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► **To cite this version:**

Samer Majdalani, Vincent Guinot. Solute transport in heterogeneous model porous media under different flow rates: Experimental and modelling study. *Journal of Hydrology*, 2023, 616, pp.128790. 10.1016/j.jhydrol.2022.128790 . hal-03881729

HAL Id: hal-03881729

<https://hal.science/hal-03881729v1>

Submitted on 2 Dec 2022

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3 **Solute transport in heterogeneous model porous media under different flow**
4 **rates: experimental and modelling study**

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13
14 **Highlights:**

- 15 – High quality experimental data set for passive transport in heterogeneous porous media
- 16 – Flow rate independent and continuity preserving formulation for MRAD parameters
17 confirmed by experiments
- 18 – Linearity of exchange and dispersion and exchange coefficients with respect to flow rate
19 confirmed by the experimental data set

20
21
22 **Keywords:** flow rate, solute transport, heterogeneous model porous media, advection-
23 dispersion, multi-region.

24
25 **Abstract**

26 The present paper focuses on solute transport behaviour in a Model Heterogeneous Porous
27 Medium (MHPM) under different flow rates. We report tracer experiments under stationary
28 hydraulic conditions, with 7 different stationary flow rates spanning two orders of magnitude.
29 Several replicates are carried out on several MHPMs, allowing for a sound statistical
30 assessment of experimental imprecision. The experimental BreakThrough Curves (BTCs)
31 exhibit a dual transport mode in agreement with previously-reported field scale experiments.
32 This dual transport mode is shown to be flow-rate independent under a suitable variable
33 change, with the BTCs superposing in the limit of experimental uncertainty. The experiment
34 is modelled using a classical Multi-Region Advection-Dispersion (MRAD) model with only
35 two mobile regions. We present a flow rate independent reformulation of the MRAD model
36 that that allows both water and solute continuity to be preserved during the calibration
37 process. Assuming a linear dependence of the dispersion and exchange coefficients on the
38 flow rate is shown to yield satisfactory model behaviour. This confirms the linearity of the
39 dispersion coefficient with respect to the flow rate, often suggested in the literature, over a
40 wide range of flow conditions.

42 1. Introduction

43 Laboratory experiments on model heterogeneous porous media MHPMs contribute to
44 understand the behaviour of solute transport in real world situations (Majdalani et al., 2015).
45 A large number of laboratory scale experimental studies on solute transport in porous media
46 involve a single flow rate, while in real world situations the flow rate may vary over one or
47 two orders of magnitude.

48 Several laboratory studies of solute transport in porous media have tested a variable flow rate
49 in order to test its effect on modelling parameters. A wide review can be found in Griffioen et
50 al. (1998), Maraqa (2001), and Haggerty et al. (2004). In these studies, the most widely used
51 model is the Mobile-Immobile Model (MIM), based on the advection-dispersion equation
52 where two regions (mobile and immobile) exchange mass between each other. The review of
53 Griffioen et al. (1998) is based on 20 experiments. It shows correlations between the flow rate
54 and the mass transfer coefficient, the mass transfer and the advection time scale, the mass
55 transfer and diffusion time scales, the mass transfer and longitudinal interaction time scales.
56 The review by Maraqa (2001) is based on 19 experiments. It shows that correlations exist
57 between the mass transfer coefficient and the flow rate, or the mass transfer coefficient and
58 the residence time. The review of Haggerty et al. (2004) is based on 316 experiments.
59 Correlations are inferred between the effective mass transfer time and other parameters such
60 as the flow rate, the capacity coefficient, the advective residence time and the experimental
61 duration.

62 Experiments reported in the literature involve porous media made of sand (Coats and Smith,
63 1964; Gaudet et al., 1977; De Smedt et al., 1986; Rambow and Lennartz, 1993, Kookana et
64 al., 1993 ; Sharma et al., 2022 ; Sutton et al., 2022), loam (van Genuchten and Wierenga,
65 1977; van Genuchten et al., 1977), loamy sand (Khan and Jury, 1990), clay (Jørgensen et al.,
66 2004), stony soil (Schulin et al., 1987), glass beads (Krupp and Elrick, 1968; De Smedt and
67 Wierenga, 1984; Berkowitz et al., 2009), field soil (Smettem, 1984, Sutton et al., 2022), loam
68 and field soil (Selim et al., 1987), aggregate (Rao et al. 1980; Seyfried and Rao, 1987; Koch
69 and Flühler, 1993; Li et al., 1994; Nkedi-Kizza et al. 1984; Brusseau et al., 1994; Bajracharya
70 and Barry, 1997), or spherical clayey inclusions in sandy media (Tran Ngoc et al., 2020).

71 In the aforementioned studies, porous media are either homogeneous or moderately
72 heterogeneous. Heterogeneity is generally obtained by introducing coarse aggregates into a
73 finer surrounding medium (e.g. glass or clay beads into sand). Li et al. (1994) introduced
74 random porous polyethylene cylinders (porosity 0.50) into silt soil (porosity 0.43).
75 Bajracharya and Barry (1997) used a porous medium consisting of fine sand and polyethylene
76 cylinders in different proportions for 3 experimental columns of different lengths, with a
77 respective total porosity of the composite medium of 0.34, 0.36, and 0.40. Berkowitz et al.
78 (2009) used a porous medium made of adjacent porous materials of fine (1 mm) and coarse (4
79 mm) glass beads, where the porosity (0.39) is the same in both fine and coarse media.
80 Therefore, in literature studies, the porosity of the introduced heterogeneity mostly belongs to
81 the range [0.5, 0.6], which is rather close to the porosity of the surrounding medium (range
82 [0.3, 0.4]).

83 In many laboratory studies the flow rate varies over a single order of magnitude (Griffioen et
84 al., 1998; Maraqa, 2001; Haggerty et al., 2004). Although reviews (Griffioen et al., 1998)
85 report flow rate variations over several orders of magnitude, they aggregate several studies
86 made on different media, that were all performed over one (or slightly more) order of
87 magnitude. Rare are the studies where the flow rate in laboratory heterogeneous porous media
88 is varied over two orders of magnitude within the same medium. One of the widest flow rate
89 ranges is reported in Li et al. (1994), where the pore velocity is varied by a factor 54 and only

90 3 different flow rates are used. In the study by Bajracharya and Barry (1997), the pore
91 velocity is varied by a factor 12.5.

92 As mentioned above, the laboratory porous medium of Li et al. (1994) and Bajracharya and
93 Barry (1997) is moderately heterogeneous. Moreover, the flow direction in these studies is
94 vertical upward (from bottom to top of the column). We argue that salt-based solute transport
95 experiments under upward flow are liable to induce density effects and that the observed
96 BreakThrough Curves (BTCs) might not reflect the real behaviour of passive transport. In
97 fact, rare are the studies of solute transport in porous media using salt tracer that take the
98 possibility of solute density effects into account and their impact on BTCs. Due to gravity,
99 strongly concentrated solute may be trapped in lower parts of the porous medium, thus
100 impacting the behaviour of solute transport and biasing the breakthrough curves compared to
101 those of purely passive transport.

102 Another issue concerning experimental data is reliability. In the aforementioned studies, rare
103 are the solute transport experiments where both the experiment and the porous medium are
104 replicated. The first point means that one should repeat the same experiment several times on
105 a given porous medium column, while the second point means that one should construct
106 several identical porous medium columns and that the ensemble of the experimental protocol
107 should be repeated on each of them. By taking the mean of all replicates, as well as the
108 minimum and maximum values, the statistical variability of the breakthrough curves
109 stemming from various sources can be assessed. Not only is statistical variability of great help
110 in estimating modelling parameters, but it also gives stable and reliable breakthrough curves
111 by minimizing realization sampling effects.

112 In this paper, we study solute transport in laboratory scale Model Heterogeneous Porous
113 Media (MHPMs) under different flow rates. The flow rate Q of tracer step experiments varies
114 over two orders of magnitudes: the ratio of the maximum to the minimum flow rate is 100.
115 The flow rate is modified across the different realizations/experiments but not within a single
116 realization (the flow in each given experiment is stationary). The Model Heterogeneous Pours
117 Medium (MHMP) used in the present study is strongly heterogeneous. A rectangular cavity
118 (porosity 100%) is introduced into surrounding glass beads (porosity 40%). The purpose is to
119 assess the applicability of standard transport models to strongly heterogeneous media, in order
120 to determine whether the degree of heterogeneity induces limitations in the model. Besides,
121 solute transport experiments are done with horizontal flow and we make sure that no solute
122 density effect is present in the MHMP. All tracer step experiments are replicated (see Section
123 2): each experiment is replicated 3 times and the ensemble of the experimental protocol is
124 replicated on 3 different MHPMs built under the same specifications.

125 We simulated the breakthrough curves by a classical approach based on the multi-region
126 advection-dispersion (MRAD) model as presented and analyzed in Majdalani et al. (2018),
127 where only two mobile regions are used. The MRAD model is a generalization of well-known
128 models such as the Two Region (TR), Mobile-Immobile (MI) and Multi-rate models (Coats
129 and Smith, 1964; Griffioen et al. 1998; Haggerty et al., 2000; van Genuchten and Wierenga,
130 1976). A number of studies have focused on how the model parameters behave with the flow
131 rates (Griffioen et al., 1998; Haggerty et al., 2004; Li et al., 1994). They do not all lead to the
132 same conclusions and a wide variety of behaviours is reported. Little is known about how the
133 parameters were constrained in the model calibration process. In particular, it is not always
134 clear whether water and solute mass conservation were enforced in the calibration process. In
135 other words, it is not always clear whether the flow rate in the model is identical to that
136 prescribed in the experiments. Not preserving this condition may yield biases in the calibrated
137 transport parameters. In the present work, mass conservation is enforced by rewriting the
138 MRAD model in terms of flow rate-independent parameters, among which a discharge
139 partition coefficient for the various regions in the model. To our best knowledge, such a

140 reformulation has not been presented in the literature before. Obviously, many other
141 modelling formalisms than the MRAD might be used. More complex models such as Multi-
142 rate models (Haggerty and Gorelick, 1995) and fractional dynamics / Continuous-Time
143 Random Walk (CTRW) models have proven efficient in the modelling of tailing effects and
144 transient dispersion (Berkowitz et al., 2008 ; Bijeljic, 2006 ; Le Borgne et al., 2011 ; Sun et
145 al., 2014 ; Moradi and Mehdinejadani, 2018). Multi-region versions of these approaches have
146 been presented recently (Sun et al., 2020; Yin et al., 2021). Such models are particularly
147 efficient in modelling the long-term behaviours and tailing effects in breakthrough curves that
148 are typical of anomalous transport. They can account for asymptotically long travel times
149 resulting from trapping as well as sudden jumps over long distances, known as Levy flights
150 (Klafter et al., 1987 ; Metzler and Klafter, 2000). However, in the present study, heavy tailing
151 was not identified as a salient characteristic of the BTCs. For this reason, using this type of
152 model was not deemed necessary.

153 The present paper is organized as follows. Section 2 presents the materials and methods.
154 Subsections 2.1 and 2.2 are devoted respectively to the experimental setup and protocol for
155 obtaining a wide range of transport conditions in a strongly porous heterogeneous medium,
156 with flow rates spanning two orders of magnitude. Subsection 2.3 presents a continuity-
157 enforcing writing of the MRAD model. Subsection 2.4 deals with the calibration approach,
158 that takes experimental imprecision into account. Section 3 presents the experimental and
159 modelling results. Sections 4 and 5 are devoted respectively to a discussion and conclusion.
160

161 **2. Material and Methods**

162 **2.1. Model heterogeneous porous medium X_i ($i = 1$ to 3) and Y_i ($i = 1$ and 2)**

163 Three parallelepiped (Length 20 cm, height 2 cm, width 10 cm) columns (X_1 , X_2 , and X_3)
164 were built manually by pasting 5 mm thick plastic plates. The X_i columns are labelled MHPM
165 A, MHPM B, and MHPM C hereafter. They all contain a parallelepiped pore (length 15 cm,
166 height 2 cm, width 1 cm) on one side. The rest of the column is filled with 1 mm glass beads
167 (Figure 1). The rectangular pore (100% porosity) plays the role of a heterogeneity where
168 water rapidly flows in comparison to the surrounding 1 mm glass beads (40% porosity). The
169 ends of the rectangular pore are covered with 500 μm sieve so that the 1 mm glass beads
170 cannot penetrate into it. The X_i columns have four inlets and four outlets. One inlet/outlet
171 faces the rectangular pore, the remaining three inlets/outlets are spread over the width of the
172 MHPM. The pore volume of each MHPM is $V_0 = 158.8$ ml.

173 To reduce solute density effect, the height of the MHPMs was taken very small (2 cm) in
174 comparison to the width (10 cm) and length (20 cm). The assumption of negligible density
175 effects was verified as follows. Two rectangular columns Y_1 (Figure 2) and Y_2 (Figure 3)
176 were designed in a manner that if they are turned upside down, the position of the
177 heterogeneity would change along the middle horizontal plane. Thus, should solute density
178 effects be present, solute transport differ for the Up and Down positions in both Y_1 and Y_2
179 columns, and the resulting BTCs would be different.
180

181 2.2. Tracer step experiment: setup and protocol

182 The solute transport is studied using tracer step experiments under saturated conditions. The
183 columns are first filled with deionized water, then a step of salty water (NaCl) with a
184 concentration of $C_0 = 0.05$ M is introduced into the column via a peristaltic pump (Lead
185 FluidTM). This yields an Atwood number $A = 2.9 \times 10^{-3}$, suggesting that density effects will be
186 negligible. The concentration at the column output is given by a conductivity meter (WTW
187 TetraCon 325TM). The flow rate is estimated by weighing the effluents on a scale (Figure 4).
188 The conductivity meter and the scale are connected to a data logger that samples the
189 measurements at regular time intervals. The step experiment is stopped when the
190 concentration at the column output reaches C_0 (concentration at the column input). The flow
191 is maintained with pure, deionized water until the conductivity of the outflowing
192 concentration returns to its initial, background level.

193 Each of the three X_i columns underwent step experiments with seven flow rates varying from
194 0.25 to 25 l/h (Table 1). The flow rate is varied across different realizations/experiments but
195 not within a single experiment (the flow is constant during a given step experiment). Since the
196 tested flow rates vary in ratios of 2, 4, 10, 20, 40, 100 and 200, they are labelled Q_2 , Q_4 , Q_{10} ,
197 Q_{20} , Q_{40} , Q_{100} , and Q_{200} hereafter. For the lowest flow rate (Q_2), the duration of the step
198 experiment was 3 hours and the data sampling interval was 10 seconds. For the higher flow
199 rate (Q_{200}), the duration of the step experiment was 2 minutes and the data sampling interval
200 was 1 second (Table 1). Each step experiment was replicated three times for each of the three
201 X_i columns, hence a total $7 \times 3 \times 3 = 63$ experimental BTCs (see Results and Discussion
202 sections).

203 The Y_1 and Y_2 columns underwent step experiments with the seven flow rates indicated in
204 Table 1 but the duration of the Y_i experiments are smaller than those of X_i because the
205 volume of Y_i columns is smaller than that of X_i columns. A selection of the BTCs for the Y_i
206 columns is commented in the Results and Discussion sections.
207

208 2.3. MRAD Model

209 2.3.1 Model presentation

210 The so-called Multi-Region Advection-Dispersion (MRAD) (Majdalani et al. 2018) model is
211 a generalization of a variety of models introduced in the literature from the 1970s. Two well-
212 known particular configurations are (i) the Two Region (TR) model (Coats and Smith, 1964;
213 Griffioen et al. 1998) and its particular implementation known as the Mobile-Immobile (MI)
214 model (van Genuchten and Wierenga, 1976), and (ii) the MultiRate (MR) model (Haggerty et
215 al., 2000). The general model consists of R regions, each of which may be mobile or
216 immobile with its own flow and dispersion characteristics, exchanging mass with each other.
217 The governing equations can be written in vector form as

$$218 \quad \frac{\partial \mathbf{c}}{\partial t} + \frac{\partial}{\partial x} \left(\mathbf{U} \mathbf{c} - \mathbf{D} \frac{\partial \mathbf{c}}{\partial x} \right) = \mathbf{K} \mathbf{c} \quad (1a)$$

$$219 \quad \mathbf{c} = [c_i], \quad \mathbf{U} = \text{diag}(u_i) \quad (1b)$$

$$220 \quad \mathbf{D} = \mathbf{U} \boldsymbol{\alpha}, \quad \boldsymbol{\alpha} = \text{diag}(\alpha_i) \quad (1c)$$

221
$$\mathbf{K} = \boldsymbol{\mu}^{-1} [k_{ij}], \quad k_{ij} = -k_{ji} \quad \forall (i,j), \quad \sum_j k_{ij} = 0 \quad \forall i \quad (1d)$$

222
$$\boldsymbol{\mu} = \text{diag}(\mu_i) \quad (1e)$$

223 Where c_i , D_i , u_i , α_i , and μ_i are respectively the concentration, dispersion coefficient, flow
 224 velocity, dispersivity and volume fraction for Region i ($i = 1, \dots, R$), and k_{ij} is a first-order
 225 exchange coefficient between Regions i and j . The antisymmetry property for the matrix \mathbf{K}
 226 and the zero sum in Equation (1d) are necessary conditions for mass conservation (Majdalani
 227 et al. 2018).

228 Specifying appropriate (μ_i, k_{ij}) combinations allow arbitrary exchange functions between the
 229 mobile and immobile regions to be modelled, including transfer functions with multiple
 230 transfer time scales and long-term memory effects (Haggerty et al. 2000, 2004). The model is
 231 also able to represent the transition from ballistic behaviour (i.e. variance of solute position
 232 growing proportionally to the square of travel time) at small spatial and time scales to normal
 233 (i.e. Fickian) dispersion at large scales (Majdalani et al. 2018). Moreover, Fickian behaviours
 234 can be obtained without including any dispersion terms by specifying appropriate velocities
 235 and exchange coefficients between parallel regions (Majdalani et al. 2018). In the most
 236 general possible layout (Figure 5), each region may exchange with all the other regions.
 237 Intuition suggests that exchange should be possible only between two regions that have
 238 similar flow velocities. This would ensure a smooth transition between low velocity (or
 239 immobile regions) and fast flowing regions. However, in a strongly heterogeneous porous
 240 medium, fast flowing regions may be located in the immediate neighbourhood of slow flow
 241 regions (Figure 5a), and the regions may not necessarily be connected. Therefore, as far as
 242 flow topology is concerned, nothing should preclude an exchange between any two different
 243 flow regions in the general case. The exchange coefficient in the model of Figure 5b reflects
 244 not only the transfer rate between the various regions, but also their degree of connectivity.
 245

246 **2.3.2 Identifying a flow rate-independent formulation for the MRAD model from**
 247 **experimental breakthrough curves**

248 The question arises of how the model parameters, i.e. the coefficients of the matrices \mathbf{U} , \mathbf{D}
 249 and \mathbf{K} vary with the flow rate Q . The simplest possible assumption is that \mathbf{D} , \mathbf{K} and \mathbf{U} are
 250 proportional to the discharge and that $\boldsymbol{\mu}$ is fixed. These assumptions can be checked easily
 251 from the experimental breakthrough curves. To do so, the following variable change $\omega =$
 252 Qt/V_0 is introduced, where V_0 is the flow volume in the domain. This volume can be
 253 determined from the experimental breakthrough curves $c_B(t)$ by noting that the inflow
 254 concentration signal c_{in} is a step function with amplitude c_0 :

255
$$Q \int_0^T (c_0 - c_B(t)) dt = V_0 c_0 \quad (2)$$

256 which yields

257
$$V_0 = Q \int_0^T \left(1 - \frac{c_B(t)}{c_0}\right) dt \quad (3)$$

258 The integral is computed from the experimental values using the trapezium rule for numerical
 259 integration. Performing the variable change $\omega = Qt/V_0$ in Equation (1a), using (1b)-(1e) leads
 260 to

261
$$\frac{\partial c}{\partial \omega} + \frac{\partial}{\partial x} \left(\frac{V_0}{Q} \mathbf{U} \mathbf{c} - \frac{V_0}{Q} \mathbf{U} \boldsymbol{\alpha} \frac{\partial c}{\partial x} \right) = \frac{V_0}{Q} \mathbf{K} \mathbf{c} \quad (4)$$

262 In the particular case where \mathbf{K} and \mathbf{U} are proportional to Q and the dispersivities
 263 α_i are independent of Q , all the matrix coefficients in equation (4) are Q -independent and all
 264 plots of $\mathbf{c}(x, \omega)$ obtained for different values of Q superimpose. From an experimental point
 265 of view, only the BTC is known:

$$266 \quad c_B(\omega) = \frac{\sum_i \mu_i u_i c_i(x_{ds}, \omega)}{\sum_i \mu_i u_i} \quad (5)$$

267 where x_{ds} is the abscissa of the downstream end of the model. Therefore, for the BTCs $c_B(\omega)$
 268 to superimpose, the volume fraction matrix $\boldsymbol{\mu}$ must be independent of Q .
 269

270 2.3.3 New MRAD formulation

271 The MRAD model studied here is not different conceptually from those presented earlier in
 272 the literature. The only difference lies in the presentation of the equations and in the
 273 identification of the model parameters. The proposed formulation brings the following
 274 improvements over previously published versions:

- 275 – the (assumed) proportionality of the dispersion and exchange coefficients to the flow rate
 276 is incorporated directly in the formulation,
- 277 – the new formulation intrinsically enforces conservation of both water and solute
 278 regardless of the flow rate. Such conservation is not enforced in usual calibration
 279 approaches (such as that described in Majdalani et al. (2018)), whereby the flow
 280 velocities and volume fractions are calibrated without constraining the conservation of
 281 water flux (let alone solute fluxes).

282 The flow is divided into R regions flowing in parallel. Let A_i and Q_i be respectively the cross-
 283 sectional area and discharge in Region i . They are related to the total area A and discharge Q
 284 with

$$285 \quad A_i = \mu_i A, \quad Q_i = A \mu_i u_i = v_i Q \quad (6)$$

286 Assuming discharge-proportional dispersion and exchange coefficients, the governing
 287 equation in Region i is

$$288 \quad A_i \frac{\partial c_i}{\partial t} + \frac{\partial}{\partial x} \left(Q_i c_i - \frac{\partial}{\partial x} (Q_i \alpha_i c_i) \right) = Q \sum_{j \neq i} k_{ij} (c_j - c_i) \quad (7)$$

289 Substituting the relationships (6) into (7) yields

$$290 \quad \mu_i A \frac{\partial c_i}{\partial t} + \frac{\partial}{\partial x} \left(v_i Q c_i - \frac{\partial}{\partial x} (v_i Q \alpha_i c_i) \right) = Q \sum_{j \neq i} k_{ij} (c_j - c_i) \quad (8)$$

291 The vector form of the equation is

$$292 \quad A \boldsymbol{\mu} \frac{\partial \mathbf{c}}{\partial t} + \frac{\partial}{\partial x} \left(Q \mathbf{v} \mathbf{c} - \frac{\partial}{\partial x} (Q \mathbf{v} \boldsymbol{\alpha} \mathbf{c}) \right) = Q \mathbf{K} \mathbf{c} \quad (9a)$$

$$293 \quad \boldsymbol{\mu} = \text{diag}(\mu_i), \quad \mathbf{v} = \text{diag}(v_i) \quad (9b)$$

$$294 \quad K_{ij} = -K_{ji} = k_{ij} \quad \forall i \neq j \quad (9c)$$

$$295 \quad K_{ii} = -\sum_{j \neq i} K_{ij} \quad (9d)$$

296 where K_{ij} and k_{ij} stand respectively for the elements of the matrix \mathbf{K} and the exchange
 297 coefficients between the regions. Equation (9a) is rewritten as

298
$$\frac{\partial \mathbf{c}}{\partial \tau} + \frac{\partial}{\partial x} \left(\frac{Q}{A} \Theta \mathbf{c} - \frac{\partial}{\partial x} \left(\frac{Q}{A} \Theta \alpha \mathbf{c} \right) \right) = \frac{Q}{A} \mu^{-1} \mathbf{K} \mathbf{c} \quad (10a)$$

299
$$\Theta = \mu^{-1} \mathbf{v} = \text{diag} \left(\frac{\mu_i}{v_i} \right) \quad (10b)$$

300 Noting that $A = V_0/L$, (L is the length of the column) one has

301
$$\frac{\partial \mathbf{c}}{\partial \tau} + \frac{\partial}{\partial x} \left(\frac{QL}{V_0} \Theta \left(\mathbf{c} - \frac{\partial}{\partial x} (\alpha \mathbf{c}) \right) \right) = \frac{QL}{V_0} \mu^{-1} \mathbf{K} \mathbf{c} \quad (11)$$

302 For a two region model as dealt with in the present work, there are 5 independent parameters:
 303 α_1 , α_2 , μ_1 , v_1 , and k_{12} . Note that $\mu_2 = 1 - \mu_1$ and $v_2 = 1 - v_1$. In the absence of dispersion and
 304 exchange ($a_1 = a_2 = k_{12} = 0$), the analytical solution for a step injection consists of two steps
 305 arriving at the downstream end of the MHPM at two different times (dashed line in [Figure 6](#),
 306 [top](#)). Increasing the dispersion coefficients α_1 and α_2 tends to smooth out these steps (solid
 307 line in [Figure 6](#), [top](#)). (μ_1 ; μ_2) act on the contrast between the arrival times of the two steps,
 308 while v_1 influences their relative sizes. Increasing k_{12} tends to smooth out the transition
 309 between the two steps ([Figure 6](#), [bottom](#)). Note that the above considerations are only
 310 indicative of the broad influence of the various parameters on the modelled solution. They do
 311 not reflect the interactions between the exchange and dispersion parameters that may have
 312 similar effects on the long term behaviour of the solution. For instance, the theoretical
 313 analysis in Majdalani et al. (2018) shows that a Fickian dispersive behaviour is obtained
 314 asymptotically for $\alpha_1 = \alpha_2 = 0$, provided that the exchange coefficient k_{12} is non-zero.

315 Note that the coefficients in matrix \mathbf{K} have the dimension of the inverse of a length. Owing to
 316 the conservation properties (9c), (9d), \mathbf{K} has at least one nil eigenvalue, while the remaining
 317 ones are all negative (Majdalani et al., 2018). The smaller of the absolute values of the
 318 remaining eigenvalues gives an order of magnitude of the distance needed for the
 319 concentrations in all regions to homogenize. Beyond this distance, the standard, single region,
 320 Fickian dispersion model becomes valid, even if the dispersion coefficients are zero in all
 321 regions (Majdalani et al., 2018). In the case of a two region model as explored in the present
 322 study, the non-zero eigenvalue is equal to $-2k_{12}$, which yields a characteristic distance $(2k_{12})^{-1}$.
 323 Note that this holds in the case of zero dispersion coefficients
 324 α_i in all regions. In the presence of dispersion, front spreading occurs faster in all regions and
 325 the normal, Fickian dispersion regime is achieved over smaller distances.
 326

327 2.4 Calibration

328 The model parameters are calibrated as introduced in Majdalani et al. (2018) by minimizing
 329 the objective function

330
$$J = \sum_k e_k^{(1)} e_k^{(2)} \quad (12a)$$

331
$$e_k^{(1)} = \left(\frac{1}{T-t_0} \int_{t_0}^T \max(0, |c_B - c_{\text{exp}}| - \delta c)^2(t) dt \right)^{1/2} \quad (12b)$$

332
$$e_k^{(2)} = \left(\frac{1}{1/T - 1/t_0} \int_{t_0}^T \max(0, |c_B - c_{\text{exp}}| - \delta c)^2(t) d\left(\frac{1}{t}\right) \right)^{1/2} \quad (12c)$$

333 where c_B and c_{exp} are respectively the simulated and experimental breakthrough
 334 concentrations, $t_0 > 0$ and T are respectively the simulation time step and simulation length,

335 and δc is the measurement precision. The $\max()$ operator ensures that the modelling error is
 336 zero if the difference between the simulated and experimental concentrations is smaller than
 337 the measurement precision δc .

338 The square root of J thus provides a measure of the difference between the modelling results
 339 and the experiments. It is to be compared with the experimental imprecision, that is measured
 340 by computing the standard deviation of the various replicas of a given experiment:

$$341 \quad \sigma_{\text{av}} = \frac{1}{N} \sum_{i=1}^N \frac{1}{T_i} \int_0^{T_i} \sigma_i(t) dt \quad (13a)$$

$$342 \quad \sigma_i(t) = \left(\frac{1}{m_i-1} \sum_{j=1}^{m_i} (c_{\text{exp},i,j}(t) - \overline{c_{\text{exp},i}}(t))^2 \right)^{1/2} \quad (13b)$$

$$343 \quad \overline{c_{\text{exp},i}}(t) = \frac{1}{m_i} \sum_{j=1}^{m_i} c_{\text{exp},i,j}(t) \quad (13c)$$

344 where $c_{\text{exp},i,j}(t)$ is the experimental concentration measured at time t for the j th replica of the
 345 i th flow rate, m_i is the number of replicas done for the i th flow rate, $N = 6$ or 7 is the number
 346 of flow rates tested, and T_i is the length of the experiment for the i th flow rate. $\overline{c_{\text{exp},i}}(t)$ is
 347 therefore the average at time t of all the concentrations obtained from the m_i replicas done for
 348 the i th flow rate, and $\sigma_i(t)$ is a measure of the experimental dispersion, at a given time t , of
 349 the various replicas for the i th flow rate. Averaging σ_i over time and over the N flow rates
 350 yields σ_{av} , a measure of the overall dispersion of the experimental concentration time series
 351 about the mean signal for all times and all flow rates.

352

353 **3. Results**

354 **3.1. Solute density effect (Y_i columns)**

355 Columns Y_1 and Y_2 are only test columns to verify the existence or the absence of solute
 356 density effect. Since the position of the heterogeneity is not the same in Y_i columns whether
 357 they are in Up or Down position (Figures 2 and 3), and since the solute has a tendency to dive
 358 to the bottom due to gravity (water + solute is denser than deionized water), gravity effects
 359 would induce differences between the BTCs of Columns Y_1 and Y_2 would be different in Up
 360 and Down positions. We made step experiments on Columns Y_1 and Y_2 in Up and Down
 361 positions with all the flow rates given in Table 1 and we noticed that the BTCs were the same
 362 (in the limit of experimental uncertainty) in Up and Down positions, regardless of the flow
 363 rate. As an illustration, Figure 7 (top) (respectively bottom) shows the breakthrough curves of
 364 column Y_1 (respectively Y_2) in Up and Down positions for Flow rate Q_{100} . Therefore, as
 365 argued in Section 2, solute density effects are negligible with the present MHPM design.
 366

367 **3.2. Flow rate effect (X_i column or MHPM A, B, and C)**

368 Each of the three X_i columns underwent step injections under the seven flow rates $Q_2 - Q_{200}$,
 369 with three replicates in each case. As suggested previously in the MRAD formulation, we
 370 adopt the variable change $\omega = Qt/V_0$ to plot the BTCs. Figure 8 shows that, for every MHPM
 371 (A, B, and C), the resulting experimental breakthrough curves superimpose in the limit of

372 experimental imprecision for all flow rates. This validates the assumption of a model
 373 formulation with discharge-independent parameters, as expressed by Eq. (4).
 374 In homogeneous porous media, BTCs classically exhibit an ‘S’ shape. The BTCs shown in
 375 Fig. 8 have a double ‘S’ shape: the lower ‘S’ is attributed to a fast solute transport mode
 376 through the heterogeneity (rectangular pore), while the higher ‘S’ is attributed to a slower
 377 transport mode within the glass beads. Other studies have also noticed that BTCs in
 378 heterogeneous porous media do not have a classical ‘S’ shape (Silliman and Simpson, 1987 ;
 379 Golfier et al., 2011 ; Majdalani et al., 2015). Double ‘S’ shaped BTCs (or double peak curves
 380 for their derivatives) have also been reported in natural/real media (Maloszewski et al., 1992 ;
 381 Goldscheider et al., 2008 ; Perrin and Luetscher, 2008 ; Field and Leij, 2012 ; Dewaide et al.,
 382 2018).
 383

384 3.3. MRAD simulations results

385 The calibration results are given in Table 2. Noting that the error J is the product of two Root
 386 Mean Square Errors (RMSEs), one with respect to t and the other with respect to $1/t$, $J^{1/2}$ gives
 387 a meaningful assessment of the difference between the simulated and experimental
 388 breakthrough curves. $J^{1/2}$ is about 3% of the total variation in the concentration, which can be
 389 deemed a very good agreement between the model and the experiment. In comparison, the
 390 experimental imprecision ranges from 0.56% to 1.56% (i.e. half of the modelling error).
 391 Figure 9 shows the experimental versus simulated breakthrough concentrations. A satisfactory
 392 alignment over the first bisector is observed. This was expected considering the values of $J^{1/2}$
 393 in Table 2.

394 Since the behaviour of the breakthrough curve for the Q_{200} setting in Figure 8 seems different
 395 from that of the other BTCs, a second calibration of the model is run by removing the Q_{200}
 396 time series from the experimental data set. This leads to slightly better calibration results
 397 (Table 3), with $J^{1/2}$ reduced by 10% to 25% compared to the calibration results in Table 2.
 398 Removing Q_{200} from the experimental data set leaves the average experimental imprecision
 399 almost unchanged. Comparing the average calibrated parameter values in Tables 2 and 3
 400 shows that the calibrated α_1 , μ_1 and k_{12} are significantly sensitive to the presence of Q_{200} in
 401 the data, while a_2 and ν exhibit a much lower sensitivity.

402 Table 4 shows the r^2 coefficients, the objective function $J^{1/2}$ and the Mean Bias Error (MBE),
 403 computed from the experimental vs. simulated C/C_0 series shown in Figure 9. The MBE is
 404 calculated accounting for experimental imprecision as

$$405 \quad \text{MBE} = \frac{1}{T-t_0} \int_{t_0}^T [\max(0, c_B - (c_{\text{exp}} + \delta c)) + \min(0, c_B - (c_{\text{exp}} - \delta c))] (t) dt \quad (14)$$

406 whereby the modelling error is calculated as the difference between the modelled
 407 concentration signal c_B and the closest bound of the experimental concentration interval
 408 $[c_{\text{expe}} - \delta c, c_{\text{expe}} + \delta c]$.

409 All r^2 coefficients are larger than 0.99, even for the Q_{200} setting. The values for $J^{1/2}$ (that is
 410 analogous to a Root Mean Squared Error) is smaller than 1.6×10^{-2} in all 21 experiments, and
 411 about 5×10^{-3} for most of them. Lastly, the MBE is smaller than 1%. For all three indicators,
 412 the Q_{200} setting does not significantly poorer values than for the other flow rates. For instance,
 413 for MHPM A, the r^2 for Q_{200} is similar to that of Q_{10} , its MBE is smaller and its $J^{1/2}$ is very
 414 similar. Similar remarks can be made for MHPM B and MHPM C. This confirms that the
 415 behaviour of the model is satisfactory, not only on the average, but also for all individual
 416 experiments for all three MHPM.
 417

418 4. Discussion

419 The linearity of the exchange coefficient k_{12} and the dispersion coefficients D_i with respect to
420 the flow rate under laminar flow was expected from theoretical considerations (Majdalani et
421 al., 2018), because these coefficients reflect the statistics of the fluctuations of the velocity
422 field about the mean values. Such fluctuations are expected to be proportional to the average
423 flow velocity (thus to the flow rate) when the flow rate is small.

424 The present experimental and modelling results confirm the theoretical assumption of a linear
425 relation between the flow rate and the mass exchange coefficients over a wide range of flow
426 rate values, even for a strongly heterogeneous MHPM. This is also true for the flow velocities
427 and dispersion coefficients in the two regions of the model. The volume fractions of the two
428 regions and the partition coefficient of the flow rate between these regions are found to be
429 flow rate independent. As a consequence, the flow velocity is proportional to the flow rate
430 and the dispersivity is flow rate independent in both regions. We note that e.g. Hansen (2022)
431 also inferred a flow velocity proportional to the flow rate and a flow rate independent
432 dispersivity using a very different experimental setup and a different model, based on
433 fractional mass exchange between the mobile and immobile regions. While Hansen (2022)
434 concludes that the exchange coefficient is flow rate independent, we obtain a linear
435 relationship between k_{12} and the flow rate. These two findings are not necessarily
436 contradictory in that the structures of the two exchange models are different.

437 The three MHPMs used in the present study were built following the same geometric
438 specifications. They are identical within a geometric precision of 1 mm (for a total length of
439 150 mm). This may be considered an excellent geometric replicability. Comparing the
440 calibration results in [Tables 2 and 3](#) gives an idea of the uncertainty in the parameters with
441 respect to MHPM manufacturing for almost indiscernible geometries. While the volume and
442 flow distribution parameters μ_i and ν_i in [Table 2](#) are remarkably stable from one MHPM to
443 the next, the dispersion coefficients in both regions vary by 150% and the exchange
444 coefficient varies by more than 300%. Dropping the largest discharge from the experimental
445 set contributes to increase the consistency of the calibration results: all model parameters,
446 including the exchange coefficient k_{12} , are remarkably consistent for all MHPMs. This seems
447 to indicate that the highest flow rate (Q_{200} pump setting) is the limit of applicability of the
448 flow rate independent model formulation. For this flow rate, the residence time of the tracer
449 within the MHPM is approximately 23 s, which corresponds to an average flow velocity of
450 6.6 mm/s. Assuming that all the flow passes through the 2 cm high central conduit yields an
451 upper bound $Re = 132$ for the Reynolds number. Turbulence effects are therefore an unlikely
452 cause. However, it is suspected that, owing to the strongly contrasted MHPM geometry, the
453 effective flow paths are not exactly the same for the Q_{200} setting as for smaller flow rates, thus
454 inducing different model calibration results.

455 In order to compare our modelling results with previous literature findings, namely Li et al.
456 (1994) and Bajracharya and Barry (1997), we recall that in the present study u varies between
457 0.2 and 20 cm/min. Li et al. (1994) found a linear relation between u and the mass exchange
458 coefficient k_{12} for $0.3 < u < 2.7$ cm/min, but for $0.05 < u < 0.1$ cm/min the relation between
459 k_{12} and u was rather quadratic ($k_{12} = 94.23 \times u^{2.3}$). In both cases, the fit of the k_{12} - u
460 relationship was based on 3 data points, for which the experimental confidence interval is not
461 known. Thus, according to Li et al. (1994), the k_{12} - u relationship is quadratic at low pore
462 water velocity and linear at higher velocities. We argue that more than 3 data points are
463 needed to deduce a good fit and this is why we use 7 flow rates in our study. In our study, the
464 k_{12} - u relationship is linear, in agreement with Li et al. (1994) for high velocities, and even
465 beyond the range of velocities explored by Li et al. (1994).

466 Bajracharya and Barry (1997) tried to fit a relation in the form $k_{12} = au^b$ to their data and
467 evaluated the fitting quality using the coefficient of determination r^2 . Since several, different
468 experimental conditions (column material, column depth, column diameter, velocity range)
469 were involved, Bajracharya and Barry (1997) obtained several values for the power b : $b =$
470 2.15 ($r^2 = 0.965$) for $0.05 < u < 0.4$ cm/min, $b = 1.79$ ($r^2 = 0.971$) for $0 < u < 0.8$ cm/min, $b =$
471 1.3 for $0 < u < 6$ cm/min ($r^2 = 0.954$). In the latter case, a linear relation with $b = 1$ was also
472 possible with $r^2 = 0.933$. Bajracharya and Barry (1997) concluded that $k_{12}-u$ relationship
473 follows a power law with a power coefficient b that ranges from 1 to 2 where k_{12} scales
474 linearly with u at low pore water velocity, and k_{12} may assume any value between 0.5 and 2 at
475 higher velocities (which contradicts the conclusions of Li et al. (1994)).
476 In the review of Maraqa et al. (2001), that is based on 19 experiments, the $k_{12}-u$ relationship
477 is found to be sublinear ($b < 1$) and the value of b depends on the type of porous medium: $b =$
478 0.85 ($r^2 = 0.57$) for a non-aggregated medium with $0.01 < u < 0.12$ cm/min, $b = 0.71$ ($r^2 =$
479 0.52) for an aggregated medium with $0.01 < u < 0.12$ cm/min, and $b = 0.76$ ($r^2 = 0.7$) for a
480 stony medium with $0.006 < u < 0.045$ cm/min.
481 The review of Griffioen et al. (1998) is based on 20 experiments. Its conclusions are that the
482 $k_{12}-u$ relationship rather follows $k_{12} = au^b$, where b has no stable value. Table 3 in
483 Griffioen et al. (1998) shows that b can take any value between -0.3568 (experiment of Khan
484 and Jury (1990)) and 4.8543 (experiment of Nielsen and Biggar (1961)).
485 The results of Bajracharya and Barry (1997), Maraqa et al. (2001), and Griffioen et al. (1998)
486 show that, even though the relationship $k_{12}-u$ is expected to be linear for theoretical reasons,
487 experimental data do not generally reflect such linearity. However, such lack of linearity may
488 stem from various sources. For instance, solute density effects may be present under vertical
489 flow conditions and induce a non-linear behaviour in the $k_{12}-u$ relationship. The lack of
490 linearity may also be explained by the absence of replicates. Not replicating the measurements
491 precludes the width of the experimental confidence interval to be assessed, thus making it
492 impossible to determine whether a linear (or another type of) law would pass through the
493 experimental error boxes. We consider that our experimental data set is reliable because the
494 absence of solute density effects has been verified experimentally and because there are 9
495 replicates for each flow rate: 3 replicates of each experiment and 3 replicates of the porous
496 medium.
497 A last discussion point is how the conclusions of the present work, carried out using a single,
498 strongly contrasted heterogeneity, can be transposed to more natural aquifers, involving much
499 larger scales and less contrasted heterogeneities. The present MHPMs were designed so as to
500 maximize the contrast between the fast and slow flow paths. The purpose was to make the
501 experimental transport process as difficult as possible to model using the standard MRAD
502 model. From the authors' experience on MHPMs placed in series (Majdalani et al., 2015),
503 increasing the number of heterogeneities tends to smooth out the transport process, bringing it
504 closer to a Fickian behaviour. This is nothing but a consequence of the central limit theorem
505 (see e.g. Klafter et al., 1987 ; Metzler and Klafter, 2000). Decreasing the contrast between the
506 permeabilities of the two media or making the volume occupied by one of them significantly
507 smaller than the other also contributes to decrease the contrast between the slow and fast
508 transport fluxes, which also brings the BTCs closer to those of a single transport mode,
509 Fickian behaviour. That the reformulated MRAD model reproduces satisfactorily the BTCs of
510 a single, highly contrasted MHPM is therefore seen as an encouraging sign for the modelling
511 of more natural aquifers containing multiple heterogeneities. Obviously, this conclusion holds
512 only provided that the properties (size, porosity, permeability) of the heterogeneities do not
513 exhibit large scale variations that would be impossible to capture by a model with uniform
514 parameters.

515 5. Conclusion

516 In this paper we studied solute transport in heterogeneous model porous medium under a wide
517 range of flow rates. We conducted tracer experiments with seven tested flow rates ranging
518 from 0.25 to 25 l/h, that is over two orders of magnitude. In comparison to other studies
519 where the porous medium is moderately heterogeneous, our experiment is characterized by a
520 high degree of heterogeneity. Solute transport experiment were carried out under horizontal
521 flow and so that no solute density effects are present in the MHPM. In order to make our
522 experimental data reliable for modelling exercise, all tracer step experiments were done with
523 replicates: 3 replicates of each experiment and the ensemble of the experimental protocol was
524 replicated on 3 identical MHPMs (A, B, and C).

525 The experimental breakthrough curves show a double ‘S’ shape behaviour in accordance with
526 other literature findings, and that the ‘S’ shape is a stable behaviour that does not vary with
527 flow rate under a suitable change of variable on the abscissa axis: $\omega = Qt/V_0$. This shows that
528 there exists a model with flow-rate independent parameters that can reproduce all
529 experimental BTCs. The BTCs are modelled successfully using a reformulated version of the
530 MRAD model with only two mobile regions. The new formulation enforces mass balance for
531 both water and the solute, and uses flow rate independent parameters. The simulated BTCs
532 are in close agreement with the experimental ones, with an error around 3%, r^2 coefficients
533 above 0.99 and a Mean Bias Error smaller than 10^{-2} . This validates the assumption of linear
534 flow velocities, dispersion coefficients and exchange coefficients with respect to the flow rate
535 in the two region model.

536 Although the assumption of linearity between transport parameters and the flow rate has been
537 suggested in previous studies, no clear experimental evidence for this can be found in the
538 literature. Our study can be considered to provide a clear experimental evidence of the
539 linearity assumption between MRAD parameters and flow rate. The variability of the model
540 parameters from one MHPM to the other is strongly reduced when the largest flow rates are
541 dropped from the experimental data sets. This may be an indication that the largest flow rate
542 is at the limit of model applicability. Our experimental data set is deemed reliable owing to its
543 high sampling rate, the use of several replicates for each experiment, all done on several
544 replicates of the MHPM.

545 We should like to conclude with a remark on the one-dimensional nature of the transport
546 model. Although MHPMs (and the resulting flow within them) are three-dimensional, most
547 experiments performed in the literature (including the present ones) involve one-dimensional
548 flow models. These are upscaled models (Farmer, 2002) in that they attempt to provide a one-
549 dimensional representation of the transport process on the (low) resolution of the MHPM size,
550 while the actual transport process is spatially variable and three-dimensional on a much
551 smaller scale. Being one-dimensional, the model includes a single (longitudinal) dispersion
552 coefficient. However, in real-world situations, dispersion involves a tensor formulation with
553 three principal directions. A logical next step in the present research should be to investigate
554 of how the MRAD model can be generalized to two- and three-dimensional modelling and
555 whether the rate of convergence to the Fickian limit and the linear dependence to the flow is
556 preserved when the MHPM is not only strongly heterogeneous but also strongly anisotropic in
557 two and three dimensions.

558
559

560 **Appendix. Numerical solution of the transport equations**

561 The present appendix details the numerical solution of the transport equation (1a), that can be
 562 rewritten in the following form under the assumption of space-independent coefficients in the
 563 equation

564
$$\frac{\partial \mathbf{c}}{\partial t} + u_i \frac{\partial c_i}{\partial x} - D_i \frac{\partial^2 c_i}{\partial x^2} = - \sum_{j \neq i} \mu_i k_{ij} c_j \quad (\text{A.1})$$

565 The equation is solved using a three step time splitting procedure (Strang, 1968). To do so,
 566 Eq. (A.1) is split into three equations:

567
$$\frac{\partial \mathbf{c}}{\partial t} + u_i \frac{\partial c_i}{\partial x} = 0 \quad (\text{A.2a})$$

568
$$\frac{\partial \mathbf{c}}{\partial t} - D_i \frac{\partial^2 c_i}{\partial x^2} = 0 \quad (\text{A.2b})$$

569
$$\frac{\partial \mathbf{c}}{\partial t} = - \sum_{j \neq i} \mu_i k_{ij} c_j \quad (\text{A.2c})$$

570 where Eqs. (A.2a-c) are solved numerically using the same computational time step Δt , and
 571 each equation (A.2b-c) uses the result of the previous one as a starting point over the time
 572 step.

573 Equation (A.2a) is solved using a finite volume procedure. Within each region i (the subscript
 574 i is dropped in the notation for the sake of readability), the following formula is used:

575
$$c_k^{n+1} = c_k^{n+1} + \frac{u \Delta t}{\Delta x} (c_{k-1/2}^{n+1/2} - c_{k+1/2}^{n+1/2}) \quad (\text{A.3})$$

576 where c_k^n is the average value for c in the k th cell at time step n , and $c_{k-1/2}^{n+1/2}$ is the average
 577 value of c at the interface between Cells $k-1$ and k between time levels n and $n+1$. The salient
 578 point of the algorithm lies in the definition of the interface values $c_{k-1/2}^{n+1/2}$. In order to
 579 minimize numerical diffusion, we used an arbitrary time step explicit method presented in
 580 Leonard (1994). This method removes the restriction on the time computational time step by
 581 allowing the dimensionless CFL number $u \Delta t / \Delta x$ to take any arbitrary large value. Δt is set up
 582 to the largest possible value allowing the fastest region to travel over the length L of the
 583 computational domain within Δt , that is

584
$$\Delta t_{\max} = \frac{L}{\max_i u_i} \quad (\text{A.4})$$

585 Equation (A.2b) is discretized using a classical centred implicit scheme

586
$$F c_{k-1}^{n+1} + (1 - 2F) c_k^{n+1} + F c_{k+1}^{n+1} = c_k^n \quad (\text{A.5a})$$

587
$$F = \frac{D \Delta t}{\Delta x^2} \quad (\text{A.5b})$$

588 Eq. (A.2c) is discretized using an implicit time marching scheme

589
$$\frac{\mathbf{c}_k^{n+1} - \mathbf{c}_k^n}{\Delta t} = \mathbf{R} \mathbf{c}_k^{n+1} \quad (\text{A.6})$$

590 where $\mathbf{c} = [c_i]$. Solving (A.6) for \mathbf{c}_k^{n+1} yields

591
$$\mathbf{c}_k^{n+1} = (\mathbf{I} - \Delta t \mathbf{R})^{-1} \mathbf{c}_k^n \quad (\text{A.7})$$

592

593 **Acknowledgements**

594 The authors thank Jean-Philippe Chazarin from the laboratory HydroSciences Montpellier –
595 France for his help in developing the electronic devices used in the experiments.
596

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737

738 **List of Tables**Table 1. Values and symbols of the flow rates tested in step experiments on columns X_i ($i = 1$ to 3) also called MHPM A, MHPM B, and MHPM C

Symbol	Flow rate (l/h)	Experiment duration (min)	Sampling Interval (s)
Q ₂	0.25	180	10
Q ₄	0.5	90	10
Q ₁₀	1.25	40	5
Q ₂₀	2.5	20	5
Q ₄₀	5	10	1
Q ₁₀₀	12.5	3	1
Q ₂₀₀	25	2	1

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Table 2. Calibration results with all flow rates. The average and standard deviations in each row are computed row from the three values obtained from MHPMs A-C.

Parameter	MHPM A	MHPM B	MHPM C	Average	Standard dev.
α_1 (cm)	2.36	2.33	1.72	2.14	0.36
α_2 (m)	0.373	0.269	0.262	0.301	0.062
μ_1 (-)	0.294	0.288	0.270	0.284	0.012
ν_1 (-)	0.598	0.546	0.593	0.579	0.029
k_{12} (m ⁻¹)	0.578	0.295	0.948	0.607	0.327
J (-)	7.05×10^{-4}	10^{-3}	1.47×10^{-3}	1.06×10^{-3}	3.9×10^{-4}
$J^{1/2}$ (-)	2.66×10^{-2}	3.17×10^{-2}	3.84×10^{-2}	3.22×10^{-2}	5.9×10^{-3}
σ_{av}	1.56×10^{-2}	0.76×10^{-2}	0.56×10^{-2}	0.96×10^{-2}	5.3×10^{-3}

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Table 3. Calibration results without Q₂₀₀. The average and standard deviations in each row are computed row from the three values obtained from MHPMs A-C.

Parameters	MHPM A	MHPM B	MHPM C	Average	Standard dev.
α_1 (cm)	1.55	1.15	1.48	1.39	0.21
α_2 (cm)	0.334	0.291	0.283	0.303	0.024
μ_1 (-)	0.271	0.228	0.264	0.254	0.023
ν_1 (-)	0.592	0.506	0.591	0.563	0.049
k_{12} (m ⁻¹)	0.898	0.707	0.823	0.809	0.096
J (-)	5.78×10^{-4}	6.86×10^{-4}	8.19×10^{-4}	6.94×10^{-4}	1.21×10^{-4}
$J^{1/2}$ (-)	2.40×10^{-2}	2.62×10^{-2}	2.87×10^{-2}	2.63×10^{-2}	2.4×10^{-3}
σ_{av}	1.68%	0.72%	0.51%	0.97×10^{-2}	6.3×10^{-3}

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Table 4. Goodness-of-fit indicators for experimental vs. modelled C/C_0 .

Flow rate	MHPM A			MHPM B			MHPM C		
	r^2	$J^{1/2}$	MBE	r^2	$J^{1/2}$	MBE	r^2	$J^{1/2}$	MBE
Q ₂	0.998	5.16×10^{-3}	1.63×10^{-3}	0.994	1.07×10^{-2}	1.13×10^{-3}	0.991	2.35×10^{-3}	7.74×10^{-4}
Q ₄	0.998	4.33×10^{-3}	1.55×10^{-3}	0.999	8.44×10^{-3}	-2.17×10^{-4}	0.997	4.34×10^{-3}	-1.71×10^{-3}
Q ₁₀	0.995	4.89×10^{-3}	3.51×10^{-3}	0.997	7.01×10^{-3}	8.39×10^{-3}	0.999	3.66×10^{-3}	9.61×10^{-4}
Q ₂₀	0.999	4.03×10^{-3}	3.74×10^{-4}	0.998	1.23×10^{-2}	9.05×10^{-3}	0.997	2.53×10^{-3}	1.23×10^{-3}
Q ₄₀	0.999	2.87×10^{-3}	3.04×10^{-4}	0.999	6.33×10^{-3}	4.83×10^{-3}	0.999	4.80×10^{-3}	2.11×10^{-3}
Q ₁₀₀	0.999	1.25×10^{-2}	-1.61×10^{-3}	0.995	8.15×10^{-3}	7.13×10^{-4}	0.997	1.83×10^{-3}	6.18×10^{-5}
Q ₂₀₀	0.995	5.04×10^{-3}	2.52×10^{-3}	0.999	1.59×10^{-2}	-1.05×10^{-3}	0.992	1.08×10^{-2}	5.17×10^{-3}

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746 Table 5. Dimensionless numbers for similarity analysis. The Reynolds number is computed as $Re = \frac{QD}{Av} = \frac{QLD}{V_0 v}$ and the

747 Peclet number in region k as $Pe_k = L/\alpha$.

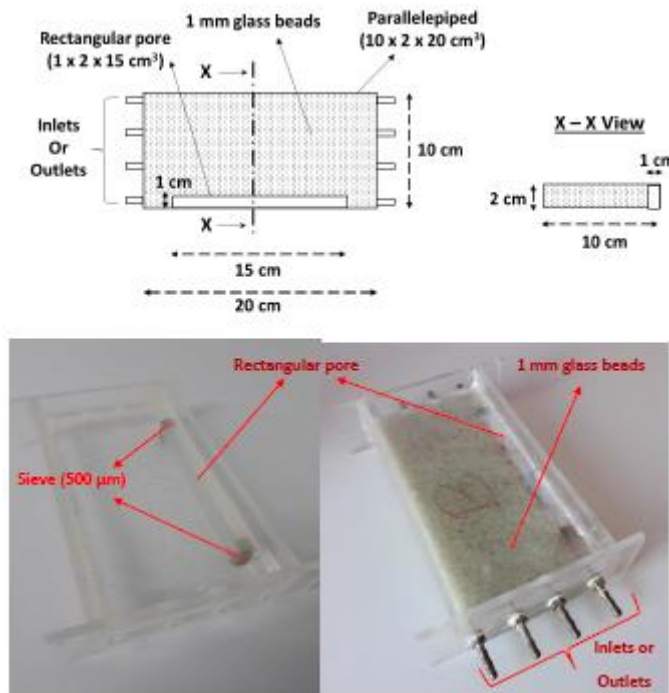
MHPM	Re (-)	Pe ₁ (-)	Pe ₂ (-)
A	1.32 – 132	9.7	44.9
B	1.32 – 132	13.0	51.5
C	1.32 – 132	10.1	53.0

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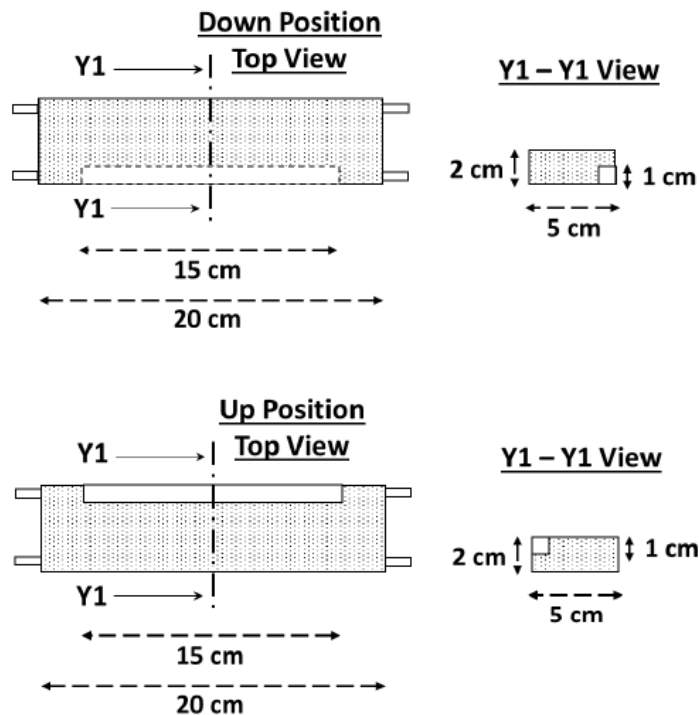
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751 **Figures**



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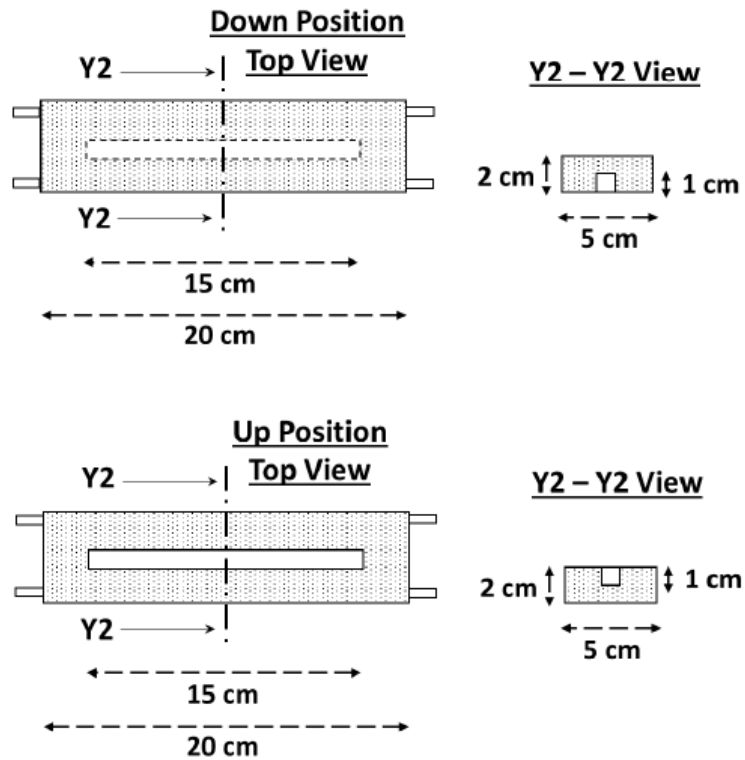
Figure 1. Model heterogeneous porous medium X_i ($i = 1$ to 3). Dashed area represents 1 mm glass beads and white area represents the heterogeneity (rectangular pore). Real photos show the column before and after filling it with 1 mm glass beads.



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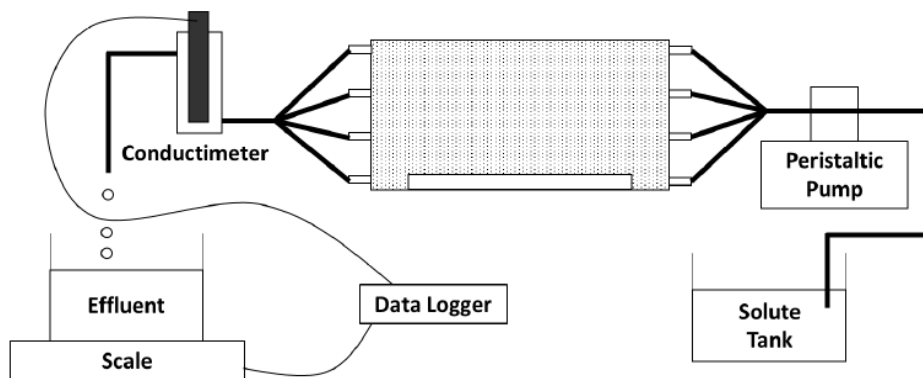
Figure 2. Model heterogeneous porous medium Y_1 where the heterogeneity (white rectangle) is located in one corner. As in Figure 1, dashed area represents 1 mm glass beads and white area represents the heterogeneity (rectangular pore).

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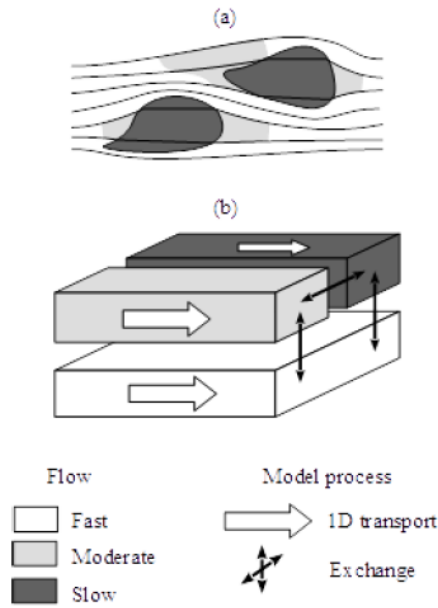
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Figure 3. Model heterogeneous porous medium Y_2 where the heterogeneity (white rectangle) is located in the center of one face. As in Figure 1, dashed area represents 1 mm glass beads and white area represents the heterogeneity (rectangular pore).



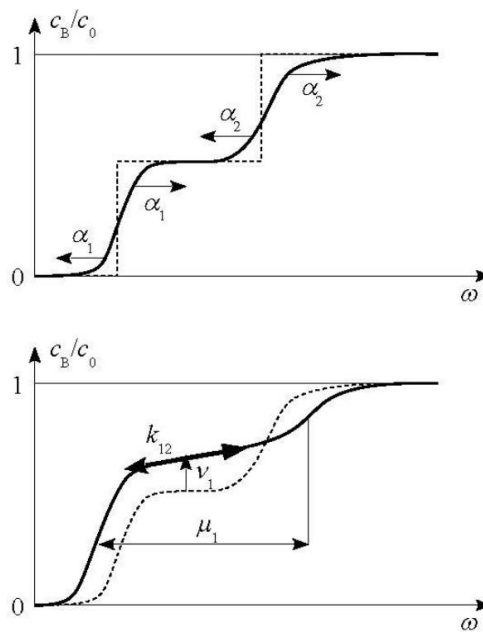
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Figure 4. Tracer step experiment setup.



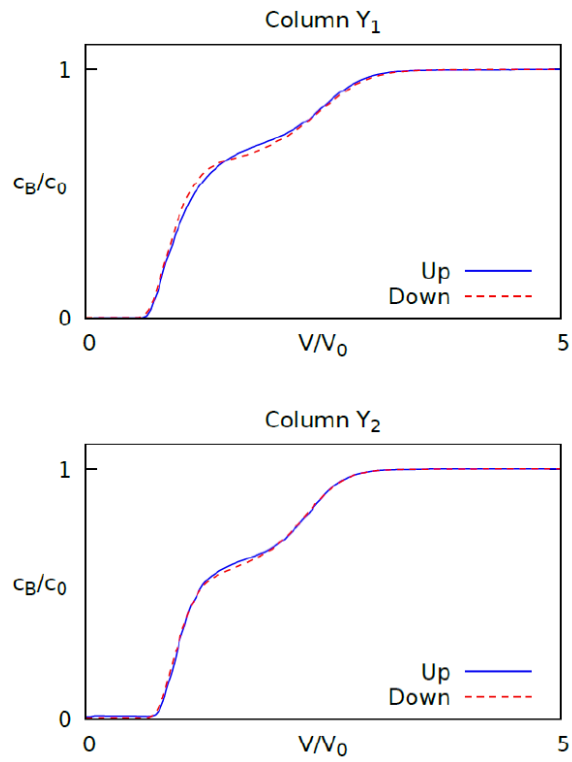
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Figure 5. MRAD model definition sketch. (a) Streamlines and partition into several regions in the presence of heterogeneities. (b) Schematization in the MRAD model. Any of the fast, moderate or slow velocity regions may be partitioned into several subregions when required by the flow physics



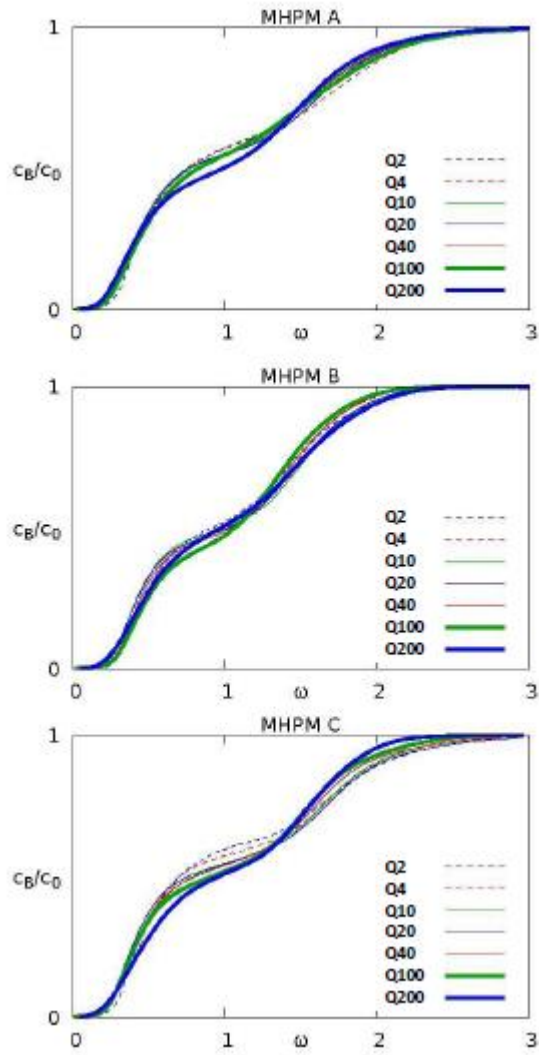
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Figure 6. Influence of the MRAD parameters on the shape of the breakthrough curve.



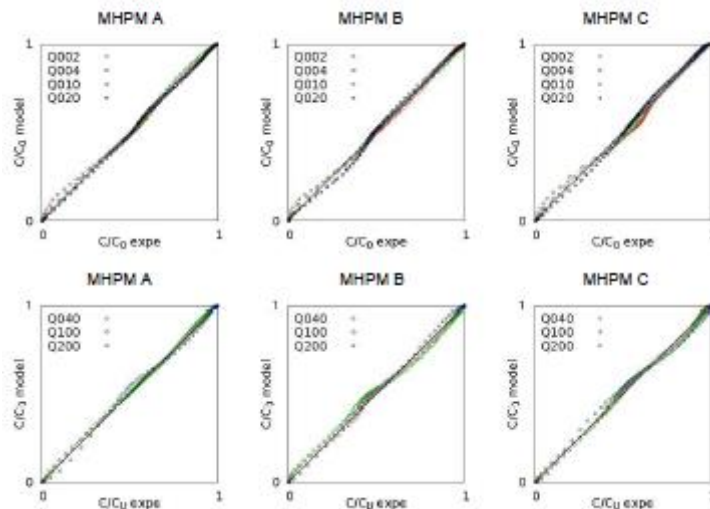
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Figure 7. Step experiments with flow rate Q_{100} . Top: Column Y_1 in Up and Down positions.
Bottom: Column Y_2 in Up and Down positions.



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Figure 8. Experimental breakthrough curves for columns MHPM A, B, and C. The variable change $\omega = Qt/V_0$ is adopted for the abscissa axis. The three digit figures in the legend refer to the peristaltic pump setting, see Table 1 for the flow rate values.



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Figure 9. Experimental vs. modelled breakthrough curves for the three MHPM (A, B, and C) and for the seven tested flow rates.

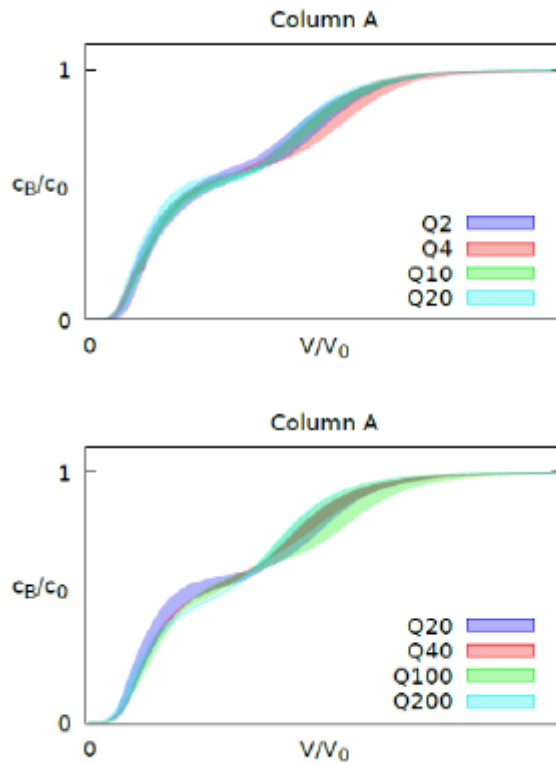


Figure S1. Experimental BTCs for MHPM A plotted along with their experimental uncertainty. Two plots are shown, with Q20 is common to both graphs for the sake of comparison.

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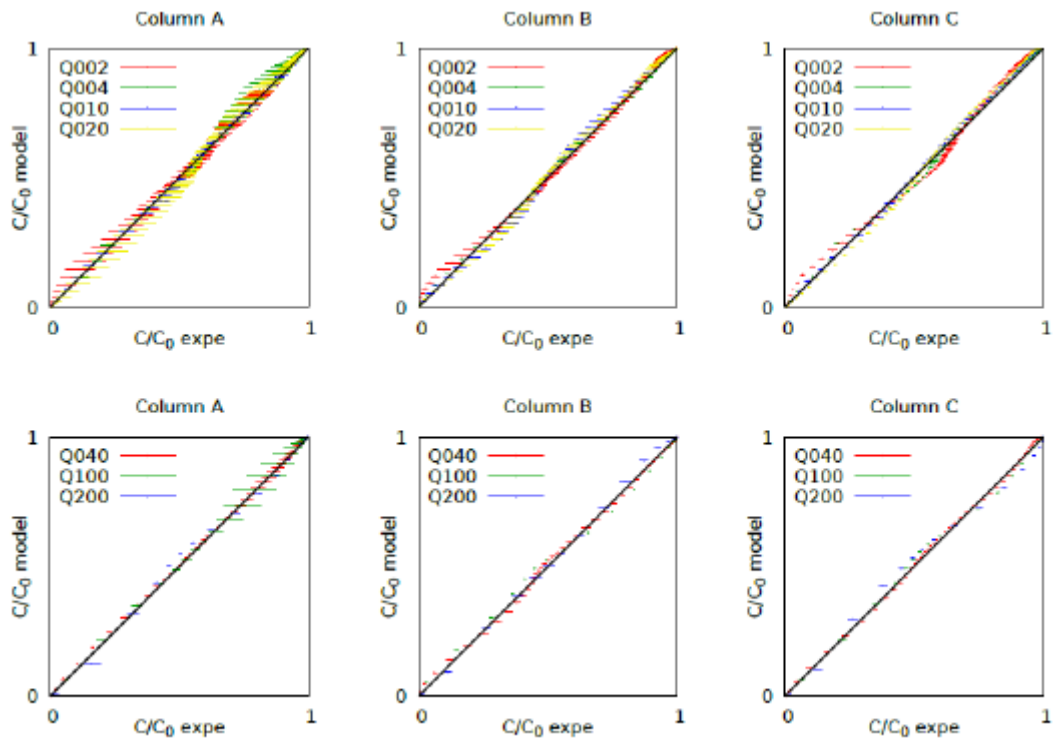


Figure S2. A modified version of Figure 9 that includes the experimental imprecision.

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