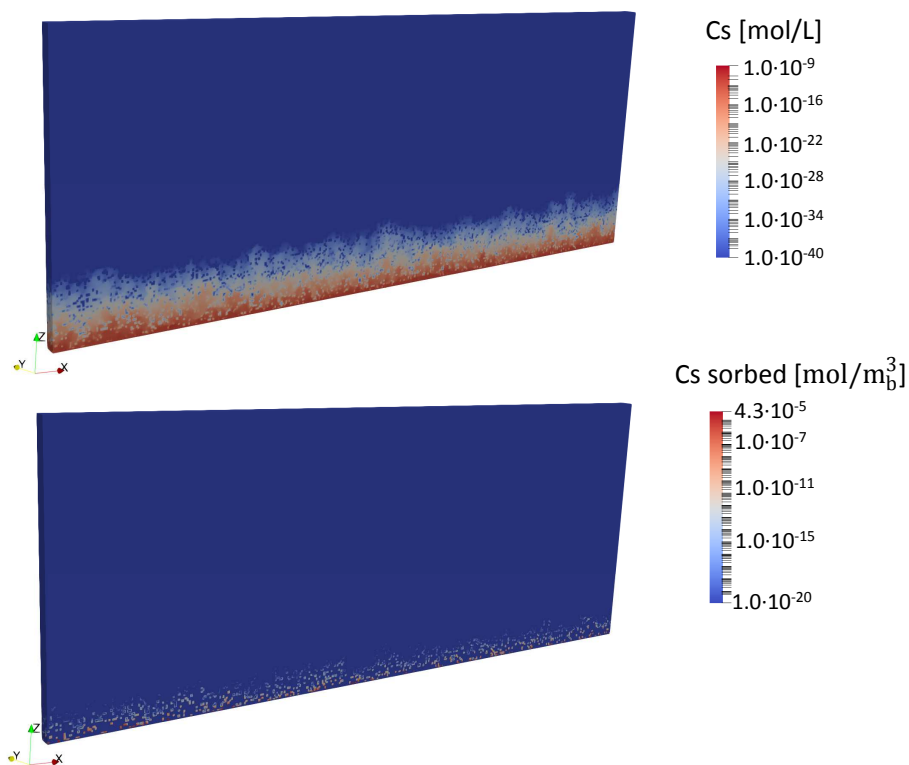


Figure 8: Snapshots of (top) cesium concentration and (bottom) cesium sorbed computed with MB after 30 yr from the beginning of the injection.

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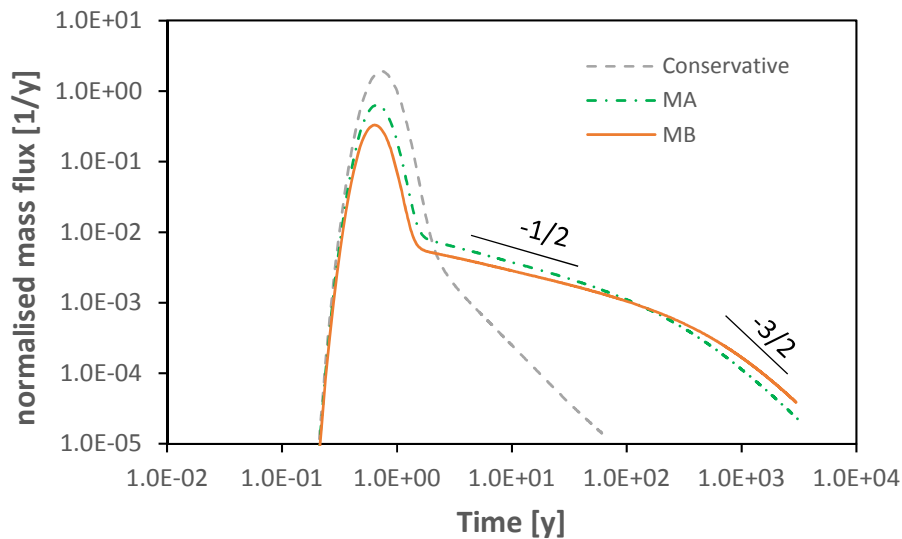


Figure 9: Cesium breakthrough curves computed with Model A (MA) and Model B (MB). The log-log slope of different parts of the tailings are also indicated.

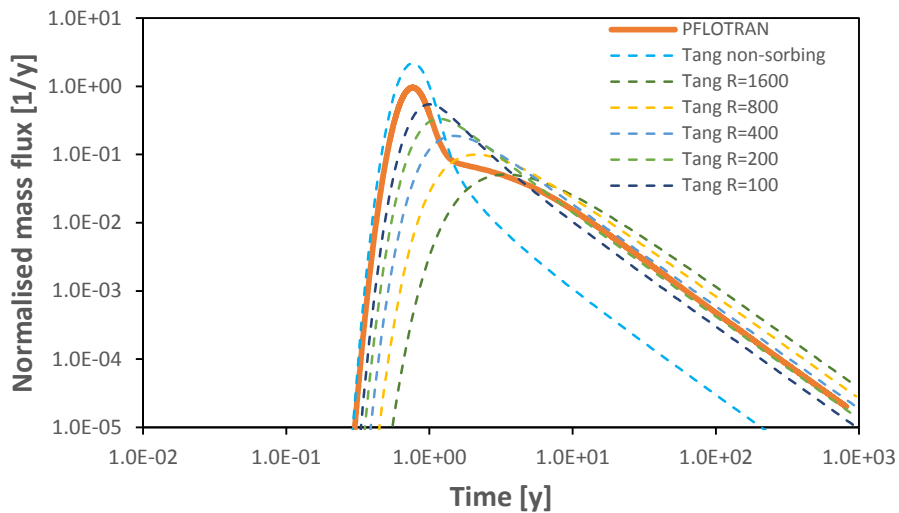


Figure 10: *Lab-scale* breakthrough curve (thick continuous orange line) computed with the 2D mineralogically heterogeneous model and with a bulk mineral volume fraction of the sorbing mineral $p = 0.16$. Homogeneous breakthrough curves computed using Tang's solution [3] and with different retardation values in the matrix are also shown.

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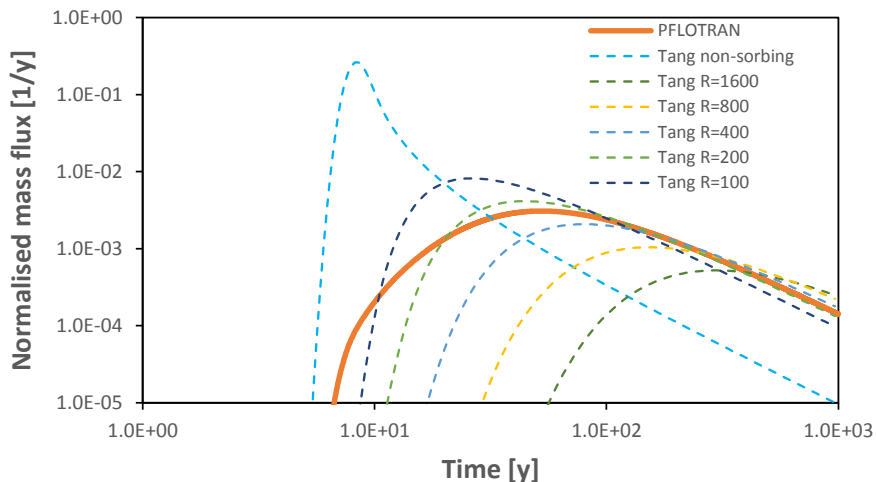


Figure 11: *Field-scale* breakthrough curve (thick continuous orange line) computed with the 2D mineralogically heterogeneous model and with $p = 0.16$. Homogeneous breakthrough curves computed using Tang's solution [3] and with different retardation values in the matrix are also shown.

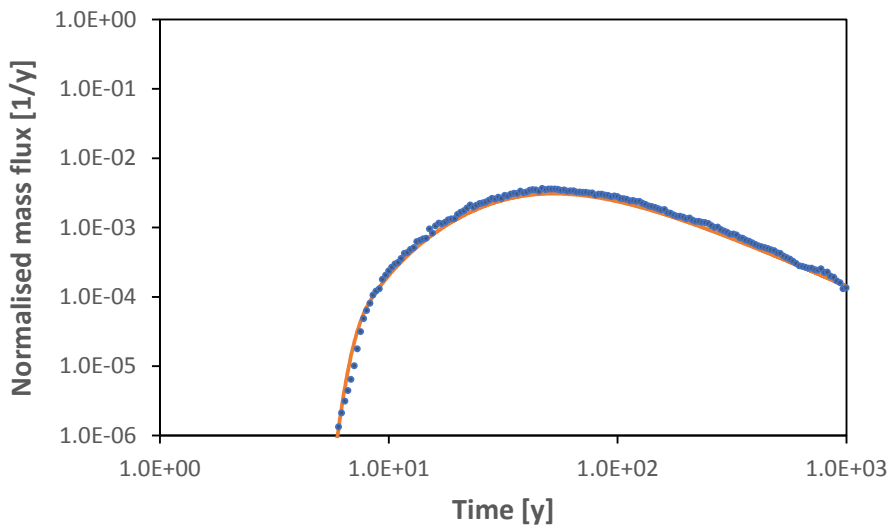


Figure 12: *Field-scale* breakthrough curve computed with (thick continuous orange line) PFLOTRAN and the 2D mineralogically heterogeneous model and with (blue dots) MARFA using the DS approach and 10 equally time-space segments.

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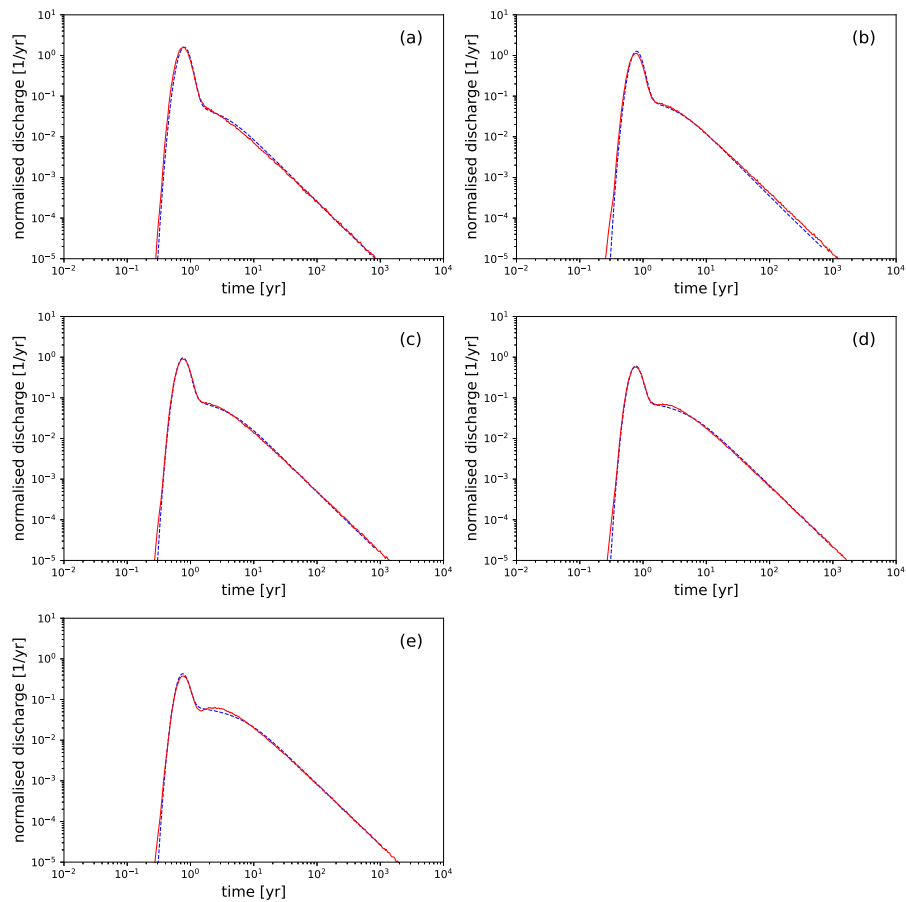


Figure 13: *Lab-scale* breakthrough curves computed with (dashed blue lines) PFLTRAN and with (continuous red lines) MARFA using the TPPM and a single segment. Different sorbing mineral volume fractions are considered; namely (a) $p = 0.04$, (b) $p = 0.08$, (c) $p = 0.16$, (d) $p = 0.32$ and (e) $p = 0.5$.

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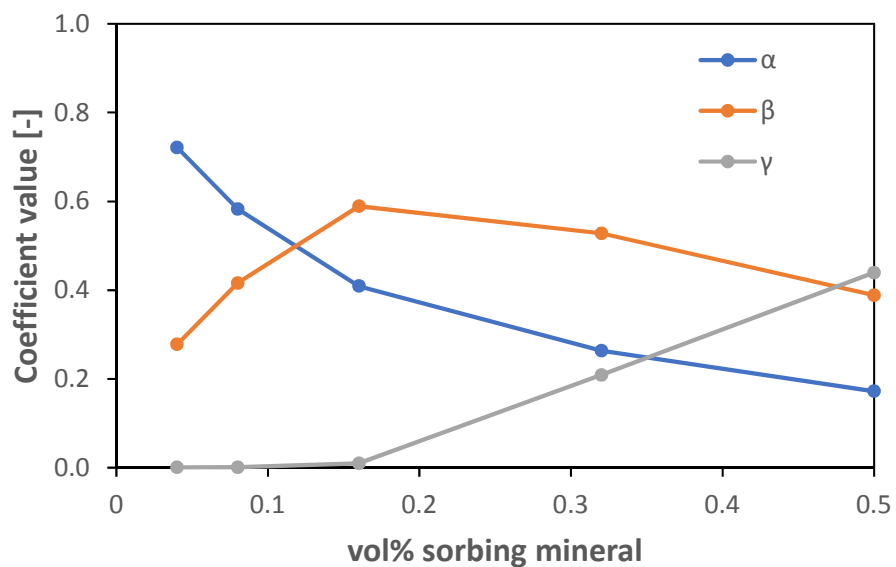


Figure 14: Coefficients of the TPPM estimated from the different *lab-scale* experiments (Figure 13).

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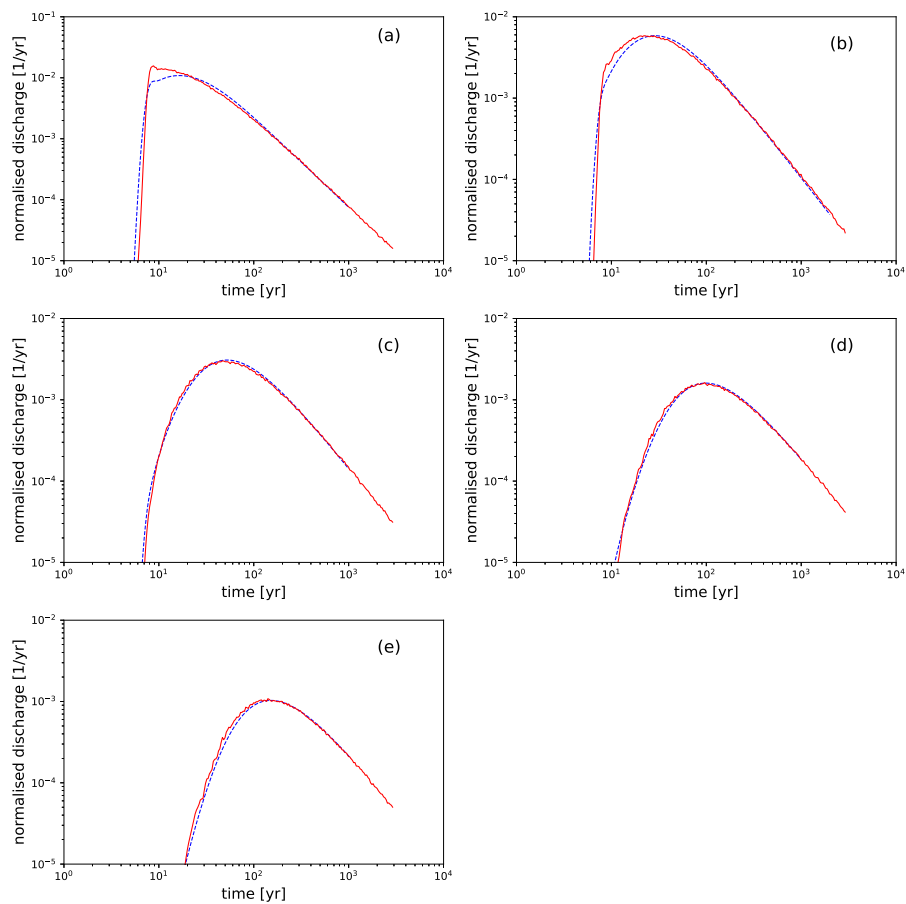


Figure 15: *Field-scale* breakthrough curves computed with (dashed blue lines) PFLOTRAN and with (continuous red lines) MARFA using the TPPM and ten equally spaced segments. Different sorbing mineral volume fractions are considered; namely (a) $p = 0.04$, (b) $p = 0.08$, (c) $p = 0.16$, (d) $p = 0.32$ and (e) $p = 0.5$. The coefficients of the TPPM used in the calculations are shown in Figure 14.

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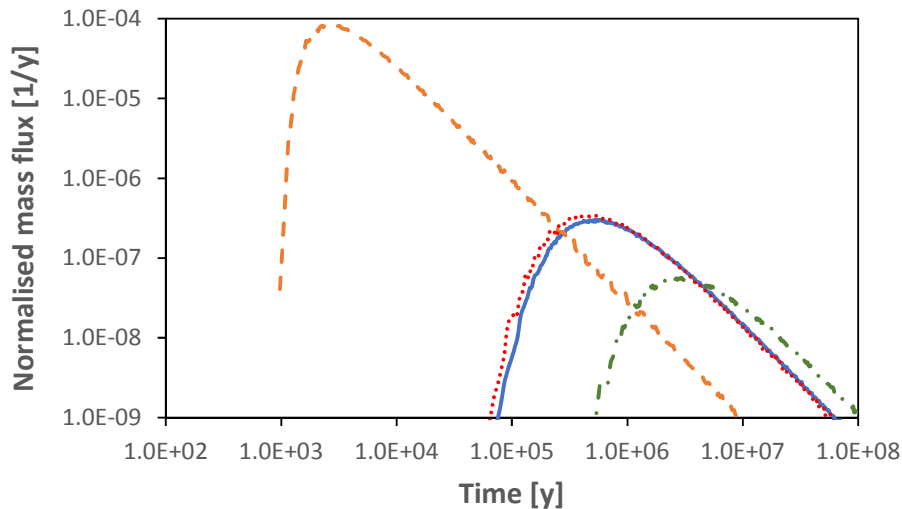


Figure 16: *Site-scale* models with constant transport properties. The heterogeneous breakthrough curve is computed with (continuous blue line) the TPPM and 1000 equally spaced segments (each segment of 0.25 m length) with $p = 0.16$. Homogeneous breakthrough curves computed with (orange dashed line) no sorption, (green dashed-dotted line) $R=1,600$ and (red dots) $R=250$ (i.e. $K_d = K_d^g \cdot p$) are also shown.

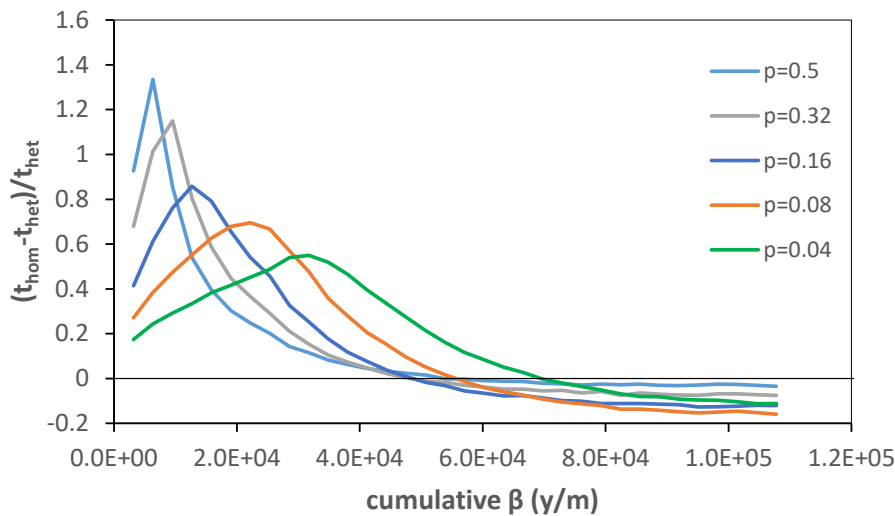


Figure 17: Relative difference between the first arrival time (1% of total injected mass) for the TPPM (t_{het}) and the equivalent homogeneous model (t_{hom}) for the five considered sorbing mineral volume fractions as a function of the cumulative transport resistance β .

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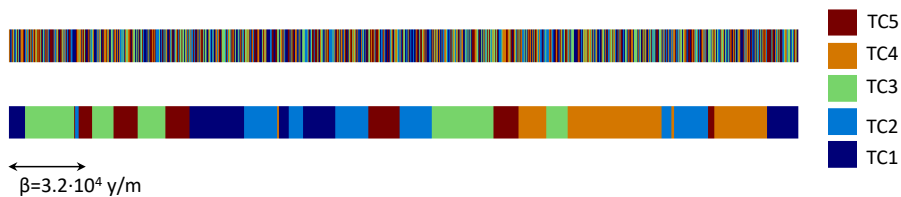


Figure 18: Distribution of the five transport classes for (top) the uncorrelated and (bottom) the correlated longitudinally heterogeneous model.

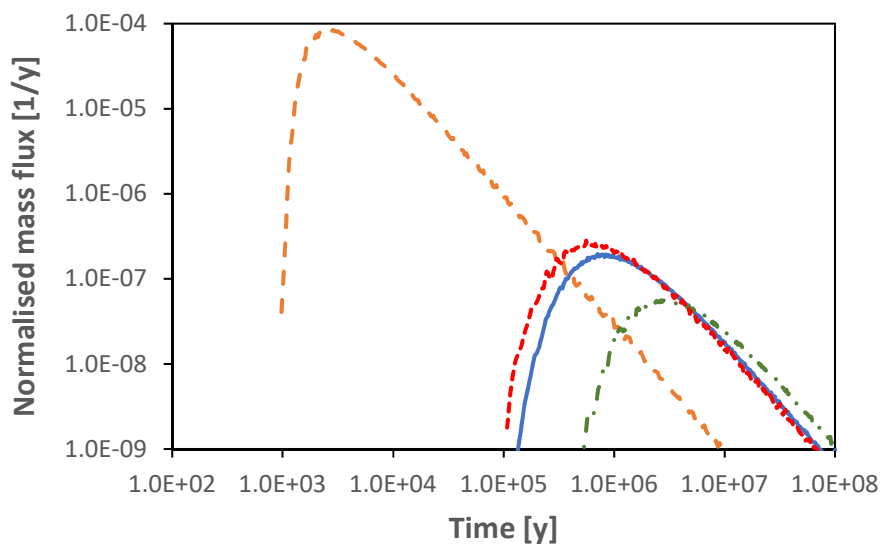


Figure 19: *Site-scale* models with different transport classes. The longitudinally heterogeneous breakthrough curve is computed with (continuous blue line) the TPPM and 1000 equally spaced segments (each segment of 0.25 m length) with the distribution of p shown in Figure 18 top. Homogeneous breakthrough curves computed with (orange dashed line) no sorption, (green dashed-dotted line) $R=1,600$ and (red dots) $R=352$ (i.e. $K_d = K_d^g \cdot \langle p \rangle$) are also shown.

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797 **Appendix A. Implementation of the TPPM in MARFA**

798 For each particle that is routed along a segment a random number is drawn,
799 $R \sim U([0, 1])$ and the conditional sampling is performed following the pseu-
800 docode listed below:

```
801 if  $R \leq \alpha$  then  
802      $f_{ret} = f_{ret}^{ns}$   
803 else if  $R \leq \alpha + \beta$  then  
804      $f_{ret} = f_{ret}^{ms}$   
805 else  
806      $f_{ret} = f_{ret}^{hs}$   
807 end if
```

808 The correct implementation of the conditional sampling scheme has been
809 verified by comparing the results of a MARFA transport calculation carried out
810 along a single segment with the results obtained using an analytical solution
811 based on Equations 6, 7 and 8 (results are not shown here for the sake of
812 brevity).