



# Modelling solute dispersion in periodic heterogeneous porous media: model benchmarking against intermediate scale experiments

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1 Modelling solute dispersion in periodic heterogeneous porous media:  
2 model benchmarking against intermediate scale experiments  
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9 **Abstract**

This paper is devoted to theoretical and experimental investigations of solute dispersion in heterogeneous porous media. Dispersion in heterogeneous porous media has been reported to be scale-dependent, a likely indication that the proposed dispersion models are incompletely formulated. A high quality experimental data set of breakthrough curves in periodic model heterogeneous porous media is presented. In contrast with most previously published experiments, the present experiments involve numerous replicates. This allows the statistical variability of experimental data to be accounted for. Several models are benchmarked against the data set: the Fickian-based advection-dispersion, mobile-immobile, multirate, multiple region advection dispersion models, and a newly proposed dispersion model based on pure advection. A salient property of the latter model is that its solutions exhibit a ballistic behaviour for small times, while tending to the Fickian behaviour for large time scales. Model performance is assessed using a novel objective function accounting for the statistical variability of the experimental data set, while putting equal emphasis on both small and large time scale behaviours. Besides being as accurate as the other models, the new purely advective model has the advantages that (i) it does not exhibit the undesirable effects associated with the usual Fickian operator (namely the infinite solute front propagation speed), and (ii) it allows dispersive transport to be simulated on every heterogeneity scale using scale-independent parameters.

10 **Keywords:** Solute transport, heterogeneous porous media, intermediate scale, Fickian behaviour,  
11 dispersion modelling.

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12 **1. Introduction**

13 In many circumstances, the classical Fickian operator fails to account correctly for the behaviour  
14 of solutes in heterogeneous porous media. The Advection-Dispersion (AD) model exhibits poor  
15 performance. Attempting to calibrate this model against field or laboratory data has been seen to  
16 lead to contradictory conclusions. Field scale dispersion data have been reported to yield a growing  
17 trend for the dispersion coefficient  $D$  with the scale of the experiment [25]. A number of laboratory

18 experiments, in contrast, indicate that no clear trend can be identified for the variations in  $D$  with  
 19 experiment scale. For instance, [58] report an increasing trend for the dispersion coefficient. In [39],  
 20 an increasing trend is found for  $D(x)$ , but the authors notice that this conclusion may be biased  
 21 by experimental noise. In [61], identifying a trend for the variations of  $D$  with distance is found  
 22 very difficult if not impossible. In [14], no scaling trend is identified for the dispersion coefficient,  
 23 even over short distances. More recently, laboratory experiments carried out on an artificial,  
 24 periodic porous medium [48] show that contradictory trends in  $D(x)$  can easily be inferred if  
 25 the breakthrough curves are not sampled with sufficient accuracy and the tracer experiments are  
 26 not replicated a sufficient number of times. Several models with scale-dependent dispersion have  
 27 been proposed in the literature [2, 40, 54, 55, 67, 68, 69, 70]. All these models have shown a  
 28 good ability to reproduce field- or laboratory-obtained experimental breakthrough curves via a  
 29 proper parameter tuning. This makes a benchmarking of their respective predictive capabilities  
 30 very difficult [22]. The following models have been used extensively for benchmarking against  
 31 experimental data sets.

32 The Fractional Advection-Dispersion (FAD) model builds up on the Continuous Time Random  
 33 Walk (CTRW) formalism [43, 49, 51]. FAD occurs when the motion of the solute molecules is  
 34 non-Brownian. Different behaviours may be obtained depending on the assumptions made on the  
 35 characteristic times and lengths of molecule jumps [43, 44, 41, 42]. In the presence of trapping  
 36 effects, an inverse power law asymptotic behaviour may be observed for the probability density  
 37 function of solute residence time in the porous media. This results in subdiffusive dispersion  
 38 processes, with a variance of molecule positions growing slower than time. Another type of non-  
 39 Fickian behaviour is that of Levy motion, whereby the characteristic time for particle motion is  
 40 finite, but the characteristic length of the jumps in molecule positions is infinite [6, 7]. The resulting  
 41 behaviour is called superdiffusion, with a variance of molecule positions growing faster than time.  
 42 All these models share the common feature that the governing equations incorporate fractional  
 43 derivatives with respect to time and/or space, hence the term "fractional". FAD models have  
 44 been tested against experimental data sets obtained from laboratory experiments [8, 13, 37, 45].  
 45 In [37] the best fit was obtained by making the dispersion parameters scale-dependent. In [62], a  
 46 FAD model was tested against in situ data obtained from experiments at the scale of 1m to 1km.  
 47 Comparisons with data observed at the metric scale [9] showed that time-varying fractional orders  
 48 of differentiation were essential in reconstructing the heavy tailing in the observed breakthrough  
 49 curves.

50 The Mobile-Immobile (MI) model [24, 64] is based on the assumption of a mobile region (where  
 51 the solute obeys a standard AD model) exchanging with an immobile region. The MI formalism  
 52 has been used to describe different physical settings. The simple structure of this model allows  
 53 analytical solutions to be obtained for a number of configurations [17, 31, 53, 65]. Several versions  
 54 of the MI model with a scale-dependent dispersion coefficient have been explored in [23]. The

55 best fit against the experimental laboratory results obtained in [38] was achieved for a dispersion  
56 coefficient varying exponentially with the travelled distance.

57 The Multiple Rate (MR) model [35] is a generalization of the MI model. Several immobile  
58 regions exchange with the mobile region according to different exchange rates. Increasing the  
59 number of regions and varying the exchange kinetics allows for anomalous diffusion processes to  
60 be reproduced via a proper distribution of the exchange rates between the mobile and immobile  
61 fractions [18].

62 Multiple Region Advection-Dispersion (MRAD) models have been proposed to account for the  
63 dispersion of solutes in heterogeneous soils in the presence of macropores, high- or low-permeability  
64 inclusions or several spatial scales of hydraulic heterogeneity. Note that the term MRAD is not  
65 the name given to these models by their authors but a term proposed by the authors of the  
66 present paper for the sake of terminology convenience. In these models, several different mobile  
67 regions, each having its own velocity fields and dispersion coefficient, exchange mass. Several  
68 closure models have been investigated for the exchange between the two regions. Although most  
69 applications include two mobile regions [1, 11, 12, 26, 27, 28, 34, 59], applications with three mobile  
70 regions have been reported [33]. Two region models have been tested against numerical experiments  
71 [11, 12, 16] and laboratory experiments [29, 30]. They are shown to become equivalent to a single  
72 region model with a Fickian behaviour (that is the AD model) in the limit of long times and travel  
73 distances [1, 16, 30]. Conversely, they are deemed more accurate than the AD model for small  
74 times and highly contrasted hydraulic properties [30].

75 All these models have shown a good ability to reproduce field- or laboratory-obtained experi-  
76 mental breakthrough curves via a proper parameter tuning. This makes a benchmarking of their  
77 respective predictive capabilities very difficult. As shown in [30], tracer tests involving a strong  
78 heterogeneity allow for a better model discrimination than tests involving weakly variable porous  
79 media. Moreover, pulse tracer tests are also deemed more discriminatory in terms of model re-  
80 sponse than step injection tests, especially for long time and/or travel distances [30]. However,  
81 most experiments report either step tracer tests [38, 39, 46, 52, 58, 61] or very long pulses that  
82 may be interpreted as a succession of two steps [56, 58, 30]. A few exceptions are reported in  
83 [30, 32, 63].

84 As shown in a previous publication [48], the AD, FAD and MI models with scale-independent  
85 parameters fail to account for the behaviour of experimental breakthrough curves at small space  
86 and time scales when the porous medium is strongly heterogeneous and periodic. Two main reasons  
87 were identified for this. Firstly, the size of the Representative Elementary Volume (REV) [5] is at  
88 least one order of magnitude larger than the spatial period of the Model Heterogeneous Porous  
89 Medium (MHPM). Dispersion models are not valid at spatial scales smaller than the REV size.  
90 Secondly, a Laplace analysis of the theoretical AD, FAD and MI modelled breakthrough curves [48]

91 shows that these models yields infinite signal propagation speeds. An infinite concentration wave  
 92 speed is clearly physically unrealistic. Besides, the finite propagation speed of the concentration  
 93 signal exerts a strong influence on the behaviour of the experimental breakthrough curves for small  
 94 times and distances [48], which explains that the above three models are more inaccurate for small  
 95 times and short distances than for long time and distances. That Fickian-based dispersion models  
 96 only seem to become more accurate as the spatial scale increases is only due to the fact that  
 97 the Peclet number increases with distance (therefore, dispersion, albeit modelled wrongly, has a  
 98 decreasing importance in the modelled signal) [48]. These conclusions are to be extended to the  
 99 FAD model with superdiffusive behaviour. Indeed, this model is obtained under the assumption of  
 100 heavy-tailed PDFs for the particle jump length [49], thus allowing for infinite particle velocities. A  
 101 conclusion of the study [48] is therefore that models where advective processes play a predominant  
 102 role should be expected to give better results than AD- and FAD-based models at small scales.

103 The experimental results in [48] also indicate that previously identified scale dependency of the  
 104 dispersion coefficient may easily be explained by the variability between the replicates of a same  
 105 experiment.

106 The objectives of the present paper are the following.

- 107 (i) Build a high-quality experimental database for Intermediate Scale Experiments (ISE) of dis-  
 108 persion of tracers in heterogeneous porous media. In [48] it was chosen to build a periodic  
 109 heterogeneous porous medium made of a series of 15 cm long columns enclosing high permeab-  
 110 ility conduits surrounded by single-sized glass beads. However, for a single period and two  
 111 periods, the results were biased by the influence of the inlet and outlet boundary conditions.  
 112 Consequently, experiments were meaningful for a minimum of three successive periods. In  
 113 the present work, the experimental setup was revised so that the experiments be meaningful  
 114 even for a single period.
- 115 (ii) Propose a model benchmarking methodology with an enhanced discriminatory power. Bear-  
 116 ing in mind the conclusions in [30], the proposed methodology consists in realizing a step  
 117 injection and using both the breakthrough curve and its time derivative to benchmark the  
 118 various models. Moreover, for each model, a single parameter set is used to reproduce the  
 119 experimental signal at all scales. This approach is retained because the ISE [48] shows that  
 120 there exists a model with scale-independent coefficients that allows the breakthrough curves  
 121 to be reproduced at all scales (although this model is unknown).
- 122 (iii) Benchmark the AD, MI, MR and MRAD models against the experimental breakthrough  
 123 curves and their time derivatives.
- 124 (iv) Determine whether a purely advective multiregion model can provide a viable alternative  
 125 to models embedding a Fickian or fractional Laplacian description of dispersion, with the

126 advantage that a purely advective model involves finite signal propagation speeds.

127 A brief description of the AD, MI, MR and MRAD models for the dispersion of tracers (that is, inert  
128 solutes not subjected to degradation, adsorption/desorption and the concentration of which does  
129 not influence the flow field) is given in Section 2 as well as the proposed Purely Advective Multiregion  
130 (PAMR) model. The experimental setup is described in Section 3. The model benchmarking  
131 procedure and experimental results are described respectively in Sections 4. Sections 5 and 6 are  
132 devoted to discussion and conclusions.

## 133 2. Models

### 134 2.1. The AD model

135 The simplest known model for passive solute transport in porous media is the Advection-  
136 Dispersion (AD) model. The governing equation is the following:

$$\partial_t c + u \partial_x c - D \partial_{xx} c = 0 \quad (1)$$

137 where  $c$  is the concentration,  $u$  is the flow velocity and  $D$  the dispersion coefficient. In the case of  
138 a constant input concentration at the upstream boundary, this model yields an S-shaped solution  
139 for the concentration and a gaussian-shaped for its derivative with respect to time.

### 140 2.2. The MI-MR model

141 The mobile-immobile (MI) model was first proposed in [64]. In what follows, owing to the  
142 assumption of passive transport, the adsorption/desorption terms are cancelled in the governing  
143 equations. Using the assumptions of constant water contents for the mobile and immobile regions,  
144 the governing equations are simplified into

$$\partial_t c_m + u \partial_x c_m - D \partial_{xx} c_m = \frac{k}{\Theta} (c_{im} - c_m) \quad (2a)$$

145

$$\partial_t c_{im} = \frac{k}{(1 - \Theta)} (c_m - c_{im}) \quad (2b)$$

146

$$\Theta = \frac{\theta_m}{\theta_m + \theta_{im}} \quad (2c)$$

147 where  $c_m$  and  $c_{im}$  are respectively the concentrations in the mobile and immobile regions,  $\theta_m$  and  
148  $\theta_{im}$  are respectively the water contents of the mobile and immobile regions,  $\Theta$  is the normalized  
149 water content of the mobile fraction, and  $k$  is the exchange rate constant between the mobile and  
150 immobile regions.

151 The MI model may be called a single rate model since it contains a single exchange rate constant  
152  $k$  between mobile and immobile regions. A generalization of the MI model, called the Multiple  
153 Rate (MR) model, was later proposed by [35]. In this model the mobile region can exchange

with multiple immobile regions, each having its own exchange rate constant  $k_j$ . Using again the assumption of passive scalar transport, normalizing the water contents of the mobile and immobile regions lead to:

$$\partial_t c_m + u \partial_x c_m - D \partial_{xx} c_m = \sum_{j=1}^N \frac{k_j}{\Theta} ((c_{im})_j - c_m) \quad (3a)$$

$$\partial_t (c_{im})_j = \frac{k_j}{\Theta_j} (c_m - (c_{im})_j) \quad j = 1, \dots, N \quad (3b)$$

Where  $N$  is the number of immobile regions with normalized water content  $\Theta_j$ , and  $k_j$  ( $j = 1, \dots, N$ ) are the multi-exchange rate constants between the mobile and the  $N$  immobile regions. For the sake of consistency, in this paper the MI and MR models designate the single-rate mobile-immobile model and the multi-rate mobile-immobile model respectively.

### 2.3. The MRAD model

The Multiple Region Advection-Dispersion (MRAD) model is based on the assumption of  $R$  regions flowing in parallel, exchanging mass according to linear kinetics [1, 11, 12, 26, 27, 28, 34, 59]. In each of these regions, the AD model is assumed valid. The original model allows for different heads in the various flow regions, thus allowing for water exchange between the regions in addition to solute exchange. In the present experiments, however, the upstream and downstream sections of each model column are connected to a single inflow and outflow pipe, thus making the head in all regions identical on the scale of the heterogeneity. Consequently, the hydraulic source term between the various regions is set to zero. Bearing in mind the assumption of passive scalar transport, any degradation or adsorption/desorption terms are set to zero. Normalizing the water contents as in the previous subsection leads to the following governing equations:

$$\partial_t c_i + u_i \partial_x c_i - D_i \partial_{xx} c_i = \sum_{j \neq i}^R \frac{k_{ij}}{\Theta_i} (c_j - c_i), \quad i = 1, \dots, R \quad (4a)$$

$$k_{ij} = k_{ji} \quad \forall (i, j) \quad (4b)$$

$$\Theta_i = \frac{\theta_i}{\sum_{j=1}^R \theta_j}, \quad \sum_{i=1}^R \Theta_i = 1 \quad (4c)$$

and the total concentration in the porous medium is defined as

$$c(x, t) \equiv \sum_{i=1}^R \Theta_i c_i(x, t) \quad (5)$$

As mentioned in the introduction, most applications involve  $R = 2$  regions, with the exception of [33] where  $R = 3$  and  $k_{ij} \neq 0$  only for  $j = i \pm 1$ . As shown in Appendix A, the variance  $c^{(2)}$  of the solute particle locations obeys the following equation

$$d_t c^{(2)} = \sum_{i=1}^R \Theta_i \left( v_i c_i^{(1)} + 2D_i \right), \quad v_i \equiv u_i - \sum_{j=1}^R \Theta_j u_j \quad (6)$$

179 where  $c_i^{(1)}$  is the average abscissa of the particle locations in the region  $i$ , obeying

$$d_t c_i^{(1)} = v_i + \sum_{j \neq i} \frac{k_{ij}}{\Theta_i} (c_j^{(1)} - c_i^{(1)}) \quad (7)$$

180 As shown in AppendixB (Result 3), all the  $c_i^{(1)}(t)$  tend to a limit value  $c_i^{(1,\infty)}$  as  $t$  tends to infinity  
 181 provided that the vector  $\mathbf{v} \equiv [v_1, \dots, v_R]$  belongs to the range of the matrix  $\mathbf{M}$  defined as

$$M_{ij} = \begin{cases} -\sum_{p \neq i} \frac{k_{ip}}{\Theta_i} & \text{if } i = j \\ \frac{k_{ij}}{\Theta_i} & \text{if } i \neq j \end{cases} \quad (8)$$

182 If this is the case,  $d_t c^{(2)}$  tends to a finite, limit value for long times, which is a Fickian (or "normal")  
 183 behaviour. The limit value of the dispersion coefficient is shown to be (AppendixA)

$$D_\infty = \sum_{i=1}^R \Theta_i \left( D_i + \frac{1}{2} v_i c_i^{(1,\infty)} \right) \quad (9)$$

184 If the vector  $\mathbf{v}$  does not belong to the range of  $\mathbf{M}$ , the  $c_i^{(1)}$  do not converge and a superdiffusive  
 185 (anomalous) behaviour is obtained.

186 A direct consequence of the above property is the following (AppendixB, Result 4): if  $r$  regions  
 187 exchange mass with each other but do not exchange mass with the  $R - r$  remaining regions, all  
 188 regions can be renumbered in such a way that  $k_{ij} = 0$  for  $(i, j) \in \{1, \dots, r\} \times \{r + 1, \dots, R\}$ . Then,  
 189 the matrix  $\mathbf{M}$  is block-diagonal and a necessary condition for the asymptotic behaviour of the  
 190 dispersion process to be Fickian is that the average speed of the first  $r$  regions be the same as that  
 191 of the remaining  $R - r$  regions. If  $\sum_{i=1}^r \Theta_i u_i \neq \sum_{i=1}^R \Theta_i u_i$ , the  $c_i^{(1)}(t)$  are not all bounded and a  
 192 superdiffusive asymptotic behaviour is obtained.

#### 193 2.4. Purely Advective Multiple Region (PAMR) model

194 The PAMR model proposed in this paper is based on the consideration that dispersion is  
 195 a purely advective process on the microscale. The Fickian model arises only as an asymptotic  
 196 property of Brownian movement [19, 20, 21, 43, 49] that is valid for a large number of solute  
 197 particle displacements (in other words, for large space and time scales compared to the typical  
 198 duration and length of the Brownian motion jumps). Although the term "Brownian" was originally  
 199 used to designate the movement of small particles suspended in fluids, its meaning has broadened  
 200 with time. The adjective "Brownian" is widely used as an equivalent to "Wiener process", a  
 201 continuous but non-differentiable [10] random process with zero mean and variance proportional  
 202 to time. Generalizing the concept has led to that of fractional Brownian motion, a useful concept  
 203 for anomalous diffusion modelling [49]. The application fields may be totally disconnected from  
 204 physics, as in e.g. financial mathematics. The first mathematical formalization of Brownian motion  
 205 is attributed to Bachelier, with his thesis on the mechanisms of stock exchange [3]. Bearing this in



206 mind, the term "Brownian" is used in the present paper to designate a Markovian random particle  
 207 displacement process. The Brownian character of solute movement in random, heterogeneous  
 208 media is easily justified by considering the individual trajectories of solute molecules, that are  
 209 assumed to travel at the same velocity as the surrounding fluid molecules (Figure 1a). If the pores  
 210 of the medium are assumed to have random and isotropic orientation, size and spacing, the velocity  
 211 field can also be assumed random at the scale of the grains/pores. Consequently, the cumulated  
 212 movement of the fluid molecules in a coordinate system moving at the average fluid velocity may  
 213 be considered random at this scale (Figure 1). Given the random pore orientation, the direction of  
 214 the movement of a particle is totally uncorrelated from one pore to the next. This corresponds to  
 215 the mathematical definition of the standard Brownian motion, whereby the particle displacement  
 216 is (i) an isotropic, random function of space (ii) a Markov process that assumes zero correlation  
 217 between successive Brownian displacements. If the medium is not totally random, however, the  
 218 Brownian assumption may not hold any more. A structured medium exhibits a certain degree of  
 219 periodicity (Figure 1c). Such periodicity may be encountered at the scale of the pore. It may  
 220 also arise at much larger scales, as in the case of e.g. low permeability lenses in an aquifer. In  
 221 such a case, the flow field cannot be considered totally random. Therefore, the cumulated particle  
 222 displacements in the coordinate system moving at the average flow velocity are also periodic to  
 223 some extent (Figure 1d).

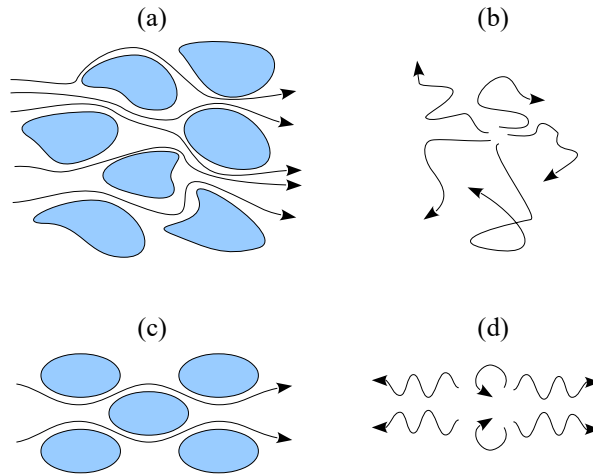


Figure 1: Solute dispersion as the result of a Brownian process. Random heterogeneous medium: (a) solute particle trajectories in the laboratory reference frame, (b) trajectories plotted in the coordinate system moving at the average solute speed. Periodic medium: (c) trajectories in the laboratory coordinate system, (d) trajectories in the coordinate system moving at the average solute speed.

224 In the extreme, totally periodic case of Figures 1c-d, the cumulated (relative) particle displace-  
 225 ments are totally periodic, with a maximum vertical amplitude equal to one half of the vertical  
 226 spatial period. Some particles travel to the left because they are slower than the mean flow velocity  
 227 on the average. Some other particles travel to the right because their average velocity is larger  
 228 than the mean flow velocity. However, despite their diverging character, the trajectories of the  
 229 particles remain deterministic because the medium is strictly periodic. One may expect a certain

amount of randomness in these trajectories because of molecular diffusion, but a long time may be necessary for the random component of the movement to predominate over the deterministic component. Real-world situations, including the experiments reported in the present paper, lie somewhere between these two extreme configurations. In the light of the considerations above, a conceptually satisfactory scale-independent model for dispersion should be expected to satisfy the following two requirements.

(R1) No Fickian fluxes should be included in the governing equations. This requirement stems from the reasoning that (i) the simplest possible scale-independent dispersion model is sought, (ii) the Fickian model has been shown in [48] to yield undesirable behaviours for small times and travel distances, (iii) consequently, Fickian fluxes must be ruled out. As far as point (ii) is concerned, the Fickian model yields infinite wave propagation speeds for the modelled solute front, an unphysical behaviour yielding zero arrival times in solute breakthrough experiments. In contrast, the delay between the inlet and the outlet was pointed out as an essential feature of the experimental breakthrough curves reported in [48].

(R2) The model should yield the Fickian behaviour as a limit, asymptotic case for large times and distances. Such a behaviour has indeed been confirmed experimentally in the case of homogeneous media, as well as periodic heterogeneous media provided a sufficient number of periods is covered [48].

The conceptual model proposed hereafter aims to fulfill these two requirements, based on the following two assumptions.

(A1) The flow velocity within an averaging volume is partitioned into  $R$  regions over which the flow velocity is homogeneous. The flow region  $i$  has a normalized water content  $\Theta_i$ ,  $\sum_{i=1}^R \Theta_i = 1$ . Under steady state flow conditions, the normalized water contents  $\Theta_i$  and the flow velocities  $u_i$  are constant and uniform.

(A2) Two adjacent regions may exchange solute particles owing to the random velocity distribution within the porous medium (Figure 1b). Consequently, the concentrations within two adjacent regions tends to even out with time. The solute exchange rate between two regions is assumed proportional to the difference between the solute concentrations in the two regions.

Assumptions (A1-2) lead to the following governing equation:

$$\partial_t (\Theta_i c_i) + \partial_x (\Theta_i u_i c_i) = \sum_{j \neq i} k_{ij} (c_j - c_i), \quad i = 1, \dots, R \quad (10)$$

The advective part of the model (left-hand side of the equation) stems from assumption (A1). The source term (right-hand side of the equation) is the simplest possible formulation satisfying assumption (A2).

262 A first advantage of this model over those reported in the previous subsections is that it satisfies  
 263 the two requirements (R1-R2). Indeed, the transport term in equation (10) is purely advective,  
 264 thus satisfying (R1). Moreover, the Fickian model is obtained as a limit case for asymptotically  
 265 long times and travel distances. This is easily shown by noticing that the model (10) is a particular  
 266 case of the MRAD model (4a). Equation (10) is obtained by setting  $D_i = 0$  in equation (4a) and  
 267 replacing  $\frac{k_{ij}}{\Theta_i}$  with  $k_{ij}\Theta_i\Theta_j$ . As shown by equation (9), a finite dispersion coefficient  $D_\infty$  may be  
 268 obtained even though the coefficients  $D_i$  are all zero. A sufficient condition for this is that the  
 269 vector  $v$  belong to the range of  $\mathbf{M}$  (see Appendices A-B for the details of the derivation).

270 Another interesting feature of the PAMR model is that it allows for (ballistic) anomalous  
 271 dispersion for small times, which is compatible with the apparent increase in the Fickian-based  
 272 dispersion coefficient with observation scale reported in a number of studies.

273 Therefore, the PAMR model is considered more satisfactory from a conceptual point of view  
 274 than the MRAD model because it does not have the drawbacks of Fickian dispersion models  
 275 for small times and/or distances, while retaining its advantages for large times and/or distances.  
 276 Nevertheless, the increased accuracy of the model for small times/distances is achieved at the  
 277 expense of model parsimony. As shown in AppendixA, at least two regions are needed to obtain an  
 278 asymptotic Fickian behaviour for dispersion. Then, the model has three independent parameters:  
 279 one of the normalized water contents  $\Theta_1, \Theta_2$ , one of the flow velocities  $v_1, v_2$  and the exchange  
 280 parameter  $k_{12}$ . In contrast, the AD model requires only two parameters (the flow velocity  $v$  and the  
 281 dispersion coefficient  $D$ ), for the same asymptotic behaviour. The increased number of parameters  
 282 was to be expected in that the Fickian behaviour is only an asymptotic property of the model.  
 283 The additional parameters control the characteristic time/distance above which Fickian behaviour  
 284 becomes a satisfactory approximation of the dispersion process.

### 285 3. Experimental setup and results

#### 286 3.1. Experimental setup

287 The MHPM consists of a PVC column (10 cm in diameter, 15 cm in length) containing a  
 288 cylindrical cavity (2.5 cm in diameter, 10 cm in length) placed in the centre of the column and  
 289 surrounded by 1 mm glass spheres. For more details about the construction of the MHPM, please  
 290 see [48]. The inflowing discharge is supplied using a peristaltic pump (Gilson MP3<sup>TM</sup>). Step  
 291 tracing experiments are done by injecting salty water (deionised water + NaCl at  $C_0 = 0.1\text{Mol/L}$ )  
 292 into the columns initially containing deionised water. A flow of 7.5 L/h salty water is induced into  
 293 the study column until the outlet concentration  $c$  stabilizes to  $C_0$ . The outlet concentration is  
 294 measured using a conductimeter (WTW TetraCon 325<sup>TM</sup>) and saved on a data logger (Campbell  
 295 CR1000<sup>TM</sup>) every 5 s. The cumulated outlet volume  $V$  is measured by weighing the effluent every  
 296 5 s and saved on the data logger. The study column consists of a series of  $N$  connected MHPM.

297 In this paper, six series were investigated with  $N = 1$  to 6. We used the 12 MHPM columns  
 298 described in [48]. For each series, four replicates of the step tracing experiment were conducted for  
 299 four  $90^\circ$  rotations of the study column. The purpose was to eliminate biases arising from possible  
 300 asymmetry in the column geometry and density effects. The various column combinations used for  
 301 the various experiments are summarized in Table 1. A mean breakthrough curve is deduced from  
 302 all the replicates.

$N$	$V_0$ (L)	$L$ (m)	Column groups	Total replicates
1	0.461	0.15	A, B, C, D, E, F, G, H, I, J, K, L	48
2	0.922	0.30	AB, CD, EF, GH, IJ, KL	24
3	1.383	0.45	ABC, DEF, GHI, JKL	16
4	1.844	0.60	ABCD, EFGH, IJKL	12
5	2.305	0.75	ABCDE, FGHIJ	8
6	2.766	0.90	ABCDEF, GHIJKL	8

Table 1: Experiment replicates.  $N$  is the number of columns,  $L$  is the total length of the porous medium,  $V_0$  is the pore volume.

303 The main difference between the present experimental setup and that in [48] is the MHPM  
 304 connection pattern (Figure 2). In [48], the first and last MHPM in the study column could not be  
 305 considered as periodical heterogeneities because they had different flow inlet and outlet connections  
 306 (Figure 2, top): the first MHPM had a divergent flow inlet and a parallel flow outlet while the  
 307 last MHPM had a parallel flow inlet and a convergent flow outlet. In the present experiment,  
 308 each MHPM of the study column can be considered as a single periodical heterogeneity because  
 309 all MHPM have identical inlet and outlet connections (Figure 2 bottom): a divergent flow inlet  
 310 and a convergent flow outlet. The advantage of the present setup is that the breakthrough curve  
 311 can be obtained directly for a single heterogeneity ( $N = 1$ ).

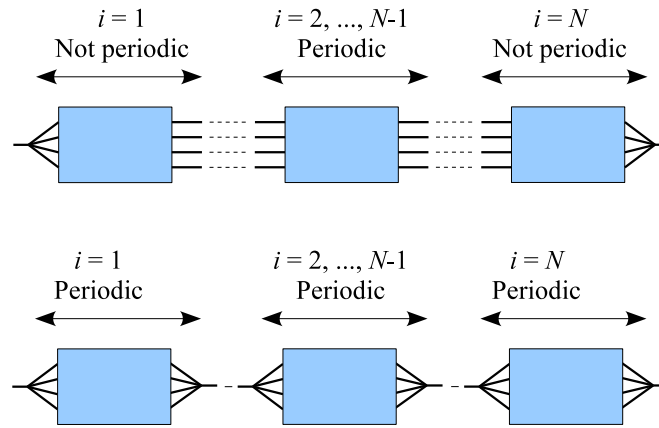


Figure 2: Definition sketch for column connection. Top: experimental setup reported in [48]. Bottom: present experimental setup.

### 312 3.2. Experimental breakthrough curves

313 Figure 3 shows the experimental breakthrough curves for  $N = 1$  to  $N = 6$  MHPM. As expected  
 314 from [48], the breakthrough concentration signal tends to the classical S-shaped solution of the AD

315 model as  $N$  increases. In the present experiments, this behaviour is achieved for fewer MHPMs  
 316 than in [48] ( $N = 5$  instead of 10). This is attributed to the different injection geometry (compare  
 317 Figure 2, top and Figure 2, bottom). Plotting the time derivative of the normalized concentration  
 318 signal allows two main transport modes to be identified. From the location of the peaks on Figure 3  
 319 for  $N = 1$ , the faster mode travels at approximately  $3 \times 10^{-3} \text{ ms}^{-1}$ , while the speed of the slower  
 320 one is approximately  $7 \times 10^{-4} \text{ ms}^{-1}$ . As time (and distance) grows, the relative amplitude of  
 321 the faster peak decreases and only one peak can be detected in the  $\partial c/\partial t$  signal for  $N = 5, 6$ .  
 322 Note that the time derivatives of the concentration signal for  $N = 1$  to 3 is strikingly similar to  
 323 experimental propagators obtained in heterogeneous porous media [50, 57] and replicated by pore-  
 324 scale modelling [10]. In contrast, the  $c(t)$  signal makes these two modes more difficult to detect,  
 325 even at early times. For this reason, the time derivative  $\partial c/\partial t$  of the concentration signal is used  
 326 all throughout this manuscript for model benchmarking.

327 The enhanced discriminatory power of the time derivative of the  $c(t)$  signal over the signal itself  
 328 should not come as a surprise. Since the injection signal is a concentration step, using its time  
 329 derivative  $\partial c/\partial t$  is equivalent to performing a breakthrough experiment using a Dirac (pulse) input  
 330 signal. From the point of view of the frequency domain analysis, the Laplace/Fourier transforms of  
 331 the Dirac signal gives an equal weight to all frequencies, while the Laplace/Fourier transform of the  
 332 step function is the inverse of the frequency, thus giving less importance to higher frequencies. Since  
 333 our earlier experiments [48] showed that high frequencies are essential in discriminating between  
 334 models, the Dirac injection should be preferred. Such an input signal, however, is extremely  
 335 difficult to generate with a good control on experimental conditions. Using the time derivative  
 336  $\partial c/\partial t$  with a step injection is an efficient way of obviating this difficulty.

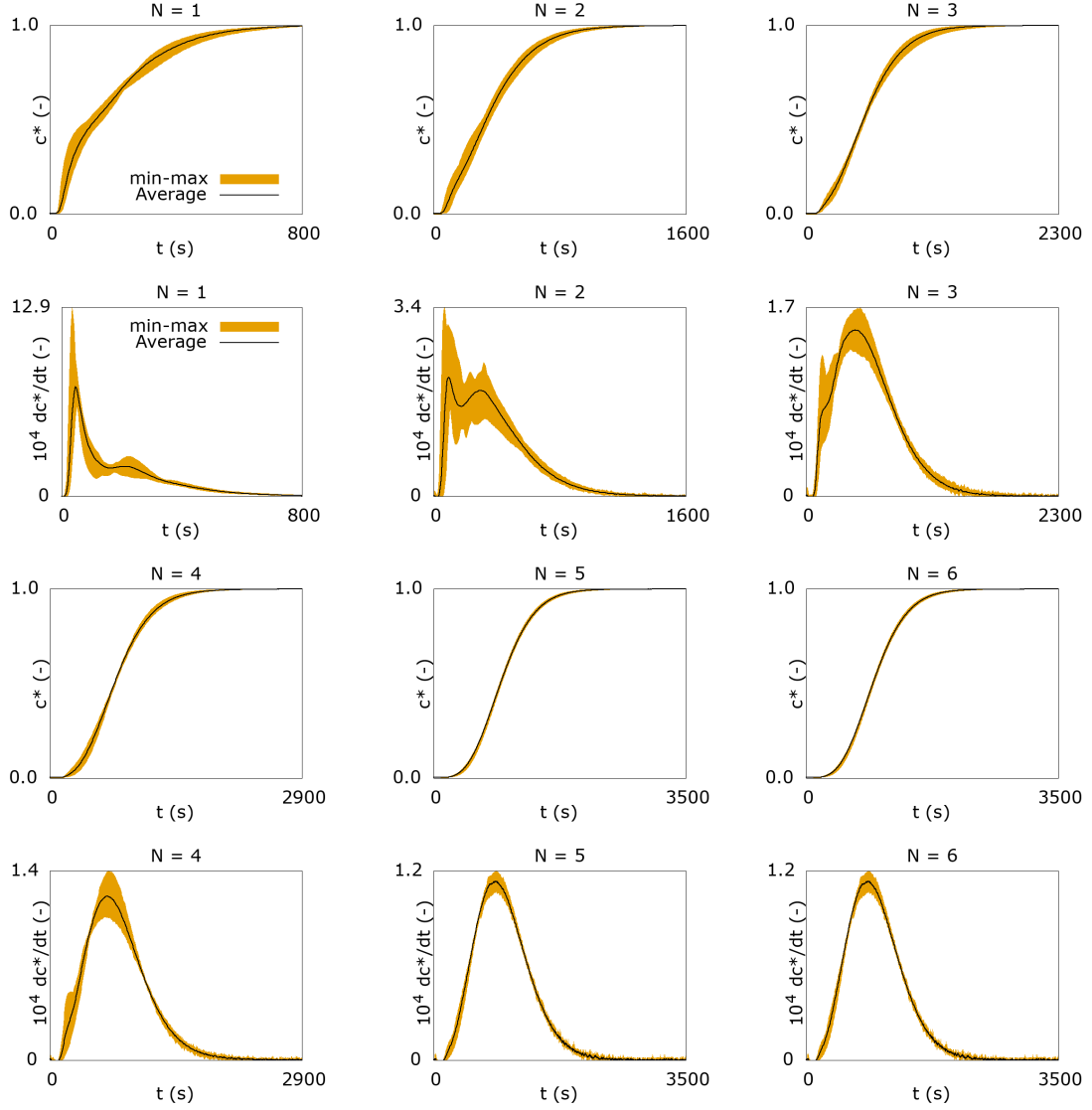


Figure 3: Experimental breakthrough curves and their time derivatives for  $N = 1, \dots, 6$  MHPM.

## 337 4. Model benchmarking

### 338 4.1. Calibration method

339 *Objective function.* As discussed in the introduction, a sound benchmarking should allow for an  
 340 efficient discrimination of both the long-time and short-time behaviours of the various models  
 341 against experimental datasets. In [48], the short-time behaviour was enhanced by using the Laplace  
 342 transforms of the experimental breakthrough curves. The Laplace transform of the signal was used  
 343 only because the unit transfer function of a single column was not accessible from the data. Since,  
 344 in the present experiments, the  $c(t)$  signal is available for  $N = 1$ , the Laplace transform can be  
 345 avoided. The governing equations were solved in the  $(x, t)$  domain. A second-order, conservative  
 346 finite volume method [60] was used. This method has proved less diffusive than the second-order-  
 347 in-time MUSCL-Hancock method for small values of the Courant-Friedrichs-Lewy (CFL) number.  
 348 In order to minimise numerical diffusion as much as possible, the computational time step was  
 349 adapted in such a way that the CFL in the fastest flow region was equal to unity. For  $\text{CFL} = 1$ ,

numerical diffusion is known to be zero and the exact solution of the advection part of the equation is obtained. Moreover, different mesh sizes were tested. Varying the computational cell size from  $\Delta x = 1.5 \times 10^{-5}$  m (i.e. 1000 cells per 15 cm long column) to  $\Delta x = 1.5 \times 10^{-4}$  m (i.e. 100 cells per column) showed no noticeable difference between the numerical solutions, showing that numerical convergence was achieved.

Let  $e(t)$  be the model error, that is, a measure of the difference between the model output and the experimentally measured concentration (see next paragraph for  $e(t)$  definitions). The usual approach consists in computing the objective function as the  $L_p$ -norm of the modelling error over the time interval  $[0, T]$  of interest. Dividing by the length of the time integration interval so as to remove the bias arising from the length of the time series yields the following objective function

$$J_1 = \left( \frac{1}{T} \int_0^T |e(t)|^p dt \right)^{\frac{1}{p}}, \quad p > 0 \quad (11)$$

In practice, the model output is discretized using a time step  $\Delta t$  over the interval  $[0, T]$ , with  $T = n\Delta t$ . In the case of a constant  $\Delta t$ , the trapezium rule leads to the following estimate:

$$J_1 = \left( \frac{1}{T} \sum_{j=1}^n \left( \frac{e_j + e_{j+1}}{2} \right)^p (t_{j+1} - t_j) \right)^{1/p} = \left( \frac{1}{n} \sum_{j=1}^n \left( \frac{e_j + e_{j+1}}{2} \right)^p \right)^{1/p} \quad (12)$$

where  $e_j$  is the error at time  $t_j$ . When the simulation is carried out over a long time, however, the objective function  $J_1$  gives a small relative weight to the early times of the model response. In order to enhance the discriminatory power of early simulated times, it is proposed that the objective function be computed not by integrating with respect to time but with respect to frequency. The lower and upper bounds of the frequency are respectively  $\nu_0 \equiv \frac{1}{T}$  and  $\nu_1 \equiv \frac{1}{\Delta t}$ . The frequency-based objective function is defined as

$$J_2 = \left( \frac{1}{\nu_1 - \nu_0} \int_{\nu_0}^{\nu_1} |e(\nu)|^p d\nu \right)^{\frac{1}{p}} = \left( \frac{1}{\nu_1 - \nu_0} \int_{\Delta t}^T \frac{1}{t^2} |e(t)|^p dt \right)^{\frac{1}{p}} \quad (13)$$

The factor  $\frac{1}{t^2}$  illustrates the stronger weight given to small times. The trapezium rule leads to the following formula for  $J_2$

$$J_2 = \left[ \frac{1}{\nu_1 - \nu_0} \sum_{j=1}^{n-1} \left( \frac{e_j + e_{j+1}}{2} \right)^p \left( \frac{1}{t_j} - \frac{1}{t_{j+1}} \right) \right]^{1/p} = \left[ \frac{n}{n-1} \sum_{j=1}^{n-1} \left( \frac{e_j + e_{j+1}}{2} \right)^p \left( \frac{1}{j} - \frac{1}{j+1} \right) \right]^{1/p} \quad (14)$$

Since the objective is to achieve a correct description of both short- and long-time behaviours, the final objective function is defined as the product  $J_1 J_2$ .

*Modelling error definition.* The measure of the modelling error was defined on the basis of the following considerations: (i) the modelling error is zero whenever the modelled variable is equal

374 to the measured one, (ii) the error must be normalized with the amplitude of the experimental  
 375 variability, assessed from several replicates of the experiment. These two conditions allow at least  
 376 two possible definitions to be proposed for the modelling error.

377 Definition 1: the error is zero when the modelled signal is within the min-max interval of the  
 378 experimental signal. When the modelled signal is outside the experimental min-max interval, the  
 379 error is taken equal to the distance to the closer interval bound:

$$e(t) = \begin{cases} \frac{\partial_t c_{\min}(t) - \partial_t c_{\text{mod}}(t)}{\Delta \partial_t c} & \text{if } \partial_t c_{\text{mod}}(t) < \partial_t c_{\min}(t) \\ 0 & \text{if } \partial_t c_{\min}(t) \leq \partial_t c_{\text{mod}}(t) \leq \partial_t c_{\max}(t) \\ \frac{\partial_t c_{\text{mod}}(t) - \partial_t c_{\max}(t)}{\Delta \partial_t c} & \text{if } \partial_t c_{\text{mod}}(t) > \partial_t c_{\max}(t) \end{cases} \quad (15a)$$

$$380 \quad \partial_t c_{\min}(t) \equiv \min_r \partial_t c_{\text{expe},r}(t), \quad \partial_t c_{\max}(t) \equiv \max_r \partial_t c_{\text{expe},r}(t), \quad \Delta \partial_t c = \partial_t c_{\max}(t) - \partial_t c_{\min}(t) \quad (15b)$$

381 where  $\partial_t c_{\text{expe},r}(t)$  is the derivative of the concentration measured at time  $t$  for the replicate number  
 382  $r$  of the experiment,  $c_{\text{mod}}(t)$  is the modelled concentration at time  $t$ . In this definition, the error  
 383 is zero whenever the modelled signal can be explained by the experimental variability between the  
 384 various replicates. Numerical experiments carried out by reducing artificially the min-max range  
 385 showed very little sensitivity of the respective performance of the various models considered in this  
 386 paper.

387 Definition 2: the error is defined as the distance from the average measurement. In this  
 388 definition the scaling factor is  $\sigma(t)$ , the standard deviation of  $\partial_t c(t)$  between the various replicates:

$$e(t) = \begin{cases} \frac{\partial_t c_{\text{av}}(t) - \partial_t c_{\text{mod}}(t)}{\sigma(t)} & \text{if } \partial_t c_{\text{mod}}(t) \leq \partial_t c_{\text{av}}(t) \\ \frac{\partial_t c_{\text{mod}}(t) - \partial_t c_{\text{av}}(t)}{\sigma(t)} & \text{if } \partial_t c_{\text{mod}}(t) \geq \partial_t c_{\text{av}}(t) \end{cases} \quad (16a)$$

$$389 \quad \partial_t c_{\text{av}}(t) \equiv \frac{1}{M} \sum_{r=1}^M \partial_t c_{\text{expe},r}(t), \quad \sigma(t) \equiv \left[ \frac{1}{M-1} \sum_{r=1}^M (\partial_t c_{\text{expe},r}(t) - \partial_t c_{\text{av}}(t))^2 \right]^{\frac{1}{2}} \quad (16b)$$

390 *Calibration algorithm.* In the following, the calibration is performed on five experiments simultan-  
 391 eously ( $N = 1 \dots 5$ ) using the definition (16a) for the error. The final objective function is taken  
 392 as the sum for each experiment of the product of the two functions  $J_1$  and  $J_2$ :

$$J = \sum_{p=1}^5 J_1(p) J_2(p) \quad (17)$$

393 A binary Genetic Algorithm (GA) [36] is used to calibrate the different models. In this kind of  
 394 algorithm, the set of parameters is represented by a "chromosome" in which each parameter is a  
 395 "gene". The gene is described by a min/max interval and a binary encoding of a given length that  
 396 determine the number of possible values taken by each of the  $N_p$  parameters (e.g  $N_{\text{bits}} = 6$  bits  
 397  $= 64$  values). As proposed in [47], the initial population is composed of  $N_{\text{pop}} = 8$  chromosomes,



each of which is the concatenation of the various genes. The population is thus represented by a  $N_{\text{pop}} \times (N_p N_{\text{bits}})$  matrix initially filled with randomly generated one and zero bits. A simulation is run for each chromosome and the results are compared in term of objective function. Half of the chromosomes that yield to the poorest results are discarded through natural selection and replaced with new offsprings. The best chromosome is kept intact, and the others are subjected to mutation (see [47] for a detailed description).

A first set of parameter bounds is defined, with physically permissible values according to the experiments. The genetic algorithm searches for the best parameter values within 64 possibilities. To ensure a wide coverage of the parameter space, the GA is run during 50,000 generations. Accuracy is improved by running the algorithm a second time over a narrower interval defined about the result of the first run, with a width about 15% that of the initial interval.

The models are calibrated using the five experiments ( $N = 1$  to 5) and validated using the sixth experiment ( $N = 6$ ). For the sake of conciseness, the results are displayed for  $N = 1, 3$  and 5 only.

#### 4.2. AD model

The best parameter values obtained for the AD model (Figure 4) are given in Table 2.

Parameter	Meaning	Numerical value
$D$	Fickian dispersion coefficient	$4.041 \times 10^{-5} \text{ m}^2\text{s}^{-1}$
$u$	Advection velocity	$7.193 \times 10^{-4} \text{ ms}^{-1}$
$J$	Objective function	7.76

Table 2: AD model. Calibration results.

As expected, the AD model is not able to reproduce the experimental results for  $N < 5$ . The modelling results improve as  $N$  increases. Owing to the single advection velocity, the model fails to represent the main two transport models at small times and distances. This is particularly visible in the frequency domain (Figure 4, bottom), where the higher frequencies are inaccurately accounted for. While the model seems to perform correctly for  $N = 5$ , the plot in the frequency domain shows that high frequencies remain underestimated by the model, since the model signal is not within the min/max confidence interval of the experimental curve. As  $N$  increases, however, the discrepancy between the modelled and experimental signals becomes smaller. This was expected from the analysis presented in the Appendices, because the Fickian dispersion model is more appropriate for large travel times and distances than for short ones.

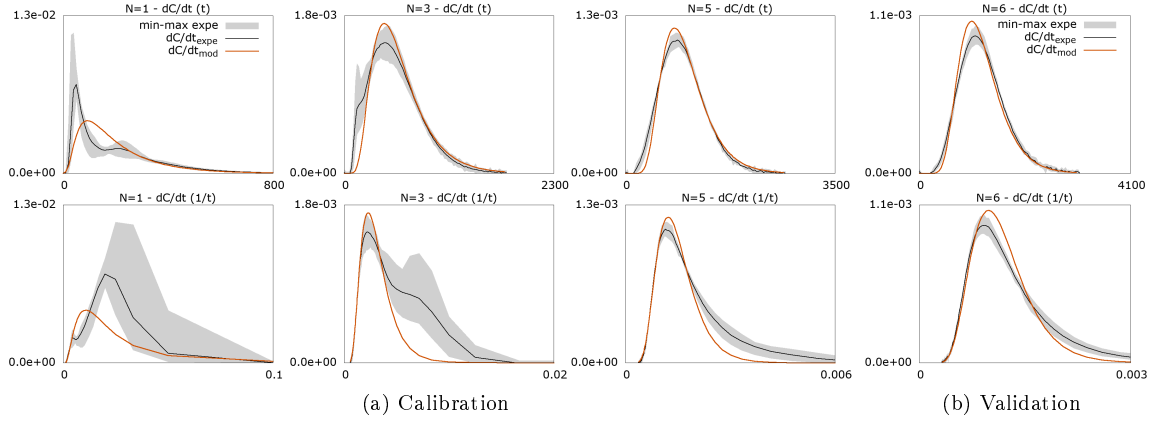


Figure 4: a) Calibration of the AD model. Top: time derivative of the concentration with respect to time. Bottom: time derivative of the concentration as a function of frequency. From left to right: best result for each experiment, obtained with the same set of parameters. b) Model validation against the 6-MHPM experiment.

#### 4.3. MI model

The four parameters to be calibrated for the MI model (2a, 2b) are  $\Theta_m$ ,  $k$ ,  $u$  and  $D$ . The remaining parameter is determined automatically,  $\Theta_{im} = 1 - \Theta_m$ . The simulation results after calibration (Figure 5), are obtained with the parameter set in Table 3.

Parameter	Meaning	Numerical value
$D$	Fickian dispersion coefficient	$3.720 \times 10^{-7} \text{ m}^2\text{s}^{-1}$
$k$	Exchange coefficient	$7.751 \times 10^{-2} \text{ s}^{-1}$
$u$	Advection velocity	$4.471 \times 10^{-3} \text{ ms}^{-1}$
$\Theta_{im}$	Normalised immobile fraction	0.8333
$\Theta_m$	Normalised mobile fraction	0.1667
$J$	Objective function	3.505

Table 3: MI model. Calibration results.

In contrast with the AD model, the MI model produces too early a peak time. The inflection points in the time signal for  $N = 1$  and in the frequency signal for  $N = 3$  are missed. For  $N = 5$ , the MI model results are within the bounds of the min/max confidence interval, which is an improvement over the AD model (compare Figs. 4, 5, second column from the right). The validation simulation (Figure 5, rightmost column) also shows a better agreement with the experimental curve than that of the AD model.

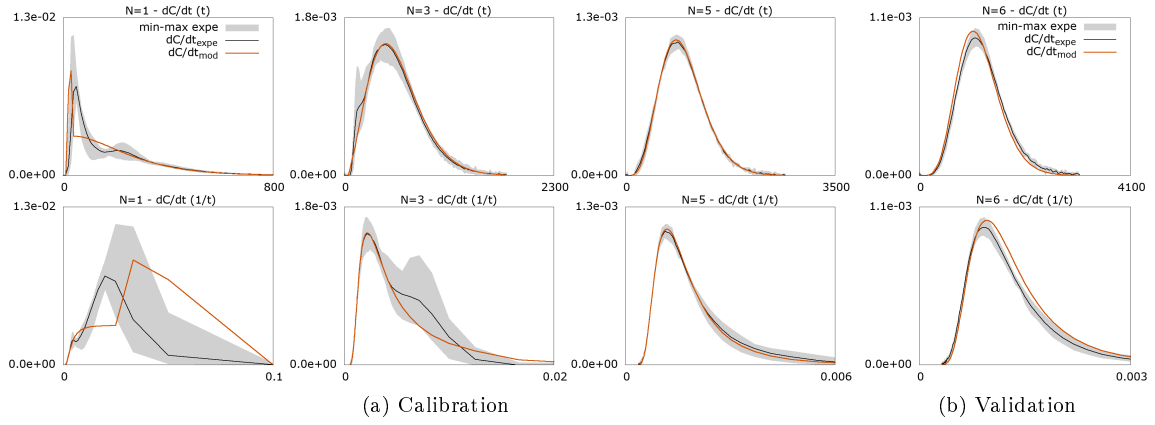


Figure 5: a) Calibration of the MI model. Top: time derivative of the concentration with respect to time. Bottom: time derivative of the concentration as a function of frequency. From left to right: best result for each experiment, obtained with the same set of parameters. b) Model validation against the 6-MHPM experiment.

#### 4.4. MR model

Calibrating the MR model (3a, 3b) with three immobile regions gives the values in Table 4.

Figure 6 shows the corresponding breakthrough curves.

Parameter	Meaning	Numerical value
$D$	Fickian dispersion coefficient	$6.200 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$
$k_1$	Exchange coefficient with region 1	$9.303 \times 10^{-1} \text{ s}^{-1}$
$k_2$	Exchange coefficient with region 2	$6.820 \times 10^{-2} \text{ s}^{-1}$
$k_3$	Exchange coefficient with region 2	$6.519 \times 10^{-2} \text{ s}^{-1}$
$u$	Advection velocity	$4.471 \times 10^{-3} \text{ ms}^{-1}$
$\Theta_1$	Normalised immobile fraction 1	0.1017
$\Theta_2$	Normalised immobile fraction 2	0.1155
$\Theta_3$	Normalised immobile fraction 3	0.5775
$\Theta_m$	Normalised mobile water content	0.1658
$J$	Objective function	1.975

Table 4: RI model. Calibration results.

While the model does not allow the inflection points in the time- and frequency-domain signals to be reconstructed for  $N = 1, 3$ , the modelled signal lies within the min/max confidence interval for all calibration runs  $N = 1, \dots, 5$ . The validation run ( $N = 6$ ) produces slightly too early a signal, just as the MI model.

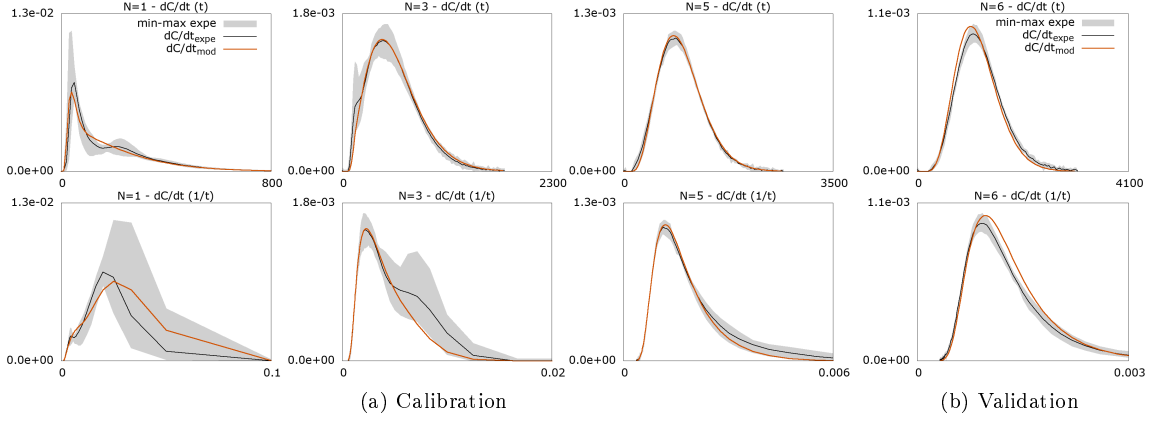


Figure 6: a) Calibration of the MR model with three immobile regions. Top: time derivative of the concentration with respect to time. Bottom: time derivative of the concentration as a function of frequency. From left to right: best result for each experiment, obtained with the same set of parameters. b) Model validation against the 6-MHPM experiment.

#### 4.5. Two region MRAD Model

The simplest possible version of the MRAD model, with two mobile regions, is used. This model has eight parameters in total, but only six of them are independent and must be calibrated:  $\Theta_1$ ,  $k_{12}$ ,  $u_1$ ,  $u_2$ ,  $D_1$  and  $D_2$ . The best parameter set (Figure 7) is given in Table 5.

Parameter	Meaning	Numerical value
$D_1$	Fickian dispersion coefficient in region 1	$1.034 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
$D_2$	Fickian dispersion coefficient in region 2	$1.897 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
$k_{12}$	Exchange coefficient	$1.570 \times 10^{-2} \text{ s}^{-1}$
$u_1$	Flow velocity in region 1	$2.406 \times 10^{-3} \text{ ms}^{-1}$
$u_2$	Flow velocity in region 2	$5.28 \times 10^{-4} \text{ ms}^{-1}$
$\Theta_1$	Normalised water content 1	0.124
$\Theta_2$	Normalised water content 2	0.876
$J$	Objective function	1.61

Table 5: MRAD model. Calibration results.

Unlike the AD, MI and MR models, the MRAD model allows the inflection points in the experimental signals to be reproduced. Although the slower peak is too early for  $N = 1$  (Figure 7, leftmost column), its location is correct for  $N = 3$ . In contrast, the faster peak is overestimated for  $N = 3$ . The small time/high frequency behaviour of the MRAD validation run ( $N = 6$ , rightmost column on Figure 7) is slightly less accurate than that of the MR model.

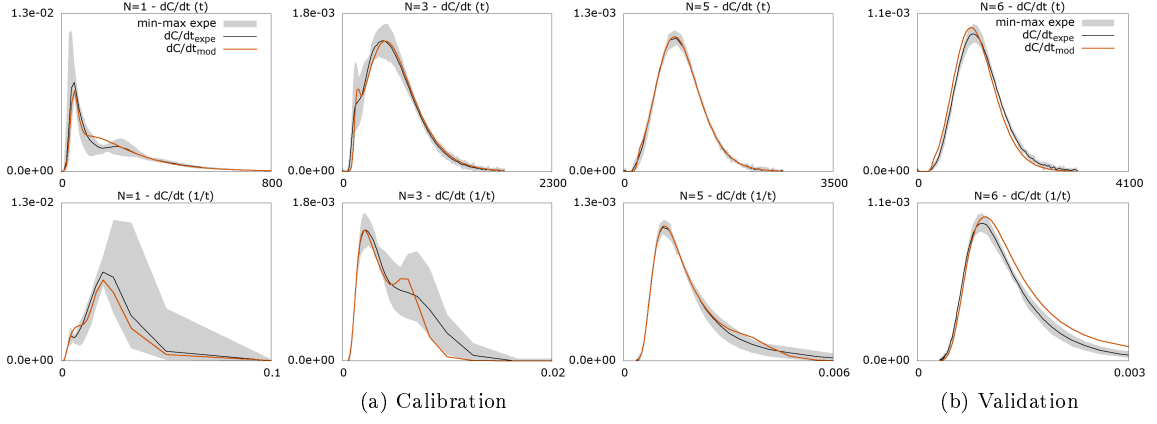


Figure 7: a) Calibration of the MRAD model with two mobile regions. Top: time derivative of the concentration with respect to time. Bottom: time derivative of the concentration as a function of frequency. From left to right: best result for each experiment, obtained with the same set of parameters. b) Model validation against the 6-MHPM experiment.

#### 4.6. Three region PAMR model

As far as the PAMR model is concerned, three regions represent the minimal level of complexity for which the model can be expected to bring an improvement over the previously tested models. This is because a two region PAMR model would be only a particular case of the two region MRAD model. In the previous paragraph, the optimal MRAD model is shown to have non-zero dispersion coefficients  $D_1$  and  $D_2$ . Consequently, a two region PAMR model (with null dispersion) can only perform worse than the two region MRAD. Proposing a PAMR model is thus meaningful only for  $R > 2$ .

The three region PAMR model requires the calibration of 6 independent parameters:  $\Theta_1$ ,  $\Theta_2$ ,  $k_{12}$ ,  $k_{13}$ ,  $k_{23}$ ,  $u_1$ ,  $u_2$  and  $u_3$ . The best parameter set (Fig 8) is given in Table 6.

As far as the calibration phase is concerned, the three region PAMR model is the only one to fit within the min/max experimental confidence intervals (albeit passing very near the upper limit for  $N = 1$ ). For  $N = 3$ , the modelled signal is improved significantly over that of the MRAD model in both the time and frequency domains. As with the previous models, the modelled validation signal is slightly too early compared to the experimental one. The large frequency behaviour of the PAMR model is better than that of the MRAD model (compare Figs. 7, 8, rightmost columns).

Parameter	Meaning	Numerical value
$k_{12}$	Exchange coefficient between regions 1 and 2	$1.518 \times 10^{-2} \text{ s}^{-1}$
$k_{13}$	Exchange coefficient between regions 1 and 3	$1.252 \times 10^{-3} \text{ s}^{-1}$
$k_{23}$	Exchange coefficient between regions 2 and 3	$5.803 \times 10^{-3} \text{ s}^{-1}$
$u_1$	Flow velocity in region 1	$3.942 \times 10^{-3} \text{ ms}^{-1}$
$u_2$	Flow velocity in region 2	$8.668 \times 10^{-4} \text{ ms}^{-1}$
$u_3$	Flow velocity in region 3	$1.079 \times 10^{-4} \text{ ms}^{-1}$
$\Theta_1$	Normalised water content 1	0.1389
$\Theta_2$	Normalised water content 2	0.1430
$\Theta_3$	Normalised water content 3	0.7271
$J$	Objective function	1.592

Table 6: Three region PAMR model. Calibration results.

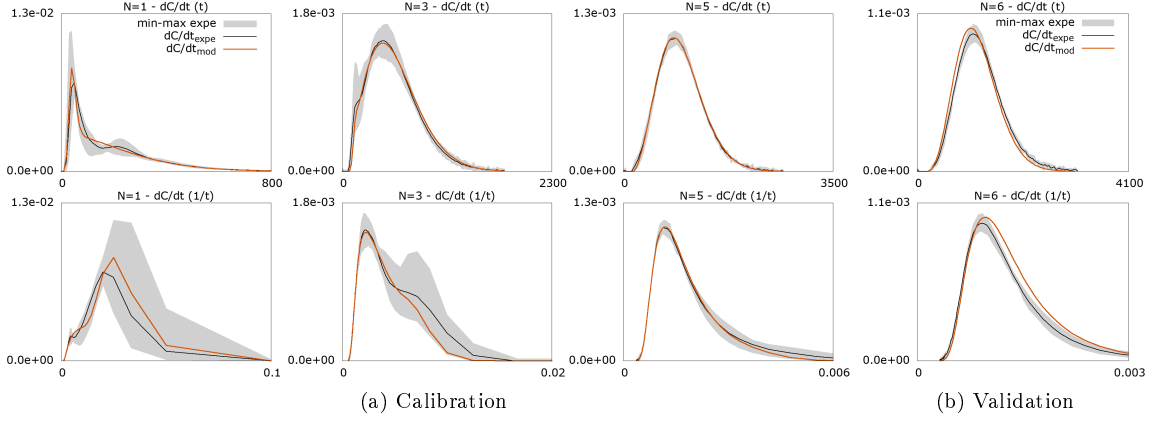


Figure 8: a) Calibration of the PAMR model with three mobile regions. Top: time derivative of the concentration with respect to time. Bottom: time derivative of the concentration as a function of frequency. From left to right: best result for each experiment, obtained with the same set of parameters. b) Model validation against the 6-MHPM experiment.

#### 4.7. Four region PAMR model

A four region PAMR model is also tested, with the following two objectives: (i) determine whether adding extra degrees of freedom allow for better calibration/validation results, (ii) investigate whether each of the two dispersion coefficients in the two region MRAD model could not be represented more efficiently using two regions exchanging mass. The rationale for this is presented in Subsection Appendix A.2.4. In this subsection, an asymptotic Fickian behaviour is shown to be obtained from two regions with identical fractions  $\Theta_p (p = 1, 2)$  exchanging mass. The consequence is that each of the two regions in the MRAD model might be subdivided into two regions of equal size, resulting in a four region PAMR model. In this version, eight independent parameters must be calibrated:  $\Theta_1, k_{12}, k_{13}, k_{34}, u_1, u_2, u_3$  and  $u_4$ . The remaining coefficients are inferred automatically because  $\Theta_2 = \Theta_1, \Theta_3 = \Theta_4 = \frac{1-\Theta_1}{2}$ , and  $k_{ij} = k_{ji} \forall (i, j)$ .

The best result (Fig. 9) is obtained for the parameter set in Table 7.

Parameter	Meaning	Numerical value
$k_{12}$	Exchange coefficient between regions 1 and 2	$2.180 \text{ s}^{-2}$
$k_{13}$	Exchange coefficient between regions 1 and 3	$1.561 \times 10^{-3} \text{ s}^{-1}$
$k_{34}$	Exchange coefficient between regions 3 and 4	$2.190 \times 10^{-1} \text{ s}^{-1}$
$u_1$	Flow velocity in region 1	$4.474 \times 10^{-3} \text{ ms}^{-1}$
$u_2$	Flow velocity in region 2	$7.624 \times 10^{-4} \text{ ms}^{-1}$
$u_3$	Flow velocity in region 3	$2.228 \times 10^{-5} \text{ ms}^{-1}$
$u_4$	Flow velocity in region 4	$1.448 \times 10^{-5} \text{ ms}^{-1}$
$\Theta_1 = \Theta_2$	Normalised water contents 1 and 2	0.1277
$\Theta_3 = \Theta_4$	Normalised water contents 3 and 4	0.3723
$J$	Objective function	1.608

Table 7: Four region PAMR model. Calibration results.

Comparing Figures 8-9 shows that the three and four region PAMR models give almost indistinguishable results. The objective functions are also extremely similar.

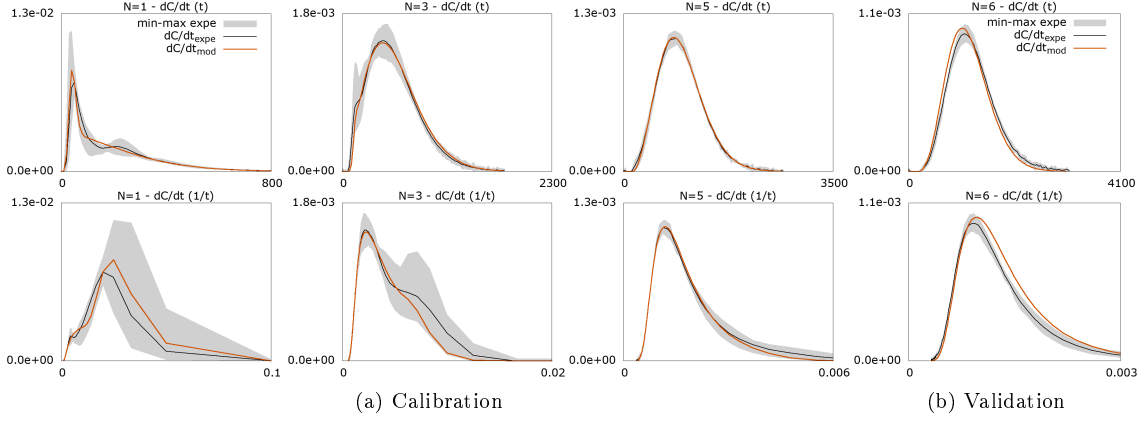


Figure 9: a) Calibration of the PAMR model with four mobile regions. Top: time derivative of the concentration with respect to time. Bottom: time derivative of the concentration as a function of frequency. From left to right: best result for each experiment, obtained with the same set of parameters. b) Model validation against the 6-MHPM experiment.

## 5. Discussion

Table 8 summarizes the results obtained after model calibration and validation. The two error definitions (15a, 16a) presented in this paper are used for the validation.

Model	No. parameters	$J$ calibration eq.(16a)	$J$ validation eq.(15a)	$J$ validation eq.(16a)
AD	2	7.750	$2.63 \times 10^{-2}$	1.660
MI	4	3.505	$3.45 \times 10^{-2}$	1.948
MR	8	1.975	$2.63 \times 10^{-2}$	1.476
MRAD	6	1.610	$6.35 \times 10^{-2}$	2.391
PAMR 3	8	1.592	$3.40 \times 10^{-2}$	1.753
PAMR 4	8	1.608	$3.43 \times 10^{-2}$	1.747

Table 8: Summary of the calibration and validation results for the 6 models. PAMR 3 and PAMR 4 correspond respectively to the three and four region PAMR models.

The following conclusions may be drawn.

Firstly, comparing the third and fifth columns in the table allows the respective predictive power of the various models at large scales to be assessed. Indeed, these two columns in the Table use the same definition (16a) for the objective function. While the AD and MI models perform poorly compared to the MR, MRAD and PAMR models in the calibration phase, their validation performance is similar in the validation phase. This may be explained by the fact that the Fickian model (towards which all models are asymptotically equivalent) becomes more valid as  $N$  increases. The MRAD model is the only one exhibiting a significantly decreasing performance in the validation phase compared to the calibration phase.

Secondly, the respective performance of the various models is the same for both model error formulae (15a, 16a). The MR and AD models, that have the smaller validation error (15a), also have the smaller validation error (16a). The MI, PAMR3 and PAMR4 models, that have intermediate validation error values with formula (15a), also have intermediate validation error values with formula (16a). Lastly, the MRAD model consistently has the larger validation error

497 values, be it with the error definition (15a) or (16a).

498 Thirdly, the error formula (15a) gives objective function values consistently 50 times as small  
499 as those obtained with the error definition (16a). These two modelling error definitions serve  
500 different purposes. The modelling error definition (15a) may be seen as a measure of the "plaus-  
501 ibility" of a model. With this definition, two different models giving output signals within the  
502 min/max experimental error range will yield identically  $J = 0$ , even if they depart signific-  
503 antly from the mean experimental signal. With this definition,  $J = 0$  means that the differ-  
504 ence between the mean experimental measurement and the model output can be fully explained  
505 by experimental imprecision. These two models may be deemed equally plausible. In contrast,  
506 the error formula (16a) is a measure of the "accuracy" of a model. With this modelling error  
507 definition, the smaller  $J$ , the better the model output fits the average experimental response.  
508 In comparison with other studies, the present work features a large number of replicates. Even  
509 though a model porous media is dealt with, the replicates show significant statistical variations  
510 in the experimental breakthrough curves, be it for a given MHPM or for the ensemble of the 12  
511 MHPM used in this study. These statistical variations are illustrated by the min-max interval on  
512 Figure 3. The interval is the widest for  $N = 1$  MHPM (single period study column) and becomes  
513 narrower as  $N$  increases. Clearly, the statistical variations are stronger at the heterogeneity scale  
514 ( $N = 1$ ) and are damped as the porous media tends to homogeneity ( $N = 6$ ). This shows the  
515 importance of replicating experiments when heterogeneous porous media are involved. Most pre-  
516 viously reported transport experiments use a limited number of replicates (a single experiment  
517 in many cases). This does not allow the experimental variability of the data set to be assessed.  
518 Given the width of the min-max cloud on Figure 3, many candidate models might fit within the  
519 experimental confidence interval, and if they do, they can all be considered as good candidate  
520 models.

521 In order to compare several modelling approaches, using high quality experimental data proves  
522 essential. A large number of replicates allows the statistical variations of the experimental data  
523 to be accounted for in the benchmarking process. Another issue in the calibration and validation  
524 process is the definition of the objective function. As shown in [48], many models provide an  
525 accurate description of the long-time behaviour of the breakthrough curves. In contrast, examining  
526 the short time behaviour of the experimental data sets leads to rule out a number of models [48].  
527 Consequently, defining an objective function that gives equal weights to small and large time  
528 behaviours, as done in the present study, is deemed essential to an efficient model assessment. To  
529 our best knowledge, this approach has been little used in transport model benchmarking. Using  
530 the time derivative of the experimental signals in the calibration and validation processes for a  
531 more efficient discrimination between models has also been little reported in the literature.

532 In this study, we compare five modelling approaches: four existing models (AD, MI, MR,  
533 MRAD) and a new model (PAMR). The originality of the PAMR model is that transport is



534 modelled on a purely advection basis, without the need for dispersion terms. The four existing,  
535 dispersion-based models use a scale-independent dispersion coefficient. We insist on this choice  
536 because as shown in [48], (i) there is no experimental evidence that dispersion varies with time  
537 and distance, (ii) there exists a model with scale-independent coefficients that allows the MHPM  
538 experiments to be reproduced. Moreover, as mentioned in [38], while some studies suggest that dis-  
539 persion may increase with time and distance, other studies suggest that dispersion may eventually  
540 tend to a constant asymptotic value.

541 If the response of the heterogeneous medium departs from the classical Fickian behaviour, we  
542 consider proposing a non-Fickian transport more appropriate than making the Fickian transport  
543 model scale-dependent (as in e.g. [23, 55]). Note that fractional advection-dispersion models were  
544 developed to eliminate the scale-dependent dispersion [6], albeit with limited success [22]. In the  
545 authors' view, the challenge tackled by the proposed PAMR model is not only to reproduce the  
546 non-Fickian transport process on the heterogeneity scale, but also to tend asymptotically towards  
547 a Fickian transport process (classical AD model) on an observation scale that is much larger than  
548 the heterogeneity scale.

549 Moreover, the PAMR model does not have the undesirable effects of the Fickian operator.  
550 As shown by Einstein [19, 20, 21], the Fickian model is valid only above a given time and space  
551 scale, under the assumption that a sufficient number of realizations of the Brownian motion have  
552 been realized and that the movement obeys a Markovian process (that is, no memory of the  
553 previous displacements is kept after a change in particle position and velocity). If the scale under  
554 consideration is such that a time or space correlation exists between the successive displacements  
555 of the solute particles (as is the case when a single MHPM is concerned), the Fickian model should  
556 be expected to be invalid. Along the same line, Benson et al. [6] insist on the fact that AD model is  
557 based on the divergence of a vector field which is evaluated by the limit of the flux of this vector on  
558 the surface of an enclosed volume when the volume shrinks towards zero. To quote these authors:  
559 "This is valid only if the flux is indeed a point vector quantity relative to the scale of observation,  
560 for example, heat flow in homogeneous material. Then the limit exists. Solute dispersion is a  
561 counterexample since it is primarily due to velocity fluctuations that arise only as an observation  
562 space grows larger, invalidating the limit".

563 This explains why the AD model fails to reproduce the experimental results at small scales  
564 (Figure 4a and Table 8). As the size of the domain increases ( $N = 6$  in Figure 4b), the AD model  
565 becomes better adapted to reproduce the experimental behaviour because the scale of observation  
566 becomes larger than the scale of one heterogeneity. The objective function for the AD model is  
567  $J = 7.76$ . The MI model (one mobile region and one immobile region) gives better results than  
568 the AD model especially for  $N \geq 3$  (Figure 5) but it still fails to reproduce the experimental  
569 behaviour for  $N = 1$  (scale of one heterogeneity). The objective function becomes  $J = 3.505$  with  
570 an improvement of 55% in comparison to AD model. The MR model, which is a generalization

571 of the MI model, gives better results than the MI model with an objective function  $J = 1.975$   
 572 and an improvement of 44% over the MI model (Figure 6). The MR used in this study has one  
 573 mobile region and three immobile regions and it starts to reproduce the experimental behaviour  
 574 at the scale of one heterogeneity (Figure 6a). The MRAD model gives better results than the MR  
 575 model (Figure 7), with an objective function of  $J = 1.61$  (an improvement of 18% in comparison  
 576 to MR). Concerning the PAMR model proposed in this study, we first used a simple version with  
 577 three mobile regions. The simulations reproduce fairly well the experimental behaviour especially  
 578 at the scale of one heterogeneity (Figure 8). With an objective function  $J = 1.592$ , the accuracy  
 579 of the PAMR model is nearly identical to that of the MRAD model. A four region version of  
 580 the PAMR gave similar simulation results (Figure 9), with  $J = 1.608$ . Adding a fourth region  
 581 thus brings no improvement over the three region PAMR. This means that the porous media of  
 582 this study (MHPM) can be well reproduced with a three region PAMR, and that a more complex  
 583 multiple region PAMR will not lead to a better simulation. We consider the PAMR simulations  
 584 very satisfactory in that (i) the PAMR model performs as satisfactorily as other existing models,  
 585 (ii) it describes quite well the experimental behaviour at the scale of both a single and several  
 586 heterogeneities, (iii) this is achieved using scale-independent parameters. Although the PAMR  
 587 model is calibrated on a small observation scale (one to five heterogeneities), it asymptotically  
 588 tends to a Fickian behaviour on a large observation scale (6 heterogeneities) with a fairly good  
 589 simulation (Table 8). This asymptotic Fickian behaviour of the PAMR model was to be expected  
 590 because the model is known to lead to the Fickian model for large scales under conditions that are  
 591 met here (see AppendixA and the stability analysis in AppendixB).

592 As far as the reported, experimental scale dependence of the dispersion coefficient is concerned,  
 593 the PAMR model allows such dependence to be explained, as shown in Subsection AppendixA.2.4.  
 594 Solving the two region PAMR equations for a Dirac initial condition shows that the apparent  
 595 dispersion coefficient obeys an exponential function of time. This is precisely the behaviour inferred  
 596 in [23], where the best fit to the experimental data set was obtained by fitting an exponential  
 597 function  $D(x)$ . The developments in Subsection AppendixA.2.4 also indicate that there exist two  
 598 different ways of fitting the dispersion coefficient from field measurements. The first consists in  
 599 adjusting  $D$  so as to fit the average spreading rate of the contaminant plume over time, yielding  
 600 a first coefficient  $D_{av}$ . The second consists in adjusting  $D$  so as to fit the time derivative of the  
 601 plume variance, yielding a local estimate  $D_{loc}$ . The variation analysis in AppendixA.2.4 shows that  
 602  $D_{loc}$  converges faster to the asymptotic value than does  $D_{av}$ . Indeed, the difference  $D_{\infty} - D_{loc}$   
 603 is a decreasing exponential function of time, while  $D_{\infty} - D_{av}$  is proportional to the inverse of  
 604 time. This was to be expected in that  $D_{av}$  incorporates the effect of all times on the dispersion  
 605 behaviour, including the times for which the dispersion behaviour is strongly non-Fickian.  $D_{loc}$   
 606 therefore provides a more accurate estimate of  $D_{\infty}$  than  $D_{av}$ . However, in practice, deriving  $D_{av}$  is  
 607 easier than  $D_{loc}$  because the determination of  $D_{loc}$  requires many more sampling times and points

608 than that of  $D_{av}$ .

609 Lastly, it is worth pointing out that all multi-region models (including the PAMR model pro-  
610 posed in this paper) exhibit a certain degree of non-local behaviour, in contrast with the AD model  
611 that is purely local. Indeed, specifying the initial and boundary conditions for any of the MI, MR,  
612 MRAD and PAMR models requires that the initial and boundary conditions be specified for each  
613 of the flow regions. In practical applications, however, this is not possible. Only the average con-  
614 centration  $c = \sum_{i=1}^R \theta_i c_i$  within the bulk porous medium is known, and the space-time distribution  
615  $c_i(x, t)$  in every region  $i$  is unknown. A straightforward solution would be to set the concentrations  
616 in all regions to the same average concentration value. However, in real-world applications, such an  
617 initial state is likely to be most inaccurate. This is because, by definition of intermediate time and  
618 space scales, the concentrations in all flow regions have not reached equilibrium and can therefore  
619 not be assumed to be identical. Consequently, the distributions  $c_i(x, t_0)$  to be used for an initial  
620 condition at a given time  $t_0$  are functions of the past behaviours of the fields  $c_i(x, t)$ ,  $t < t_0$  and the  
621 way the various flow regions have been exchanging solute. This is typically a non-local behaviour,  
622 a common feature shared by all widely admitted anomalous transport models.

## 623 6. Conclusions

624 In this paper, solute dispersion in model periodical heterogeneous media is studied from both  
625 an experimental and modelling perspective. The following, main results are found.

626 A large number of solute transport experiments through periodic heterogeneous porous media  
627 is presented. The significant number of experiment replicates yield high quality breakthrough  
628 curves, while allowing the experimental uncertainty to be characterized accurately. The authors  
629 are willing to make the data sets available to the scientific community.

630 A calibration procedure putting the emphasis on both small time and large time behaviours is  
631 set up. It allows for the benchmarking of several transport and dispersion models: the Advection-  
632 Dispersion (AD), Mobile-Immobile (MI), Multi-Rate (MR), Multi-Region Advection-Dispersion  
633 (MRAD) and Purely Advective Multi Region (PAMR) models.

634 Applying the AD model shows that, at the scale of a single heterogeneity, the dispersion pro-  
635 cess is non-Fickian. It tends asymptotically to a Fickian behaviour for an increasing number of  
636 heterogeneity periods. Even without a Fickian dispersion term, the PAMR model is seen to per-  
637 form as well as the AD, MI, MR and MRAD models. The PAMR is able to simulate transport on  
638 every heterogeneity scale: on the single heterogeneity scale, PAMR can reproduce a non-Fickian  
639 behaviour while it tends to the observed, classical Fickian behaviour on the scale of several het-  
640 erogeneities. Another advantage of the PAMR model is the absence of the undesirable effects of  
641 the Fickian term, such as the physically unsound infinite propagation speed of the solutions of the  
642 diffusion equation.

### 643 AppendixA. Equations of moments

#### 644 AppendixA.1. Spatial moments for the AD model

645 The present subsection is devoted to the development of the equations for the spatial moments  
 646 of the propagator in the AD model. The propagator is the solution  $c(x, t)$  of the AD equation (1)  
 647 for the initial condition  $c(x, 0) = \delta(x)$ . The governing equation is first rewritten in the coordinate  
 648 system moving at speed  $u$ :

$$\partial_t c - D \partial_{xx} c = 0 \quad (\text{A.1})$$

649 Denoting by  $c^{(p)}$  the  $p$ th-order spatial moment of the concentration

$$c^{(p)} \equiv \int_{-\infty}^{+\infty} x^p c(x, t) dx \quad (\text{A.2})$$

650 the governing equations for the moments are obtained by multiplying equation (A.1) by  $x^p$  and  
 651 integrating over the real axis:

$$\int_{-\infty}^{+\infty} x^p (\partial_t c - D \partial_{xx} c) dx = 0 \quad (\text{A.3})$$

652 Using integration by parts to eliminate the higher-order derivatives, using the property  $\lim_{x \rightarrow \pm\infty} c(x, t) =$   
 653 0, the following equations are obtained

$$d_t c^{(0)} = 0 \Rightarrow c^{(0)}(t) = 1 \quad (\text{A.4a})$$

654

$$d_t c^{(1)} = u \Rightarrow c^{(1)}(t) = 0 \quad (\text{A.4b})$$

$$d_t c^{(2)} - 2D = 0 \Rightarrow c^{(2)}(t) = 2Dt \quad (\text{A.4c})$$

655 The well-known property of a variance of particle locations proportional to time is retrieved.  
 656 Note however that equation (A.4c) leads to two expressions for the dispersion coefficient, a local  
 657 dispersion ( $D_{\text{loc}}$ ) and an average dispersion ( $D_{\text{av}}$ ):

$$D_{\text{loc}} = \frac{1}{2} d_t c^{(2)} \quad (\text{A.5a})$$

658

$$D_{\text{av}} = \frac{1}{2t} c^{(2)} \quad (\text{A.5b})$$

659 The first is obtained from the differential equation (A.4c), the second is obtained from its solution  
 660 under the assumption of a constant  $D$ . Eq. (A.5a) reflects a local behaviour at time  $t$  while Eq.  
 661 (A.5b) reflects an average behaviour over the time interval  $[0, t]$ . Both expressions are equivalent  
 662 when  $D$  is constant. When  $D$  is not constant (as e.g. in the MRAD model considered in Section

A.2),  $D_{av}$  incorporates the influence of early times when the behaviour is non-Fickian and can be expected to take a longer time to converge to the asymptotic value than the local coefficient  $D_{loc}$ .

## Appendix A.2. Spatial moments for the MRAD model

### Appendix A.2.1. Governing equations

For the sake of simplicity, the behaviour is analyzed in the coordinate system that moves at the average speed  $\bar{u} = \frac{\sum_{i=1}^R \Theta_i u_i}{\sum_{i=1}^R \Theta_i}$ . In this coordinate system, the governing equations are

$$\Theta_i \partial_t c_i + \Theta_i v_i \partial_x c_i - \Theta_i D_i \partial_{xx} c_i = \sum_{j \neq i} k_{ij} (c_j - c_i) \quad (\text{A.6a})$$

669

$$k_{ij} = k_{ji}, \quad \sum_{i=1}^R \Theta_i v_i = 0 \quad (\text{A.6b})$$

where the  $v_i$  are defined as in (6). Integrating (A.6a) with respect to  $x$  over  $(-\infty, +\infty)$ , using the property  $\lim_{x \rightarrow \pm\infty} c(x, t) = \lim_{x \rightarrow \pm\infty} \partial_x c(x, t) = 0$  yields

$$d_t c_i^{(0)} = \sum_{j \neq i}^R \frac{k_{ij}}{\Theta_i} (c_j^{(0)} - c_i^{(0)}) \quad (\text{A.7})$$

Since  $c_i^{(0)}(t=0) = 1 \forall i$ ,  $d_t c_i^{(0)}$  remains identically zero at all times, which results in

$$c_i^{(0)}(t) = 1 \forall t \geq 0 \quad (\text{A.8})$$

Multiplying equation (A.6a) by  $x$ , integrating with respect to  $x$  over  $(-\infty, +\infty)$ , using integration by parts and the property  $\lim_{x \rightarrow \pm\infty} c(x, t) = \lim_{x \rightarrow \pm\infty} \partial_x c(x, t) = 0$  yields

$$d_t c_i^{(1)} = v_i c_i^{(0)} + \sum_{j \neq i}^R \frac{k_{ij}}{\Theta_i} (c_j^{(1)} - c_i^{(1)}) = v_i + \sum_{j \neq i}^R \frac{k_{ij}}{\Theta_i} (c_j^{(1)} - c_i^{(1)}) \quad (\text{A.9})$$

Multiplying equation (A.6a) by  $x^2$ , integrating with respect to  $x$  over  $(-\infty, +\infty)$ , using integration by parts and the property  $\lim_{x \rightarrow \pm\infty} c(x, t) = \lim_{x \rightarrow \pm\infty} \partial_x c(x, t) = \lim_{x \rightarrow \pm\infty} \partial_{xx} c(x, t) = 0$  yields

$$d_t c_i^{(2)} = v_i c_i^{(1)} + 2D_i c_i^{(0)} + \sum_{j \neq i}^R \frac{k_{ij}}{\Theta_i} (c_j^{(2)} - c_i^{(2)}) = v_i c_i^{(1)} + 2D_i + \sum_{j \neq i}^R \frac{k_{ij}}{\Theta_i} (c_j^{(2)} - c_i^{(2)}) \quad (\text{A.10})$$

Multiplying by  $\Theta_i$  and summing over  $i = 1, \dots, R$ , using the property  $\sum_{i=1}^R \Theta_i v_i = 0$  yields equation (6).

679 *Appendix A.2.2. Small time behaviour*

680 At  $t = 0$ ,  $c_i^{(1)} = 0 \forall i$  and the governing equation (A.9) simplifies to

$$\left( d_t c_i^{(1)} \right)_{t=0} = v_i \quad (\text{A.11})$$

681 Consequently the following equivalence holds

$$c_i^{(1)}(t) \sim_0 v_i t \quad (\text{A.12})$$

682 Moreover,  $c_i^{(2)}(t = 0) = 0 \forall i$  and equation (6) becomes

$$d_t c^{(2)} = \sum_{i=1}^R \Theta_i (v_i^2 + 2D_i) \quad (\text{A.13})$$

683 with an equivalent dispersion coefficient obtained from (A.5a, A.5b):

$$D_{\text{loc}} = \sum_{i=1}^R \Theta_i (v_i^2 t + D_i) \quad (\text{A.14a})$$

684

$$D_{\text{av}} = \sum_{i=1}^R \Theta_i \left( \frac{1}{2} v_i^2 t + D_i \right) \quad (\text{A.14b})$$

685 For small times, the equivalent dispersion coefficient is observed to increase linearly with distance.

686 However the growth rate of the average dispersion coefficient is smaller than that of the local one.

687 *Appendix A.2.3. Long time behaviour*

688 The solution is asymptotically stable (see Appendix B), consequently there exists a set of finite  
689 asymptotic values  $c_i^{(1,\infty)}$  such that

$$c_i^{(1)} \xrightarrow[t \rightarrow +\infty]{} c_i^{(1,\infty)} \forall i \quad (\text{A.15})$$

690 Substituting the property (A.15) into equation (A.10) gives the following long time, asymptotic

691 behaviour

$$d_t c^{(2)} = \sum_{i=1}^R \Theta_i \left( v_i c_i^{(1,\infty)} + 2D_i \right) \quad (\text{A.16})$$

692 The time derivative of the variance of particle locations becomes constant and a classical Fickian

693 behaviour is achieved, with (A.5a) simplifying into Equation (9).

694 *Appendix A.2.4. A particular case: the two region model*

695 The simplest possible model consists of two regions :

$$R = 2, \Theta_2 = 1 - \Theta_1, v_2 = -\frac{\Theta_1}{\Theta_2} v_1 \quad (\text{A.17})$$

696 Solving equations (A.9, 6) under assumptions (A.17) yields the following solution

$$c_i^{(1)} = \frac{\Theta_1 \Theta_2}{k_{12}} \left( 1 - \exp \left( -\frac{k_{12}}{\Theta_1 \Theta_2} t \right) \right) v_i, \quad i = 1, 2 \quad (\text{A.18a})$$

$$c^{(2)} = \frac{\Theta_1 \Theta_2}{k_{12}} (\Theta_1 v_1^2 + \Theta_2 v_2^2) \left( t + \frac{\Theta_1 \Theta_2}{k_{12}} \left[ \exp \left( -\frac{k_{12}}{\Theta_1 \Theta_2} t \right) - 1 \right] \right) + 2(\Theta_1 D_1 + \Theta_2 D_2) t \quad (\text{A.18b})$$

698 which yields

$$D_{\text{loc}} = \frac{1}{2} \frac{\Theta_1 \Theta_2}{k_{12}} (\Theta_1 v_1^2 + \Theta_2 v_2^2) \left( 1 - \exp \left( -\frac{k_{12}}{\Theta_1 \Theta_2} t \right) \right) + \Theta_1 D_1 + \Theta_2 D_2 \quad (\text{A.19a})$$

$$D_{\text{av}} = \frac{1}{2} \frac{\Theta_1 \Theta_2}{k_{12}} (\Theta_1 v_1^2 + \Theta_2 v_2^2) \left( 1 + \Theta_1 \Theta_2 \frac{\exp \left( -\frac{k_{12}}{\Theta_1 \Theta_2} t \right) - 1}{kt} \right) + \Theta_1 D_1 + \Theta_2 D_2 \quad (\text{A.19b})$$

700 with the following limit behaviours

$$D_{\text{loc}} \underset{0}{\sim} \Theta_1 D_1 + \Theta_2 D_2 + \frac{1}{2} \Theta_1 \Theta_2 (\Theta_1 v_1^2 + \Theta_2 v_2^2) t \quad (\text{A.20a})$$

$$D_{\text{av}} \underset{0}{\sim} \Theta_1 D_1 + \Theta_2 D_2 + \frac{1}{4} \Theta_1 \Theta_2 (\Theta_1 v_1^2 + \Theta_2 v_2^2) t \quad (\text{A.20b})$$

$$D_{\text{loc}} \underset{\infty}{\sim} D_{\text{av}} \underset{\infty}{\sim} D_{\infty} = \Theta_1 D_1 + \Theta_2 D_2 + \frac{1}{2} \frac{\Theta_1 \Theta_2}{k_{12}} (\Theta_1 v_1^2 + \Theta_2 v_2^2) \quad (\text{A.20c})$$

703 *Long time and small time behaviours.* A further restriction of the model (A.17) is obtained under  
 704 the particular assumption  $D_1 = D_2 = 0, \Theta_1 = \Theta_2 = \frac{1}{2}, v_1 = -v_2 = -a$ . This leads to a particular  
 705 case of the telegraph equation [4]. Its first mention as a model for turbulent dispersion is attributed  
 706 to Davydov [15]. It gives a formula similar to the well-known formula established by Einstein in  
 707 its publications on Brownian movement [19, 20, 21]:

$$D_{\infty} = \frac{a^2}{8k_{12}} \quad (\text{A.21})$$

708 with  $k_{12} = \frac{1}{4\tau}$ ,  $\tau$  being the time scale of the Brownian movement. For small times, the advective  
 709 process is predominant, with a so-called ballistic behaviour (a variance growing proportionally  
 710 to the square of time). For large times, an asymptotic Fickian regime is reached. The Fickian  
 711 behaviour is reached after a few times  $k_{12}^{-1}$ . This shows that a Fickian behaviour can be obtained  
 712 from a purely advective model beyond a certain time scale. At smaller times, the dispersion  
 713 process is anomalous. The advantage of the purely advective model over the Fickian model is that  
 714 it implicitly rules out infinite signal propagation speeds.

715 *Convergence rate to the asymptotic value  $D_{\infty}$ .* Equations (A.19a, A.19b) can be rewritten as

$$D_{\infty} - D_{\text{av}} = A \frac{\exp(-Kt)}{Kt} \underset{t \rightarrow \infty}{\sim} \frac{A}{Kt} \quad (\text{A.22a})$$

$$D_\infty - D_{\text{loc}} = A \exp(-Kt) \quad (\text{A.22b})$$

716

$$A = \frac{K}{2}(\Theta_1 v_1^2 + \Theta_2 v_2^2), K = \frac{k_{12}}{\Theta_1 \Theta_2} \quad (\text{A.22c})$$

717 Comparing equations (A.22a, A.22b) shows that the local estimate  $D_{\text{loc}}$  of the dispersion coefficient  
 718 tends faster to the asymptotic value  $D_\infty$  than does the average estimate  $D_{\text{av}}$ .

## 719 AppendixB. Stability of the solution

720 The purpose of this Appendix is to study the stability properties of the system (A.9). Note  
 721 first that this system can be written in vector form as

$$\mathrm{d}_t \mathbf{x} = \mathbf{v} + \mathbf{M} \mathbf{x} \quad (\text{B.1a})$$

722

$$\mathbf{x} \equiv [\mathbf{c}_1^{(1)}, \dots, \mathbf{c}_R^{(1)}]^T, \mathbf{v} \equiv [\mathbf{v}_1, \dots, \mathbf{v}_R]^T, \mathbf{M} = [M_{ij}] \quad (\text{B.1b})$$

723 where the elements  $M_{ij}$  are defined as in (8). As shown in AppendixA, if the solutions of (B.1a)  
 724 are stable, a Fickian behaviour leading to normal diffusion is obtained in the limit of long times.

725 It is first noticed that the matrix  $\mathbf{M}$  can be written in the form  $\mathbf{M} = -\mathbf{S}\mathbf{D}$ , with

$$\mathbf{D} = \text{diag}[\Theta_i], S_{ij} = -\frac{M_{ij}}{\Theta_j} = \begin{cases} \sum_{p \neq i} \frac{k_{ip}}{\Theta_i \Theta_j} & \text{if } i = j \\ -\frac{k_{ij}}{\Theta_i \Theta_j} & \text{if } i \neq j \end{cases} \quad (\text{B.2})$$

726 Consequently, the matrix  $\mathbf{S}$  is symmetric.

727 *Result 1.* The matrix  $\mathbf{S}$  is positive semidefinite.

728 *Proof.* For any vector  $\mathbf{x} = [x_1, \dots, x_R]^T$ , rearranging and noting that  $k_{ij} \geq 0 \forall (i, j)$  gives

$$\mathbf{x}^T \mathbf{S} \mathbf{x} = \sum_{i=1}^R \sum_{j>i} k_{ij} \left( \frac{x_i}{\Theta_i} - \frac{x_j}{\Theta_j} \right)^2 \geq 0 \forall \mathbf{x} \quad (\text{B.3})$$

729  $\square$

730 *Corollary 1.* The eigenvalues of  $\mathbf{S}$  are all positive.

731 *Proof.* Let  $\lambda$  be an eigenvalue of  $\mathbf{S}$  and  $\mathbf{x}$  a corresponding eigenvector. Then

$$\mathbf{x}^T \mathbf{S} \mathbf{x} = \mathbf{x}^T \lambda \mathbf{x} = \lambda \mathbf{x}^T \mathbf{x} = \lambda \|\mathbf{x}\|^2 \geq 0 \quad (\text{B.4})$$

732  $\square$

733 *Theorem 1.* Let  $\mathbf{S}$  and  $\mathbf{D}$  be symmetric and positive definite matrices. Then the eigenvalues of  $\mathbf{S}\mathbf{D}$   
 734 are all strictly positive.



735 *Proof.* There exists an orthogonal matrix  $\mathbf{C}$  such that  $\mathbf{S} = \mathbf{C} \text{diag} [\lambda_i] \mathbf{C}^T$ . Defining  $\mathbf{S}^{1/2} \equiv$   
736  $\mathbf{C} \text{diag} [\sqrt{\lambda_i}] \mathbf{C}^T$ , it is noted that the matrices  $\mathbf{S}^{1/2} \mathbf{D} \mathbf{S}^{1/2}$  and  $\mathbf{S} \mathbf{D}$  are similar because  $\mathbf{S} \mathbf{D} =$   
737  $\mathbf{S}^{1/2} \mathbf{S}^{1/2} \mathbf{D} \mathbf{S}^{1/2} \mathbf{S}^{-1/2}$  (note that  $\mathbf{S}^{-1/2}$  exists because the  $\sqrt{\lambda_i}$  are all nonzero). Therefore the ei-  
738 genvalues of  $\mathbf{S} \mathbf{D}$  are the same as the eigenvalues of  $\mathbf{S}^{1/2} \mathbf{D} \mathbf{S}^{1/2}$ . Moreover, the matrix  $\mathbf{S}^{1/2} \mathbf{D} \mathbf{S}^{1/2}$  is  
739 symmetric and positive definite because  $\mathbf{D}$  is symmetric, positive definite and  $\mathbf{S}^{1/2}$  is symmetric.  
740 Consequently, the eigenvalues of  $\mathbf{S} \mathbf{D}$  are all strictly positive.  $\square$

741 *Corollary 2.* The eigenvalues of  $-\mathbf{S} \mathbf{D}$  are all strictly negative.

742 *Theorem 2.* Let  $\mathbf{S}$  and  $\mathbf{D}$  be symmetric and positive semidefinite matrices. Then the eigenvalues  
743 of  $\mathbf{S} \mathbf{D}$  are all positive.

744 *Proof.* Let  $\lambda_1, \dots, \lambda_R$  be the (positive) eigenvalues of  $\mathbf{S}$ . There exists an orthogonal matrix  $\mathbf{C}$   
745 such that  $\mathbf{S} = \mathbf{C} \text{diag} [\lambda_i] \mathbf{C}^T$ . Defining  $\mathbf{S}_\epsilon = \mathbf{C} \text{diag} [\lambda_i + \epsilon] \mathbf{C}^T, \epsilon > 0$ . Following the reasoning of  
746 Theorem 1,  $\mathbf{S}_\epsilon^{-1/2}$  exists and the eigenvalues of  $\mathbf{S}_\epsilon \mathbf{D}$  are the same as the eigenvalues of  $\mathbf{S}_\epsilon^{1/2} \mathbf{D} \mathbf{S}_\epsilon^{1/2}$ .  
747 Consequently, they are all positive. Since  $\mathbf{S}_\epsilon \mathbf{D} \rightarrow \mathbf{S} \mathbf{D}$  as  $\epsilon \rightarrow 0$ , it follows from the continuity of  
748 the spectrum of a matrix that the eigenvalues of  $\mathbf{S} \mathbf{D}$  are all positive.

749 *Corollary 3.* The eigenvalues of  $\mathbf{M} = -\mathbf{S} \mathbf{D}$  are all negative.

750 *Result 2.* The solutions of the differential system  $d_t \mathbf{x} = \mathbf{M} \mathbf{x}$  converge to an equilibrium solution.

751 *Proof.* Since  $\mathbf{M}$  and  $\mathbf{M}^T$  have the same spectrum, their eigenvalues are all negative. Therefore,  
752 the solutions of  $d_t \mathbf{x} = \mathbf{M} \mathbf{x}$  and  $d_t \mathbf{x} = \mathbf{M}^T \mathbf{x}$  have the same asymptotic behaviour. Let  $\mathbf{x}$  be the  
753 solution of  $d_t \mathbf{x} = \mathbf{M}^T \mathbf{x}$ . Defining  $Q \equiv \frac{1}{2} \sum_{i=1}^R \frac{1}{\Theta_i} x_i^2$ , one has

$$d_t Q = \sum_{i=1}^R \frac{1}{\Theta_i} x_i d_t x_i = (\mathbf{D}^{-1} \mathbf{x})^T d_t \mathbf{x} = (\mathbf{D}^{-1} \mathbf{x})^T \mathbf{M}^T \mathbf{x} = \mathbf{x}^T \mathbf{D}^{-1} \mathbf{M}^T \mathbf{x} = -\mathbf{x}^T \mathbf{S} \mathbf{x} \quad (\text{B.5})$$

754 From Result 1, the matrix  $-\mathbf{S}$  is negative, semidefinite. Consequently,  $d_t Q \leq 0$  and  $0 \leq Q(t) \leq$   
755  $Q(0)$  for  $t > 0$ . Consequently, the solution  $\mathbf{x}(t)$  is bounded. Since the eigenvalues of  $\mathbf{M}^T$  are  
756 real and negative (from Corollary 3), it follows from the theory of linear differential equations that  
757 there exists a vector  $\mathbf{x}_\infty$  such that  $\mathbf{x} \xrightarrow[t \rightarrow \infty]{} \mathbf{x}_\infty$ .  $\square$

758 *Result 3.* If  $\mathbf{v} \in \text{rge} \mathbf{M}$ , the solution of the non-homogeneous system  $d_t \mathbf{x} = \mathbf{v} + \mathbf{M} \mathbf{x}$  converge to an  
759 equilibrium solution.

760 *Proof.* By assumption, there exists  $\mathbf{a}$  such that  $\mathbf{M} \mathbf{a} = \mathbf{v}$ . Then  $d_t \mathbf{x} = \mathbf{v} + \mathbf{M} \mathbf{x} \iff d_t (\mathbf{a} + \mathbf{x}) =$   
761  $\mathbf{v} + \mathbf{M} \mathbf{x} = \mathbf{M} (\mathbf{a} + \mathbf{x})$ . Consequently,  $\mathbf{a} + \mathbf{x}$  satisfies the homogeneous system  $d_t \mathbf{x} = \mathbf{M} \mathbf{x}$  and  
762 converges to an equilibrium solution, hence the result.

763 *Result 4.* If  $\mathbf{M}$  is block-diagonal,  $\mathbf{M} = \begin{bmatrix} \begin{bmatrix} M_{11} & \cdots & M_{1r} \\ \vdots & & \vdots \\ M_{r1} & \cdots & M_{rr} \end{bmatrix} & 0 \\ 0 & \mathbf{A} \end{bmatrix}$ , a necessary condition for

764  $\mathbf{v} = [v_1, \dots, v_R]^T$  to belong to  $\text{rge}\mathbf{M}$  is

$$\sum_{i=1}^r \Theta_i v_i = 0 \quad (\text{B.6})$$

765 *Proof.* If  $\mathbf{v}$  belongs to the range of  $\mathbf{M}$ , there exists a vector  $\mathbf{a}$  such that  $\mathbf{v} = \mathbf{M}\mathbf{a}$ . Then, using the  
766 symmetry property  $k_{ij} = k_{ji} \forall (i, j)$ , one has

$$\sum_{i=1}^r \Theta_i v_i = \sum_{i=1}^r \Theta_i \sum_{j=1}^r M_{ij} a_j = \sum_{i=1}^r \Theta_i \sum_{\substack{j=1 \\ j \neq i}}^r \frac{k_{ij}}{\Theta_i} (a_j - a_i) = \sum_{i=1}^r \sum_{\substack{j=1 \\ j \neq i}}^r k_{ij} (a_j - a_i) = 0 \quad (\text{B.7})$$

767  $\square$

768 *Corollary 4.* The same result holds for the  $R - r$  remaining elements of  $\mathbf{v}$ ,  $\sum_{i=r+1}^R \Theta_i v_i = 0$ .

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