

# 1    **On the reliability of analytical models to predict solute transport in a fracture** 2    **network**

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## 7    **Abstract**

8    In hydrogeology, the application of reliable tracer transport model approaches is a key issue to  
9    derive the hydrodynamic properties of aquifers.

10   Laboratory and field – scale tracer dispersion breakthrough curves (BTC) in fractured media are  
11   notorious for exhibiting early time arrivals and late – time tailing that are not captured by the  
12   classical advection – dispersion equation (ADE). These “non – Fickian” features are proved to be  
13   better explained by a mobile – immobile (MIM) approach. In this conceptualization the fractured  
14   rock system is schematized as a continuous medium in which the liquid phase is separated into  
15   flowing and stagnant regions.

16   The present study compares the performances and reliabilities of the classical Mobile – Immobile  
17   Model (MIM) and the Explicit Network Model (ENM) that takes expressly into account the  
18   network geometry for describing tracer transport behaviour in a fractured sample at bench scale.  
19   Though ENM shows better fitting results than MIM, the latter remains still valid as it proves to  
20   describe the observed curves quite well.

21   The results show that the presence of nonlinear flow plays an important role in the behaviour of  
22   solute transport. Firstly the distribution of solute according to different pathways is not constant but  
23   it is related to the flow rate. Secondly nonlinear flow influences advection, in that it leads to a delay  
24   in solute transport respect to the linear flow assumption. Whereas nonlinear flow does not show to  
25   be related with dispersion. The experimental results show that in the study case the geometrical  
26   dispersion dominates the Taylor dispersion. However the interpretation with the ENM model shows  
27   a weak transitional regime from geometrical dispersion to Taylor dispersion for high flow rates.  
28   Incorporating the description of the flowpaths in the analytical modeling has proved to better fit the  
29   curves and to give a more robust interpretation of the solute transport.

## 30 **Introduction**

31 In fractured rock formations, the rock mass hydraulic behaviour is controlled by fractures. In such  
32 aquifers, open and well – connected fractures constitute high permeability pathways and are orders  
33 of magnitude more permeable than the rock matrix (Bear & Berkowitz, 1987; Berkowitz, 2002;  
34 Bodin et al., 2003; Cherubini, 2008; Cherubini & Pastore, 2011, Geiger et al., 2012, Neuman,  
35 2005).

36 In most studies examining hydrodynamic processes in fractured media, it is assumed that flow is  
37 described by Darcy's law, which expresses a linear relationship between pressure gradient and flow  
38 rate (Cherubini & Pastore, 2010). Darcy's law has been demonstrated to be valid at low flow  
39 regimes ( $Re < 1$ ). For  $Re > 1$  a nonlinear flow behaviour is likely to occur.

40 But in real rock fractures, microscopic inertial phenomena can cause an extra macroscopic  
41 hydraulic loss (Kløv, 2000) which deviates flow from the linear relationship among pressure drop  
42 and flow rate.

43 To experimentally investigate fluid flow regimes through deformable rock fractures, Zhang &  
44 Nemcik (2013) carried out flow tests through both mated and non – mated sandstone fractures in  
45 triaxial cell. For water flow through mated fractures, the experimental data confirmed the validity of  
46 linear Darcy's law at low velocity. For larger water flow through non – mated fractures, the  
47 relationship between pressure gradient and volumetric flow rate revealed that the Forchheimer  
48 equation offers a good description for this particular flow process. The obtained experimental data  
49 show that Izbash's law can also provide an excellent description for nonlinear flow. They concluded  
50 that further work was needed to study the dependency of the two coefficients on flow velocity.

51 In fracture networks heterogeneity intervenes even in solute transport: due to the variable aperture  
52 and heterogeneities of the fracture surfaces the fluid flow will seek out preferential paths (Gylling et  
53 al., 1995) through which solutes are transported.

54 Generally the geometry of fracture network is not well known and the study of solute transport  
55 behaviour is based on multiple domain theory according to which the fractured medium is separated  
56 in two distinct domains: high velocity zones such as the network of connected fractures (mobile  
57 domain) where solute transport occurs predominantly by advection, and lower velocity zones such  
58 as secondary pathways, stagnation zones (almost – immobile domain), such as the rock matrix.

59 The presence of steep concentration gradients between fractures and matrix causes local  
60 disequilibrium in solute concentration which gives rise to dominantly diffusive exchange between

fracture and matrix. This explains the non – Fickian nature of transport, which is characterized by breakthrough curves with early first arrival and long tails.

Quantifying solute transport in fractured media has become a very challenging research topic in hydrogeology over the last three decades (Nowamooz et al., 2013).

Tracer tests are commonly conducted in such aquifers to estimate transport parameters such as effective porosity and dispersivity, to characterize subsurface heterogeneity, and to directly delineate flow paths. Transport parameters are estimated by fitting appropriate tracer transport models to the breakthrough data.

In this context, analytical models are frequently employed, especially for analyzing tests obtained under controlled conditions, because they involve a small number of parameters and provide physical insights into solute transport processes (Liu et al 2012).

The advection – dispersion equation (ADE) has been traditionally applied to model tracer transport in fractures. However extensive evidence has shown that there exist two main features that cannot be explained by the ADE: the early first arrival and the long tail of the observed BTCs curves. (Neretnieks et al, 1982; Becker and Shapiro, 2000; Jiménez-Hornero et al. 2005; Bauget and Fourar, 2008).

Several other models have been used to fit the anomalous BTCs obtained in laboratory tracer tests carried out in single fractures. Among those, the Mobile-Immobile (MIM) model (van Genuchten and Wierenga, 1976), has showed to provide better fits of BTC curves (Gao et al., 2009, Schumer et.al 2003, Feehley et al, 2010).

In the well – controlled laboratory tracer tests carried out by Qian et al. (2011) a mobile– immobile (MIM) model proved to fit both peak and tails of the observed BTCs better than the classical ADE model.

Another powerful method to describe non – Fickian transport in fractured media is the continuous time random walk (CTRW) approach (Berkowitz et al. 2006) which is based on the conceptual picture of tracer particles undergoing a series of transitions of length  $s$  and time  $t$ .

Together with a master equation conserving solute mass, the random walk is developed into a transport equation in partial differential equation form. The CTRW has been successfully applied for describing non – Fickian transport in single fractures (Berkowitz et al.2001; Jiménez – Hornero et al. 2005).

Bauget and Fourar (2008) investigated non – Fickian transport in a transparent replica of a real single fracture. They employed three different models including ADE, CTRW, and a stratified model to interpret the tracer experiments.

94 As expected, the solution derived from the ADE equation appears to be unable to model long-time  
95 tailing behaviour. On the other hand, the CTRW and the stratified model were able to describe non  
96 – Fickian dispersion. The parameters defined by these models are correlated to the heterogeneities  
97 of the fracture.

98 Nowamooz et al., (2013) carried out experimental investigation and modeling analysis of tracer  
99 transport in transparent replicas of two Vosges sandstone natural fractures.

100 The obtained breakthrough curves were then interpreted using a stratified medium model that  
101 incorporates a single parameter permeability distribution to account for fracture heterogeneity,  
102 together with a CTRW model, as well as the classical ADE model.

103 The results confirmed poorly fitting breakthrough curves for ADE. In contrast, the stratified model  
104 provides generally satisfactory matches to the data (even though it cannot explain the long-time  
105 tailing adequately) while the CTRW model captures the full evolution of the long tailing displayed  
106 by the breakthrough curves.

107 Qian et al (2011) experimentally studied solute transport in a single fracture (SF) under non –  
108 Darcian flow condition which was found to closely follow the Forchheimer equation.

109 They also investigated on the influence of the velocity contrast between the fracture wall and the  
110 plane of symmetry on the dispersion process, which was called ‘boundary layer dispersion’ by  
111 Koch and Brady (1985). They affirmed that this phenomenon had to be considered if the thickness  
112 of the boundary layer was greater than the roughness of the fracture. On the other hand, if the  
113 thickness of the boundary layer was smaller than the roughness of the fractures, the recirculation  
114 zones inside the roughness cavities rather than the boundary layer would be more relevant for the  
115 dispersion process, thus the hold – up dispersion would become important. Since smooth parallel  
116 planes were used for constructing the SF in their experiment, the fracture roughness and the hold –  
117 up dispersion were negligible.

118 Bodin et al (2007) developed the SOLFRAC program, which performs fast simulations of solute  
119 transport in complex 2D fracture networks using the Time Domain Random Walk (TDRW)  
120 approach (Delay & Bodin, 2001) that makes use of a pipe network approximation. The code  
121 accounts for advection and hydrodynamic dispersion in channels, matrix diffusion, diffusion into  
122 stagnant zones within the fracture planes, mass sharing at fracture intersections, and other  
123 mechanisms such as sorption reactions and radioactive decay. Comparisons between numerical  
124 results and analytical breakthrough curves for synthetic test problems have proven the accuracy of  
125 the model.

126 Zafarani & Detwiler (2013) presented an alternate approach for efficiently simulating transport  
127 through fracture intersections. Rather than solving the two – dimensional Stokes equations, the

128 model relies upon a simplified velocity distribution within the fracture intersection, assuming local  
129 parabolic velocity profiles within fractures entering and exiting the fracture intersection. Therefore,  
130 the solution of the two – dimensional Stokes equations is unnecessary, which greatly reduces the  
131 computational complexity. The use of a time – domain approach to route particles through the  
132 fracture intersection in a single step further reduces the number of required computations. The  
133 model accurately reproduces mixing ratios predicted by high – resolution benchmark simulations.

134 As most of previous investigations of flow and transport in fracture networks considered Darcian  
135 flow, the behaviour of the solute transport in fracture networks under non – darcian flow conditions  
136 has been therefore poorly investigated. In fracture networks different pathways can be identified  
137 through which solute is generally distributed in function of the energy spent by solute particles to  
138 cross the path. In this context the presence of nonlinear flow could play an important role in the  
139 distribution of the solutes according to the different pathways. In fact the energy spent to cross the  
140 path should be proportional to the resistance to flow associated to the single pathway, which in  
141 nonlinear flow regime is not constant but depends on the flow rate. This means that changing the  
142 boundary conditions the resistance to flow varies and as a consequence the distribution of solute in  
143 the main and secondary pathways also changes giving rise to a different behaviour of solute  
144 transport.

145 In previous studies by Cherubini et al (2012, 2013) the presence of nonlinear flow and non fickian  
146 transport in a fractured rock formation has been analyzed at bench scale in laboratory tests. The  
147 effects of nonlinearity in flow have been investigated by analyzing hydraulic tests on an artificially  
148 created fractured limestone block of parallelepiped ( $0.60 \times 0.40 \times 0.8 \text{ m}^3$ ) shape.

149 The volumes of water passing through different paths across the fractured sample. The inlet flow  
150 rate and the hydraulic head difference between the inlet and outlet ports have been measured. The  
151 experimental results have shown evidence of a non-Darcy relationship between flow rate and  
152 hydraulic head differences that is best described by a polynomial expression. Transition from  
153 viscous dominant regime to inertial dominant regime has been detected. The experiments has been  
154 compared with a 3d numerical model in order to evaluate the linear and non-linear terms of  
155 forchheimer equation for each paths.

156 Moreover, a tortuosity factor has been determined which is a measure of the deviation of each flow  
157 path from the parallel plate model. A power law has been detected between the Forchheimer terms  
158 and the tortuosity factor, which means that the latter influences flow dynamics.

159 The non fickian nature of transport has been investigated by means of tracer tests that regard the  
160 measurement of breakthrough curves for saline tracer pulse across a selected path varying the flow  
161 rate. The observed experimental breakthrough curves of solute transport have proved to be better

162 modeled by the 1d analytical solution of MIM model. The carried out experiments show that there  
163 exists a pronounced mobile–immobile zone interaction that cannot be neglected and that leads to a  
164 non-equilibrium behaviour of solute transport. The existence of a non-Darcian flow regime has  
165 showed to influence the velocity field in that it gives rise to a delay in solute migration with respect  
166 to the predicted value assuming linear flow. Furthermore the presence of inertial effects has proved  
167 to enhance non-equilibrium behaviour. Instead, the presence of a transitional flow regime seems not  
168 to exert influence on the behaviour of dispersion.

169 Herein, in order to give a more physical interpretation of the flow and transport behaviour, we build  
170 on the work by Cherubini et al (2013) by interpreting the obtained experimental results of flow and  
171 transport tests by means of the comparison of two conceptual models: the 1d single rate mobile –  
172 immobile model (MIM) and the 2d Explicit Network Model (ENM). Differently from the former,  
173 the latter expressly takes the fracture network geometry into account.

174 When applied to fractured media, the MIM approach does not explicitly take the fracture network  
175 geometry into account, but it conceptualizes the shape of fractures as 1d continuous media in which  
176 the liquid phase is separated into flowing and stagnant regions. The convective dispersive transport  
177 is restricted to the flowing region, and the solute exchange is described as a first – order process.

178 Unlike MIM, the ENM model may allow to know the physical meaning of flow and transport  
179 phenomena (i.e the meaning of long – time behaviour of BTC curves that characterize fractured  
180 media) and permits to obtain a more accurate estimation of flow and solute transport parameters. In  
181 this model the fractures are represented as 1d – pipe elements and they form a 2d – pipe network.

182 It is clear that ENM needs to address the problem of parameterization. In fact the transport  
183 parameters of each individual fracture should be specified and this leads to more uncertainty in the  
184 estimation.

185 Our overarching objective is therefore of investigating the performances and the reliabilities of  
186 MIM and ENM approaches to describe conservative tracer transport in a fractured rock sample.

187 In particular way the present paper focuses the attention on the effects of nonlinear flow regime on  
188 different features that depict the conservative solute transport in a fracture network such as mean  
189 travel time, dispersion, dual porosity behaviour, distribution of solute into different pathways.

## 190 **Theoretical background**

### 191 **Nonlinear flow**

192 In the literature different laws are reported that account for the nonlinear relationship between  
193 velocity and pressure gradient.

194 A cubic extension of Darcy's law that describes pressure loss versus flow rate for low flow rates is  
 195 the weak inertia equation:

$$196 \quad -\frac{dp}{dx} = \frac{\mu}{k} \cdot v + \frac{\gamma p^2}{\mu} \cdot v^3 \quad (1)$$

197 Where  $p$  ( $\text{ML}^{-1}\text{T}^{-2}$ ) is the pressure,  $k$  ( $\text{L}^2$ ) is the permeability,  $\mu$  ( $\text{ML}^{-1}\text{T}^{-1}$ ) is the viscosity,  $\rho$  ( $\text{ML}^{-3}$ )  
 198 is the density,  $v$  ( $\text{LT}^{-1}$ ) is the velocity and  $\gamma$  ( $\text{L}$ ) is called the weak inertia factor.

199 In case of higher Reynolds numbers ( $\text{Re} \gg 1$ ) the pressure losses pass from a weak inertial to a  
 200 strong inertial regime, described by the Forchheimer equation (Forchheimer, 1901), given by:

$$201 \quad -\frac{dp}{dx} = \frac{\mu}{k} \cdot v + \rho \beta \cdot v^2 \quad (2)$$

202 Where  $\beta$  ( $\text{L}^{-1}$ ) is called the inertial resistance coefficient, or non – Darcy coefficient.

203 Forchheimer law can be written in terms of hydraulic head:

$$204 \quad -\frac{dh}{dx} = a' \cdot v + b' \cdot v^2 \quad (3)$$

205 Where  $a'$  ( $\text{TL}^{-1}$ ) and  $b'$  ( $\text{TL}^{-2}$ ) are the linear and inertial coefficient respectively equal to:

$$206 \quad a' = \frac{\mu}{\rho g k}; \quad b' = \frac{\beta}{g} \quad (4)$$

207 In the same way the relationship between flow rate  $Q$  ( $\text{L}^3\text{T}^{-1}$ ) and hydraulic head gradient can be  
 208 written as:

$$209 \quad -\frac{dh}{dx} = a \cdot Q + b \cdot Q^2 \quad (5)$$

210 Where  $a$  ( $\text{TL}^{-3}$ ) and  $b$  ( $\text{T}^2\text{L}^{-6}$ ) are related to  $a'$  and  $b'$ :

$$211 \quad a = \frac{a'}{\omega_{eq}}; \quad b = \frac{b'}{\omega_{eq}} \quad (6)$$

212 Where  $\omega_{eq}$  ( $\text{L}^2$ ) represents the equivalent cross sectional area of fracture.

### 213 **Mobile Immobile Model**

214 The mathematical formulation of the MIM for non - reactive solute transport is usually given as  
 215 follows:

$$\begin{aligned}
216 \quad & \frac{\partial c_m}{\partial t} = D \frac{\partial^2 c_m}{\partial x^2} - v \frac{\partial c_m}{\partial x} - \alpha (c_m - c_{im}) \\
& \beta \frac{\partial c_{im}}{\partial t} = \alpha (c_m - c_{im})
\end{aligned} \tag{7}$$

217 Where  $t$  (T) is the time,  $x$  (L) is the spatial coordinate along the direction of the flow,  $c_m$  and  $c_{im}$   
 218 ( $\text{ML}^{-3}$ ) are the cross - sectional averaged solute concentrations respectively in the mobile and  
 219 immobile domain,  $v$  ( $\text{LT}^{-1}$ ) is the average flow velocity and  $D$  ( $\text{L}^2\text{T}^{-1}$ ) is the dispersion coefficient,  $\alpha$   
 220 ( $\text{T}^{-1}$ ) is the mass exchange coefficient,  $\beta$  [-] is the mobile water fraction. For a non – reactive solute  
 221  $\beta$  is equivalent to the ratio between the immobile and mobile cross – sectional area (-).

222 The solution of system Equation (7) describing one – dimensional (1d) non – reactive solute  
 223 transport in an infinite domain for instantaneous pulse of solute injected at time zero at the origin is  
 224 given by (Goltz & Roberts, 1986):

$$225 \quad c_m(x, t) = e^{-\alpha t} c_0(x, t) + \alpha \int_0^t H(t, \tau) c_0(x, \tau) d\tau \tag{8}$$

226 Where  $c_0$  represents the analytical solution for the classical advection – dispersion equation (Crank,  
 227 1956):

$$228 \quad c_0(x, t) = \frac{M_0}{\omega_{eq} \sqrt{\pi D t}} e^{-\frac{(x-vt)^2}{4Dt}} \tag{9}$$

229 Where  $M_0$  (M) is the mass of the tracer injected instantaneously at time zero at the origin of the  
 230 domain. The term  $H(t, \tau)$  presents the following expression:

$$231 \quad H(t, \tau) = e^{-\frac{\alpha}{\beta}(t-\tau) - \alpha \tau} \frac{\tau I_1 \left( \frac{2\alpha}{\beta} \sqrt{\beta(t-\tau)\tau} \right)}{\sqrt{\beta(t-\tau)\tau}} \tag{10}$$

232 Where  $I_1$  represents the modified Bessel function of order 1.

233 In order to fit the BTCs curves with the MIM model the assumption of representative 1d length ( $L$ )  
 234 of the fracture network should be made. However this matter can be solved by the introduction of  
 235 the normalized velocity ( $v/L$ ) and normalized dispersion ( $D/L^2$ ). The MIM model is defined by four  
 236 parameters regarding the whole fracture network ( $v/L$ ,  $D/L^2$ ,  $\alpha$ ,  $\beta$ ).



## 237 **Explicit Network Model**

238 Assuming that a single fracture  $j$  can be represented by a 1d – pipe element, the relationship  
239 between head loss  $\Delta h_j$  (L) and flow rate  $Q_j$  ( $L^3T^{-1}$ ) can be written in finite terms on the basis of  
240 Forchheimer model:

$$241 \frac{\Delta h_j}{l_j} = aQ_j + bQ_j^2 \Rightarrow \Delta h_j = \left[ l_j (a + bQ_j) \right] Q_j \quad (11)$$

242 Where  $l_j$  (L) is the length of fracture,  $a$  ( $TL^{-3}$ ) and  $b$  ( $T^2L^{-6}$ ) are the Forchheimer parameters in finite  
243 terms.

244 The term in the square brackets represents the resistance to flow  $R_j(Q_j)$  ( $TL^{-3}$ ) of  $j$  fracture.

245 For steady – state condition and for a 2d simple geometry of the fracture network, the solution of  
246 flow field can be obtained in a straightforward manner applying the first and second Kirchhoff's  
247 laws.

248 The first law affirms that the algebraic sum of flow in a network meeting at a point is zero:

$$249 \sum_{j=1}^n Q_j = 0 \quad (12)$$

250 Whereas the second law affirms that the algebraic sum of the head losses along a closed loop of the  
251 network is equal to zero:

$$252 \sum_{j=1}^n \Delta h_j = 0 \quad (13)$$

253 Generally in a 2d fracture network, the single fracture can be set in series and/or in parallel.

254 In particular the total resistance to flow of a network in which the fractures are arranged in a chain  
255 is found by simply adding up the resistance values of the individual fractures.

256 In a parallel network the flow breaks up by flowing through each parallel branch and re –  
257 combining when the branches meet again. The total resistance to flow is found by adding up the  
258 reciprocals of the resistance values and then taking the reciprocal of the total. The flow rate crossing  
259 the generic fracture  $j$  belonging to parallel circuits  $Q_j$  can be obtained as:

$$Q_j = \sum Q \left( \frac{1}{R_j} \frac{\prod_{i=1}^n R_i}{\sum_{i=1}^n R_i} \right) \quad (14)$$

Where  $\sum Q$  ( $\text{LT}^{-3}$ ) is the sum of the discharge flow evaluated for the fracture intersection located in correspondence of the inlet bond of  $j$  fracture, whereas the term in brackets represents the probability of water distribution of  $j$  fracture  $P_{Q,j}$ .

The BTC curves at the outlet of the network  $c_{out}(t)$  ( $\text{ML}^{-3}$ ), for an instantaneous injection, can be obtained as the summation of BTCs of each elementary path in the network. The latter can be expressed as the convolution product of the probability density functions of residence times in each individual fracture belonging to the elementary path. Using the convolution theorem,  $c_{out}(t)$  can be expressed as:

$$c_{out}(t) = \frac{M_0}{Q_0} F^{-1} \left[ \sum_{i=1}^{N_{ep}} \prod_{j=1}^{n_{f,i}} P_{c,j} F(s_j(l_j, t)) \right] \quad (15)$$

Where  $M_0$  (M) is the injected mass of solute,  $F$  is the Fourier transform operator,  $N_{ep}$  is the number of elementary paths,  $n_{f,i}$  is the number of fractures in  $i$  elementary path,  $P_{c,j}$  and  $s_j(l_j, t)$  ( $\text{T}^{-1}$ ) represent the fraction of solute crossing the single fracture and the probability density function of residence time respectively.

$P_{c,j}$  can be estimated as the probability of the particle transition in correspondence of the inlet bond of each individual single fracture. The rules for particle transition through fracture intersections play an important role in mass transport. In literature several models have been developed and tested in order to represent the mass transfer within fracture intersections. The simplest rule is represented by the “perfect mixing model” in which the mass sharing is proportional to the relative discharge flow rates.

The perfect mixing model assumes that the probability of particle transition of the fraction of solute crossing the single fracture can be written as:

$$P_{c,j} = \frac{Q_j}{\sum Q} \quad (16)$$

283 Where  $Q_j$  represents the flow rate in the single  $j$  fracture. Note that if assuming valid the perfect  
 284 mixing model  $P_{Q,j}$  is equal to  $P_{c,j}$ .

285 It is clear that in order to know  $s_j(l_j, t)$  the transport model and consequently the transport  
 286 parameters of each single fracture need to be defined.  $s_j(l_j, t)$  can be evaluated in a simple way  
 287 using the 1D analytical solution of the Advection Dispersion Equation model (ADE) for pulse  
 288 input:

$$289 \quad s_j(l_j, t) = \frac{Q_j}{\omega_{eq,j} \sqrt{\pi D_j t}} e^{-\frac{(l_j - v_j t)^2}{4 D_j t}} \quad (17)$$

290 in which the velocity  $v_j$  and dispersion  $D_j$  relating to the generic  $j$  fracture can be estimated through  
 291 the following expression:

$$292 \quad v_j = \frac{Q_j}{\omega_{eq,j}} \quad (18)$$

$$293 \quad D_j = \alpha_{L,j} v_j \quad (19)$$

294 Where  $\omega_{eq,j}$  and  $\alpha_{L,j}$  are the equivalent crossing area and the dispersion coefficient of  $j$  fracture  
 295 respectively.

296 The ENM is defined by six parameters regarding each single fracture ( $a$ ,  $b$ ,  $P_Q$ ,  $\omega_{eq}$ ,  $\alpha_L$  and  $P_c$ ).

## 297 **Material and methods**

### 298 **Flow and tracer tests**

299 The experimental setup has been already extensively discussed in Cherubini et al. (2013), however  
 300 for the completeness in this section a summary is reported. The analysis of flow dynamics through  
 301 the selected path (Fig 2) regards the observation of water flow from the upstream tank to the flow  
 302 cell with a circular cross-section of  $0.1963 \text{ m}^2$  and  $1.28 \times 10^{-4} \text{ m}^2$  respectively.

303 Initially at time  $t_0$ , the valves ‘ $a$ ’ and ‘ $b$ ’ are closed and the hydrostatic head in the flow cell is equal  
 304 to  $h_0$ . The experiment begins with the opening of the valve ‘ $a$ ’ which is reclosed when the hydraulic  
 305 head in the flow cell is equal to  $h_I$ . Finally the hydraulic head in the flow cell is reported to  $h_0$   
 306 through the opening of the valve ‘ $b$ ’. The experiment procedure is repeated changing the hydraulic

307 head of the upstream tank  $h_c$ . The time  $\Delta t = (t_1 - t_0)$  required to fill the flow cell from  $h_0$  to  $h_1$  has  
308 been registered.

309 Given that the capacity of the upstream tank is much higher than that of the flow cell it is  
310 reasonable to assume that during the experiments the level of the upstream tank ( $h_c$ ) remains  
311 constant. Under this hypothesis the flow inside the system is governed by the equation:

$$312 \quad S_1 \frac{dh}{dt} = \Gamma(\Delta h)(h_c - h) \quad (20)$$

313 Where  $S_1$  ( $L^2$ ) and  $h$  (L) are respectively the section area and the hydraulic head of the flow cell;  $h_c$   
314 (L) is the hydraulic head of upstream tank,  $\Gamma(\Delta h)$  represents the hydraulic conductance term  
315 representative of both hydraulic circuit and the selected path.

316 The average flow rate  $\bar{Q}$  can be estimated by means of the volumetric method:

$$317 \quad \bar{Q} = \frac{S_1}{t_1 - t_0} (h_1 - h_0) \quad (21)$$

318 Whereas the average hydraulic head difference  $\bar{\Delta h}$  is given by:

$$319 \quad \bar{\Delta h} = h_c - \frac{h_0 + h_1}{2} \quad (22)$$

320 In correspondence of the average flow rate and head difference is it possible to evaluate the average  
321 hydraulic conductance as:

$$322 \quad \bar{\Gamma}(\Delta h) = \frac{S_1}{t_1 - t_0} \ln \left( \frac{h_0 - h_c}{h_1 - h_c} \right) \quad (23)$$

323 The inverse of  $\bar{\Gamma}(\Delta h)$  represents the average resistance to flow  $\bar{R}(\bar{Q})$ .

324 The study of solute transport dynamics through the selected path has been carried out by means of a  
325 tracer test using sodium chloride. Initially a hydraulic head difference between the upstream tank  
326 and downstream tank is imposed. At  $t = 0$  the valve 'a' is closed and the hydrostatic head inside the  
327 block is equal to the downstream tank. At  $t = 10$  s the valve 'a' is opened while at time  $t = 60$  s a  
328 mass of solute equal to  $5 \times 10^{-4}$  kg is injected into the inlet port through a syringe. The source release  
329 time (1 s) is very small therefore the instantaneous source assumption can be considered valid.

330 In correspondence of the flow cell in which the multi - parametric probe is located it is possible to  
 331 measure the tracer breakthrough curve and the hydraulic head; in the meanwhile the flow rate  
 332 entering the system is measured by means of an ultrasonic velocimeter. For different flow rates a  
 333 BTC curve can be recorded at the outlet port.

334 Time moment analysis has been applied in order to characterize the BTC curves in terms of mean  
 335 breakthrough time, degree of spread and asymmetry.

336 The mean residence time  $t_m$  is given by:

$$337 \quad t_m = \frac{\int_0^{\infty} t^n c(t) dt}{\int_0^{\infty} c(t) dt} \quad (24)$$

338 The  $n^{\text{th}}$  normalized central moment of distribution of solute concentration versus time is defined as:

$$339 \quad \mu_n = \frac{\int_0^{\infty} [t - t_m]^n c(t) dt}{\int_0^{\infty} c(t) dt} \quad (25)$$

340 The second moment  $\mu_2$  represents the degree of spread relative to  $t_m$ . whereas the degree of  
 341 asymmetry measured by the skewness coefficient is defined as:

$$342 \quad S = \mu_3 / \mu_2^{3/2} \quad (26)$$

## 343 Discussion

### 344 Estimation of flow model parameters

345 The flow field in each single fracture of the network can be solved in analytical way by means of  
 346 Kirchhoff laws. In Figure 2 is represented the 2d – pipe network conceptualization.

347 The resistance to flow of each single  $j$  fracture is described by the Equation (12). The Forchheimer  
 348 parameters are assumed constant for the whole fracture network.

349 The application of the Kirchhoff's first law at the node 3 can be written as:

$$350 \quad Q_0 - Q_1 - Q_2 = 0 \quad (27)$$

351 Whereas the application of the Kirchhoff's second law at the loop 3 – 4 – 5 – 6 can be written as:

$$R_6(Q_1)Q_1 - (R_3(Q_2) + R_4(Q_2) + R_5(Q_2))Q_2 = 0 \quad (28)$$

Substituting Equation (27) into Equation (28) the iterative equation of flow rate  $Q_I$  can be obtained:

$$Q_1^{k+1} = Q_0 \left[ \frac{R_3(Q_0 - Q_1^k) + R_4(Q_0 - Q_1^k) + R_5(Q_0 - Q_1^k)}{R_3(Q_0 - Q_1^k) + R_4(Q_0 - Q_1^k) + R_5(Q_0 - Q_1^k) + R_6(Q_1^k)} \right] \quad (29)$$

The Forchheimer parameters representative of whole fracture network can be derived matching the average resistance to flow derived experimentally with the resistance to flow evaluated for the whole network:

$$\bar{R}(\bar{Q}) = R_1(Q_0) + R_2(Q_0) + \left( \frac{1}{R_6(Q_1)} + \frac{1}{R_3(Q_2) + R_4(Q_2) + R_5(Q_2)} \right)^{-1} + R_7(Q_0) + R_8(Q_0) + R_9(Q_0) \quad (30)$$

Figure 3 shows the fitting of observed resistance to flow determined by the inverse of Equation (23) and the theoretical resistance to flow (Equation 30). The linear and nonlinear terms of Forchheimer model in Equation (12) have been estimated and they are respectively equal to  $a = 7.345 \times 10^4 \text{ sm}^{-3}$  and  $b = 11.65 \times 10^9 \text{ s}^2 \text{ m}^{-6}$ . It is evident that the 2d - pipe network model closely matches the experimental results ( $r^2 = 0.9913$ ). Flow characteristics can be studied through the analysis of Forchheimer number  $F_0$  which represents the ratio of nonlinear to linear hydraulic gradient contribution:

$$F_o = \frac{bQ}{a} \quad (31)$$

Inertial forces dominate over viscous ones at the critical Forchheimer number ( $F_o=1$ ) corresponding in our case to a flow rate equal to  $Q_{crit} = 6.30 \times 10^{-6} \text{ m}^3/\text{s}$ , which is coherent with the results obtained in the previous study (Cherubini et al., 2013a).

The term in square brackets in Equation (30) represents the probability of water distribution  $P_Q$  evaluated for the branch 6. Note that it is not constant but it depends on the flow rate crossing the parallel branch. Figure 4 shows  $P_Q$  as function of  $Q_0$ . The probability of water distribution decreases as the injection flow rate increases. This means that when the injection flow rate increases the resistance to flow of the branch 6 increases faster than the resistance to flow of the branch 3 – 4 – 5 and therefore the solute choses the secondary pathway.

## 376 **Fitting of breakthrough curves and interpretation of estimated transport model** 377 **parameters**

378 Several tests have been conducted in order to observe solute transport behaviour varying the  
379 injection flow rate in the range  $1.20 \times 10^{-6}$  -  $9.34 \times 10^{-6}$   $\text{m}^3 \text{s}^{-1}$ . For each experimental BTCs the mean  
380 travel time  $t_m$  and the coefficient of Skewness  $S$  have been estimated.

381 Figure 5 shows  $t_m$  as function of  $Q_0$ . Travel time decreases more slowly for high flow rates. In  
382 particular a change of slope is evident in correspondence of the injection flow rate equal to  $4 \times 10^{-6}$   
383  $\text{m}^3 \text{s}^{-1}$  (Cherubini et al., 2013a), which means the setting up of a transitional flow regime; the  
384 diagram of velocity profile is flattened because of inertial forces prevailing on viscous one, as  
385 already showed by Cherubini et al (2013a). The presence of a transitional flow regime leads to a  
386 delay on solute transport with respect to the values that can be obtained under the assumption of a  
387 linear flow field. Note that this behaviour occurs before  $Q_{crit}$ .

388 The skewness coefficient does not exhibit a trend upon varying the injection flow rate, but its mean  
389 value is equal to 2.018. A positive value of skewness indicates that BTCs are asymmetric with early  
390 first arrival and long tail. This behaviour seems not to be dependent on the presence of the  
391 transitional regime.

392 The measured breakthrough curves for different flow rates have been individually fitted by MIM  
393  $(\nu/L, D/L^2, \alpha, \beta)$  and ENM  $(\omega_{eq}, \alpha_L, P_Q, P_C)$  models.

394 In particular for the ENM model the parameters  $\omega_{eq}$  (equivalent area) and  $\alpha_L$  are representative of  
395 all fracture network, whereas the parameters  $P_Q$  and  $P_C$  are associated only to the parallel branches.  
396 For the considered fracture network the Equation (15) becomes:

$$397 \quad c_{out} = \frac{M_0}{Q_0} F^{-1} \left[ \begin{aligned} &P_c \cdot F(s_1) \cdot F(s_2) \cdot F(s_6) \cdot F(s_7) \cdot F(s_8) \cdot F(s_9) + \\ &+ (1 - P_c) \cdot F(s_1) \cdot F(s_2) \cdot F(s_3) \cdot F(s_4) \cdot F(s_5) \cdot F(s_7) \cdot F(s_8) \cdot F(s_9) \end{aligned} \right] \quad (32)$$

398 The velocity and dispersion that characterize the probability density function  $s$  are related to the  
399 flow rate that crosses each branch by Equations (18) and (19). This one is equal to the injection  
400 flow rate  $Q_0$  except for branch 6 and branches 3 – 4 – 5 for which it is equal to  $Q = P_Q Q_0$  and  
401  $Q = (1 - P_Q) Q_0$  respectively.

402 Furthermore three parameter configurations have been tested for the ENM model. The  
403 configurations are distinguished on the basis of the number of fitting parameters and assumptions

404 made on  $P_C$  and  $P_Q$  parameters. The first configuration named ENM2 has two fitting parameters  
 405  $\omega_{eq}$  and  $\alpha_L$ . In this configuration  $P_C$  is imposed equal to  $P_Q$  and is derived as the square brackets  
 406 term in Equation (29).

407 The second configuration named ENM3 has three fitting parameters  $\omega_{eq}$ ,  $\alpha_L$  and  $P_C(P_Q)$ .  $P_C$  is still  
 408 equal to  $P_Q$  but they are evaluated by the interpretation of BTC curves.

409 In the third configuration named ENM4 all four parameters  $(\omega_{eq}, \alpha_L, P_Q, P_C)$  are determined  
 410 through the fitting of BTCs.

411 To compare all the considered models, both the determination coefficient ( $r^2$ ) and the root mean  
 412 square error (RMSE) were used as criteria to determine the goodness of the fitting, which can be  
 413 expressed as:

$$414 \quad r^2 = 1 - \frac{\sum_{i=1}^N (C_{i,o} - C_{i,e})^2}{\sum_{i=1}^N (C_{i,o} - \bar{C}_{i,o})^2} \quad (33)$$

$$415 \quad RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (C_{i,o} - C_{i,e})^2} \quad (34)$$

416 Where  $N$  is the number of observations,  $C_{i,e}$  is the estimated concentration,  $C_{i,o}$  is the observed  
 417 concentration and  $\bar{C}_{i,o}$  represents the mean value of  $C_{i,o}$ .

418 Tables 1, 2, 3 and 4 show the estimated values of parameters, root mean square error RMSE and the  
 419 determination coefficient  $r^2$  for all the considered models varying the inlet flow rate  $Q_0$ .

420 Figure 6 shows the fitting results of BTC curves for different injection flow rates.

421 For higher flow rates ( $7.07 \times 10^{-6}$  and  $4.80 \times 10^{-6} \text{ m}^3/\text{s}$ ) the fitting is poorer than for lower flow rates  
 422 ( $3.21 \times 10^{-6}$  and  $1.96 \times 10^{-6} \text{ m}^3/\text{s}$ ). However, all models provide a satisfactory fitting. The ENM4  
 423 model provides the highest values of  $r^2$  varying in the range 0.9921 – 1.000 and the smallest values  
 424 of RMSE in the range 0.0033 – 0.0252. This is expected for two reasons. First this model has more  
 425 fitting parameters than ENM2 and ENM3, thus it is more flexible. Second, compared to MIM  
 426 model, it takes explicitly into account the presence of the secondary path.



427 The MIM model considers the existence of immobile and mobile domains and a rate – limited mass  
428 transfer between these two domains. In the present context this conceptualization can be a weak  
429 assumption especially for high flow rates when the importance of secondary path increases.  
430 However the fitting of BTCs shows that MIM model remains valid as it proves to describe the  
431 observed curves quite well.

432 The extent of solute mixing can be assessed from the analysis of MIM first-order mass transfer  
433 coefficient  $\alpha$  and the fraction of mobile water  $\beta$ .

434 Several authors have observed the variation of the mass-transfer coefficient between mobile and  
435 immobile water regions with pore-water velocity (van Genuchten and Wierenga, 1977; Nkedi-Kizza  
436 et al., 1984; De Smedt and Wierenga, 1984; De Smedt et al., 1986; Schulin et al., 1987). The  
437 increase in  $\alpha$  with increasing water velocity is attributed to higher mixing in the mobile phase at  
438 high pore water velocities (De Smedt and Wierenga, 1984) or to shorter diffusion path lengths as a  
439 result of a decrease in the amount of immobile water (van Genuchten and Wierenga, 1977).

440 As concerns  $\beta$ , various authors have observed different behaviour of the mobile water fraction  
441 parameter. Gaudet et al. (1977) reported increasing mobile water content with increasing pore water  
442 velocity. However, studies have also found that  $\beta$  appears to be constant with varying pore-water  
443 velocity (Nkedi-kizza et al. 1983). However, lower  $\beta$  values can be attributed to faster initial  
444 movement of the solute as it travels through a decreasing number of faster flow paths. As a result,  
445 some authors have related  $\beta$  values to the initial arrival of the solute. In fact, Gaudet et al. (1977)  
446 and Selim and Ma (1995) observed that the mobile water fraction parameter affects the time of  
447 initial appearance of the solute.

448 In general, the initial breakthrough time increases as  $\beta$  increases (Gao et al., 2009) which can also  
449 be evidenced from Fig 6. For lower flow rates the initial arrival time is higher than for higher flow  
450 rates. As the fraction of mobile water increases, the breakthrough curves are shifted to longer times  
451 because the solute is being transported through larger and larger fractions of the fracture volume. In  
452 the limiting case that the fraction of mobile water reaches one, the MIM reduces to the equilibrium  
453 ADE (no immobile water) (Mulla & Strock, 2008).

454 The evidence of dual porosity behaviour on solute transport is clearly shown by the analysis of the  
455 two MIM parameters: the ratio of mobile and immobile area  $\beta$  and the mass exchange coefficient  $\alpha$ ,  
456 shown in Figure 7 as a function of velocity.

457 A different behaviour of these two coefficients to varying the injection flow rate is observed in the  
458 present study. At Darcian-like flow conditions the mass exchange coefficient remains constant,

459 whereas the ratio of mobile and immobile area decreases as velocity increases. When nonlinear  
460 flow starts to become dominant a different behaviour is observed:  $\alpha$  increases in a potential way,  
461 whereas  $\beta$  assumes a weakly growing trend as velocity increases with a mean value equal to 0.56.

462 In order to better explain this behaviour, the transport time (reciprocal of normalized velocity) and  
463 the exchange time (reciprocal of the exchange term) varying the flow rate for the MIM model are  
464 showed in Figure 8. In analogous way in Figure 9 is showed the comparison between the mean  
465 travel time for the main path and the secondary path varying the injection flow rate for the ENM4  
466 model.

467 For the MIM model at high flow rates the exchange time joins the transport time; analogously for  
468 the ENM4 as the flow rate increases the secondary path reaches the main path in terms of mean  
469 travel time. This analogy between MIM and ENM enhances the concept that the mass transfer  
470 coefficient is dependent on flow velocity.

471 In Darcian-like flow conditions the main path is dominant on the secondary path. The latter can be  
472 considered as an immobile zone. In this condition the fracture network behaves as a single fracture  
473 and the observed dual porosity behaviour can be attributable only to the fracture – matrix  
474 interactions of the main path.

475 For higher velocities, a higher contact area between the mobile and immobile region is evidenced,  
476 enhancing solute mixing between these two regions (Gao et al, 2009). The increase in  $\alpha$  with  
477 increasing water velocity is therefore attributable to nonlinear flow that enhances the exchange  
478 between the main and secondary flow paths. Increasing the injection flow rate the importance of the  
479 secondary path grows and the latter cannot be considered as an immobile zone, as a consequence  
480 the dual porosity behaviour becomes stronger.

481 As showed in figure 10 and 11  $P_Q$  as function of  $Q_0$  evaluated by means the fitting of BTCs by  
482 ENM3 and ENM4 models presents a different trend respect to  $P_Q$  determined by means of flow  
483 tests.  $P_Q$  evaluated by transport tests decreases more rapidly than  $P_Q$  determined by flow tests  
484 (Figure 10). In the ENM4 model  $P_Q$  and  $P_C$  show a different behaviour, especially for higher  
485 velocity  $P_C$  presents values higher than  $P_Q$  (Figure 11). In other words the interpretation of BTC  
486 curves evidences more enhanced nonlinear flow behaviour than the flow tests.

487 In Figure 12 is reported the relationship between velocity  $v$  and injection flow rate  $Q_0$ . Note that, in  
488 order to compare the results, the velocities for MIM are evaluated assuming the length of the

medium equal to the length of main path ( $L = 0.601$  m). Instead for ENM4 model the velocities are evaluated dividing  $Q_0$  for the equivalent area  $\omega_{eq}$ . The models present the same behaviour, and similarly to the mean travel time a change of slope is evident again in correspondence of flow rate equal to  $4 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . This result confirms the fact that the presence of nonlinear flow regime leads to a delay on solute transport with respect to the values that can be obtained under the assumption of a linear flow field.

In order to better represent the nonlinear flow regime, Figure 13 shows water pressure as a function of velocity. A change of slope is evident for  $v = 1.5 \times 10^{-2} \text{ ms}^{-1}$  which corresponds to the flow rate equal to  $4 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ .

Moreover as shown in Figure 14 a linear trend of dispersion with the injection flow rate both for MIM and ENM models has been observed. This is coherent with what obtained in the previous study (Cherubini et al. 2013a) where a linear relationship is found between velocity and dispersion both for ADE and MIM models with the conclusion that geometrical dispersion dominated the effects of Aris – Taylor dispersion. The values of the coefficient of dispersion obtained for ENM models do not depend on flow velocity but assume a somehow scattered but fluctuating value. Being  $\alpha_L$  values constant, geometrical dispersion dominates the mixing processes along the fracture network. Therefore, the presence of a nonlinear flow regime does not prove to exert any influence on dispersion except for high velocities for the ENM model where a weak transitional regime appears.

This does not happen for MIM dispersion values whose rates of increase are smaller than those of ENM dispersion values.

The values of dispersion coefficient are in order of magnitude of decimeter, which is comparable with the values obtained for darcian condition (Qian et al, 2011), and the dispersion values of MIM are much lower than those of ENM.

This may be attributable to the fact that the MIM separates solute spreading into dispersion in mobile region and mobile-immobile mass transfer. The dispersive effect is therefore partially taken into account by the mass transfer between the mobile zone and the immobile zone (Qian et al, 2011; Gao et al, 2009).

## Conclusion

Flow and tracer test experiments have been carried out in a fracture network. The aim of the present study is that of comparing the performances and reliabilities of two model paradigms: the Mobile -

520 Immobile Model (MIM) and the Explicit Network Model (ENM) to describe conservative tracer  
521 transport in a fractured rock sample.

522 Fluid flow experiments show a not negligible nonlinear behaviour of flow best described by the  
523 Forchheimer law. The solution of the flow field for each single fracture highlights that the  
524 probabilities of water distribution between the main and the secondary path are not constant but  
525 decrease as the injection flow rate increases. In other words varying the injection flow rate the  
526 conductance of the main path decreases more rapidly than the conductance of the secondary path.

527 The BTCs curves determined by transport experiments have been fitted by MIM model and three  
528 versions of ENM model (ENM2, ENM3, ENM4) which differ on the basis of the assumptions made  
529 on the parameters  $P_Q$  and  $P_C$ . All models show a satisfactory fitting. The ENM4 model provides the  
530 best fit which is expectable because it has more fitting parameters than ENM2 and ENM3, thus it is  
531 more flexible. Secondly, compared to MIM model, it takes explicitly into account the presence of  
532 the secondary path. Furthermore for the ENM model the parameter  $P_Q$  decreases more rapidly  
533 varying the injection flow rate than the same parameter determined by flow tests. The relationship  
534 between transport time and exchange time for MIM model and mean travel time for main path and  
535 secondary path for the ENM4 model varying the injection flow rate has shown similarity of  
536 behaviour: for higher values of flow rate the difference between transport time and exchange time  
537 decreases and the secondary path reaches the main path in terms of mean travel time. This analogy  
538 between MIM and ENM explains the fact that the mass transfer coefficient is dependent on flow  
539 velocity. The mass transfer coefficient increases as the importance of secondary path over the main  
540 path increases.

541 The velocity values evaluated for MIM and ENM model show the same relationship with the  
542 injection flow rate. In particular a change of slope is evident in correspondence of the flow rate  
543 equal to  $4 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . This behaviour occurs before the critical flow rate estimated by flow tests  
544 equal to  $6.3 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . Therefore the interpretation of BTCs curves evidences more enhanced  
545 nonlinear behaviour than flow tests. These results confirm the fact that the presence of transitional  
546 flow regime leads to a delay on solute transport with respect to the values that can be obtained  
547 under the assumption of a linear flow field (Cherubini et al., 2013a).

548 As concerns dispersion, a linear trend varying the velocity for both MIM and ENM models has been  
549 observed -coherently with the previous results- (Cherubini et al., 2013a), the MIM model  
550 underestimating the dispersion respect to ENM4 model.

551 The dispersivity values obtained for ENM models do not depend on flow velocity but assume a  
552 somehow scattered but fluctuating value. Being  $\alpha_L$  values constant, geometrical dispersion  
553 dominates the mixing processes along the fracture network. Therefore, the presence of a nonlinear  
554 flow regime does not prove to exert any influence on dispersion except for high velocities for the  
555 ENM model where a weak transitional regime seems to appear. This result demonstrates that for our  
556 experiment geometrical dispersion still dominates Taylor dispersion.

557 A major challenge for tracer tests modeling in fractured media is the adequate choice of the  
558 modeling approach for each different study scale.

559 When dealing with large scales, tracer tests breakthrough curves are generally modeled by a  
560 relatively small number of model parameters (Becker and Shapiro, 2000).

561 At laboratory scale, the definition of the network of fractures by means of discrete approaches  
562 (DFN) can permit to identify transport pathways and mass transport coefficients, in order to better  
563 define heterogeneous advective phenomena (Cherubini et. al, 2013b).

564 At an intermediate local field scale (1-100m), recognition that heterogeneous environments contain  
565 fast and slow paths led to the development of the MIM formulation applied successfully in a variety  
566 of hydrogeologic settings. However, the assumed velocity partitioning into flowing and not-flowing  
567 zones is not an accurate representation of the true velocity field (Gao et al., 2009). Especially when  
568 the rock mass is sparsely fractured, the breakthrough curves are characterized by early breakthrough  
569 and long tailing behaviour and a simple mobile-immobile conceptualization may be an over  
570 simplification of the physical transport phenomenon.

571 Solute transport in fractured aquifers characterized by highly non-Fickian behaviour is therefore  
572 better described by an Explicit Network Model rather than by a simple MIM. Applying a discrete  
573 model in such a case can permit to determine if transport occurs through one or several fractures  
574 and if multiple arrivals are caused by fracture heterogeneity, in such a way as to yield a more robust  
575 interpretation of the subsurface transport regime.

576 In such a context, geophysical imaging may provide detailed information about subsurface structure  
577 and dynamics (Dorn et al, 2012).

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<i>MIM 1</i>							
$n^{\circ}$	$Q (m^3/s) \times 10^{-6}$	$v/L (s^{-1}) \times 10^{-2}$	$D/L^2 (s^{-1}) \times 10^{-2}$	$\alpha (s^{-1}) \times 10^{-2}$	$\beta (-)$	RMSE	$r^2$
1	1.319	$0.73 \pm 0.05$	$0.15 \pm 0.01$	$0.43 \pm 0.09$	$0.95 \pm 0.14$	0.022	0.979
5	2.209	$1.05 \pm 0.05$	$0.16 \pm 0.01$	$0.50 \pm 0.12$	$0.51 \pm 0.07$	0.021	0.991
10	2.731	$1.26 \pm 0.05$	$0.18 \pm 0.01$	$0.60 \pm 0.12$	$0.51 \pm 0.06$	0.021	0.994
15	3.084	$1.74 \pm 0.06$	$0.19 \pm 0.01$	$1.03 \pm 0.16$	$0.56 \pm 0.05$	0.023	0.995
20	3.365	$1.75 \pm 0.06$	$0.20 \pm 0.01$	$1.06 \pm 0.17$	$0.54 \pm 0.05$	0.022	0.996
25	3.681	$2.49 \pm 0.10$	$0.25 \pm 0.02$	$1.67 \pm 0.32$	$0.51 \pm 0.06$	0.030	0.995
30	4.074	$2.57 \pm 0.11$	$0.26 \pm 0.02$	$1.67 \pm 0.35$	$0.50 \pm 0.06$	0.033	0.994
35	4.536	$2.25 \pm 0.09$	$0.21 \pm 0.02$	$1.58 \pm 0.29$	$0.57 \pm 0.06$	0.031	0.994
40	5.382	$3.20 \pm 0.13$	$0.26 \pm 0.02$	$2.68 \pm 0.44$	$0.61 \pm 0.06$	0.035	0.994
45	5.895	$3.32 \pm 0.15$	$0.26 \pm 0.02$	$2.82 \pm 0.50$	$0.57 \pm 0.06$	0.036	0.995
50	6.168	$3.02 \pm 0.15$	$0.26 \pm 0.02$	$2.52 \pm 0.52$	$0.51 \pm 0.07$	0.031	0.996
55	8.345	$3.54 \pm 0.29$	$0.35 \pm 0.04$	$3.05 \pm 1.07$	$0.41 \pm 0.11$	0.038	0.995

Table 1. Estimated values of parameters, root mean square error RMSE and determination coefficient  $r^2$  for mobile – immobile model MIM at different injection flow rates in the fractured medium.

<i>ENM 2</i>					
$n^{\circ}$	$Q (m^3/s) \times 10^{-6}$	$\omega_{eq} (m^2) \times 10^{-4}$	$\alpha_L (m) \times 10^{-1}$	RMSE	$R^2$
1	1.3194	$3.10 \pm 0.14$	$1.92 \pm 0.86$	0.033	0.952
5	2.2090	$3.22 \pm 0.04$	$0.98 \pm 0.06$	0.020	0.993
10	2.7312	$3.29 \pm 0.04$	$0.92 \pm 0.05$	0.019	0.995
15	3.0842	$2.81 \pm 0.03$	$0.79 \pm 0.03$	0.020	0.996
20	3.3648	$3.06 \pm 0.03$	$0.79 \pm 0.03$	0.019	0.997
25	3.6813	$2.35 \pm 0.02$	$0.74 \pm 0.03$	0.026	0.996
30	4.0735	$2.49 \pm 0.02$	$0.75 \pm 0.03$	0.027	0.996
35	4.5356	$3.27 \pm 0.04$	$0.74 \pm 0.04$	0.028	0.995
40	5.3824	$2.76 \pm 0.02$	$0.75 \pm 0.02$	0.023	0.998
45	5.8945	$2.90 \pm 0.02$	$0.69 \pm 0.02$	0.027	0.997
50	6.1684	$3.30 \pm 0.04$	$0.68 \pm 0.02$	0.032	0.995
55	8.3455	$3.56 \pm 0.05$	$0.78 \pm 0.02$	0.041	0.994

Table 2. Estimated values of parameters, root mean square error RMSE and determination coefficient  $r^2$  for ENM2 at different injection flow rates in the fractured medium.

**ENM 3**

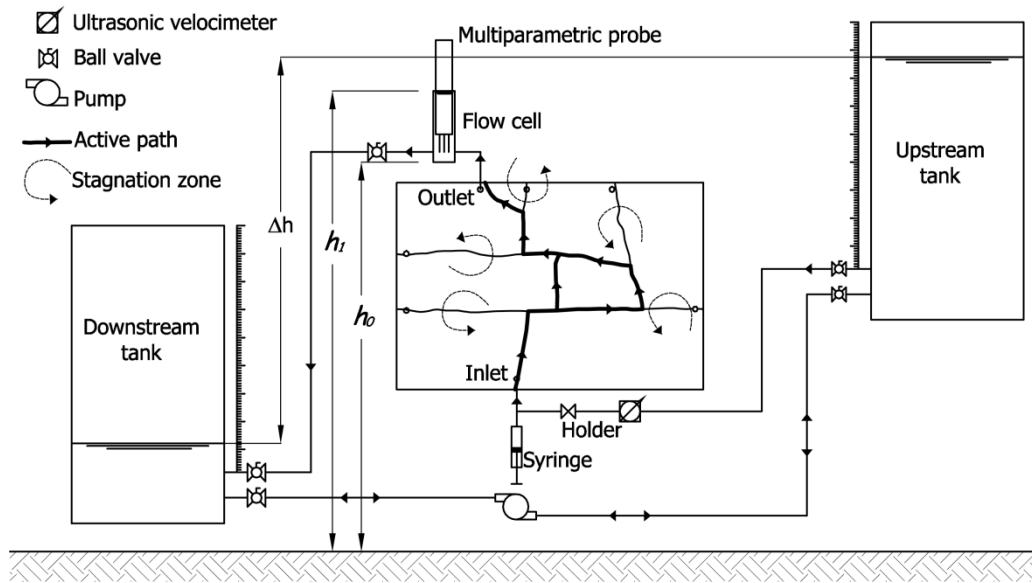
n°	Q (m <sup>3</sup> /s)×10 <sup>-6</sup>	ω <sub>eq</sub> (m <sup>2</sup> )×10 <sup>-4</sup>	α <sub>L</sub> (m)×10 <sup>-1</sup>	P <sub>Q</sub> /P <sub>C</sub> (-)	RMSE	R <sup>2</sup>
1	1.319	3.43 ± 1.28	1.92 ± 0.86	0.82 ± 0.17	0.032	0.954
5	2.209	3.18 ± 0.11	0.98 ± 0.06	0.76 ± 0.02	0.020	0.993
10	2.731	3.28 ± 0.09	0.92 ± 0.05	0.75 ± 0.02	0.019	0.995
15	3.084	2.73 ± 0.05	0.79 ± 0.03	0.73 ± 0.01	0.019	0.997
20	3.365	2.94 ± 0.05	0.79 ± 0.03	0.72 ± 0.01	0.017	0.997
25	3.681	2.22 ± 0.04	0.74 ± 0.03	0.71 ± 0.01	0.023	0.997
30	4.074	2.37 ± 0.04	0.75 ± 0.03	0.71 ± 0.01	0.025	0.997
35	4.536	3.13 ± 0.06	0.74 ± 0.04	0.71 ± 0.01	0.026	0.995
40	5.382	2.61 ± 0.03	0.75 ± 0.02	0.70 ± 0.01	0.016	0.999
45	5.895	2.70 ± 0.03	0.69 ± 0.02	0.68 ± 0.01	0.016	0.999
50	6.168	2.98 ± 0.03	0.68 ± 0.02	0.66 ± 0.01	0.017	0.999
55	8.345	3.13 ± 0.02	0.78 ± 0.02	0.63 ± 0.01	0.016	0.999

**Table 3. Estimated values of parameters, root mean square error RMSE and determination coefficient r<sup>2</sup> for ENM3 at different injection flow rates in the fractured medium.**

**ENM 4**

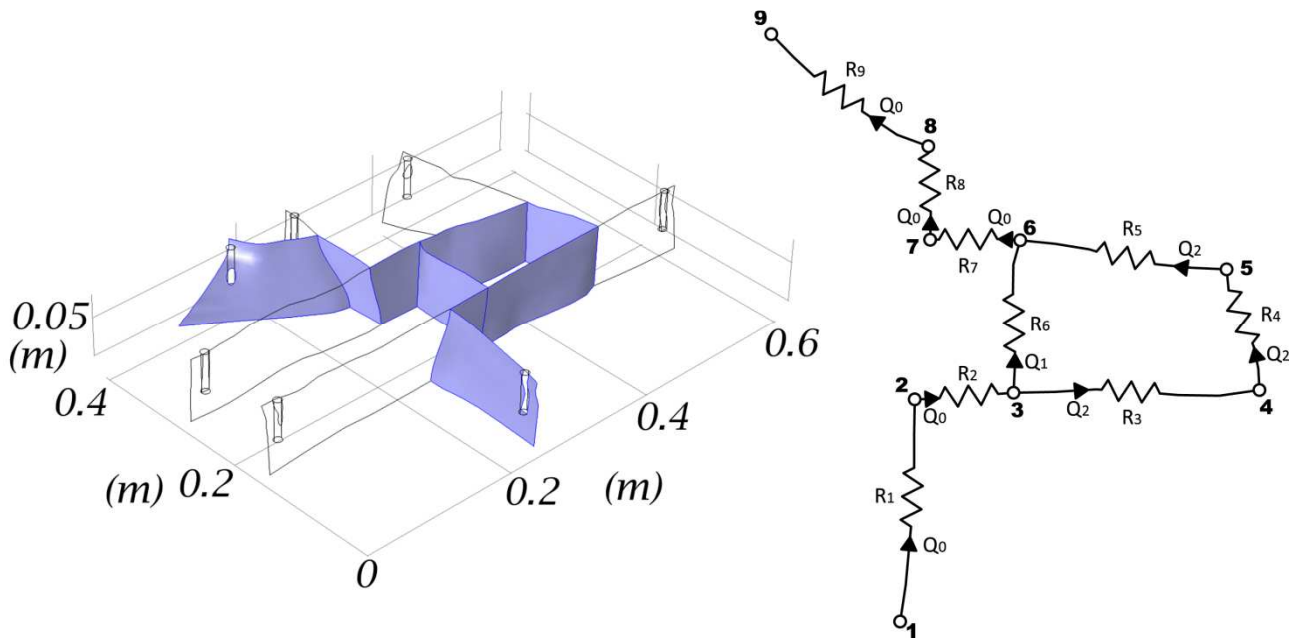
n°	Q (m <sup>3</sup> /s)×10 <sup>-6</sup>	ω <sub>eq</sub> (m <sup>2</sup> )×10 <sup>-4</sup>	α <sub>L</sub> (m)×10 <sup>-1</sup>	P <sub>Q</sub> (-)	P <sub>C</sub> (-)	RMSE	R <sup>2</sup>
1	1.319	2.67 ± 0.13	1.18 ± 0.11	0.85 ± 0.02	0.67 ± 0.02	0.020	0.981
5	2.209	3.15 ± 0.12	0.96 ± 0.07	0.76 ± 0.02	0.75 ± 0.03	0.020	0.993
10	2.731	3.28 ± 0.10	0.92 ± 0.06	0.75 ± 0.02	0.76 ± 0.02	0.019	0.995
15	3.084	2.74 ± 0.06	0.80 ± 0.04	0.73 ± 0.01	0.74 ± 0.02	0.019	0.997
20	3.365	2.97 ± 0.06	0.81 ± 0.04	0.72 ± 0.01	0.73 ± 0.02	0.017	0.997
25	3.681	2.28 ± 0.05	0.80 ± 0.04	0.70 ± 0.01	0.74 ± 0.02	0.020	0.998
30	4.074	2.43 ± 0.06	0.80 ± 0.04	0.71 ± 0.01	0.74 ± 0.02	0.022	0.997
35	4.536	3.18 ± 0.08	0.76 ± 0.05	0.71 ± 0.01	0.73 ± 0.02	0.025	0.996
40	5.382	2.62 ± 0.04	0.76 ± 0.03	0.70 ± 0.01	0.70 ± 0.01	0.016	0.999
45	5.895	2.76 ± 0.03	0.73 ± 0.02	0.68 ± 0.01	0.71 ± 0.01	0.014	0.999
50	6.168	3.12 ± 0.04	0.76 ± 0.02	0.66 ± 0.01	0.71 ± 0.01	0.012	0.999
55	8.345	3.46 ± 0.02	0.96 ± 0.01	0.63 ± 0.00	0.73 ± 0.01	0.003	1.000

**Table 4. Estimated values of parameters, root mean square error RMSE and determination coefficient r<sup>2</sup> for ENM4 at different injection flow rates in the fractured medium.**



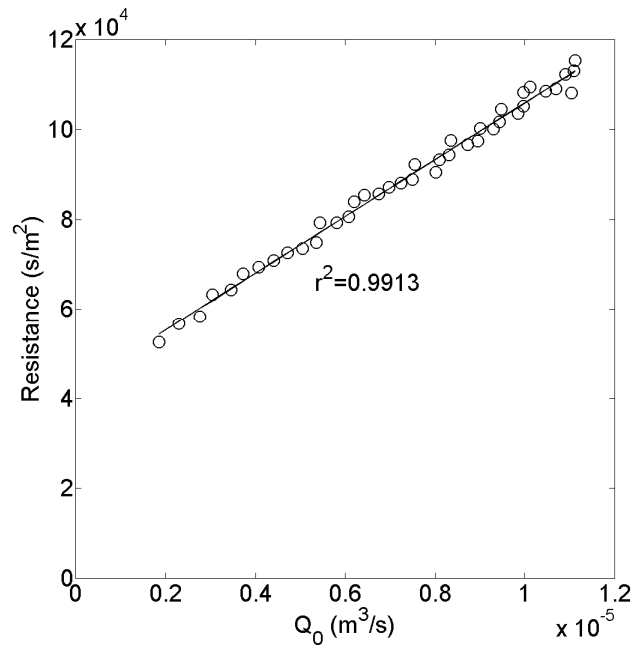
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708 **Figure 1. Schematic diagram of experimental setup.**



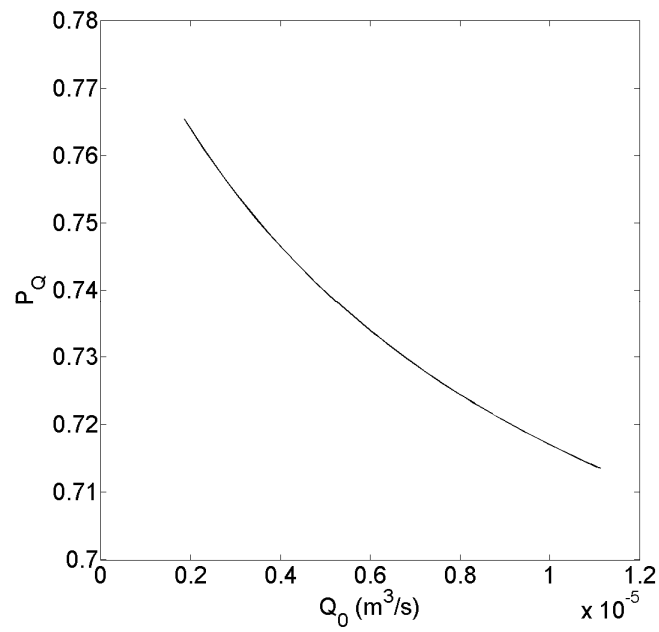
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710 **Figure 2. 2d pipe network conceptualization of the fractured medium.**



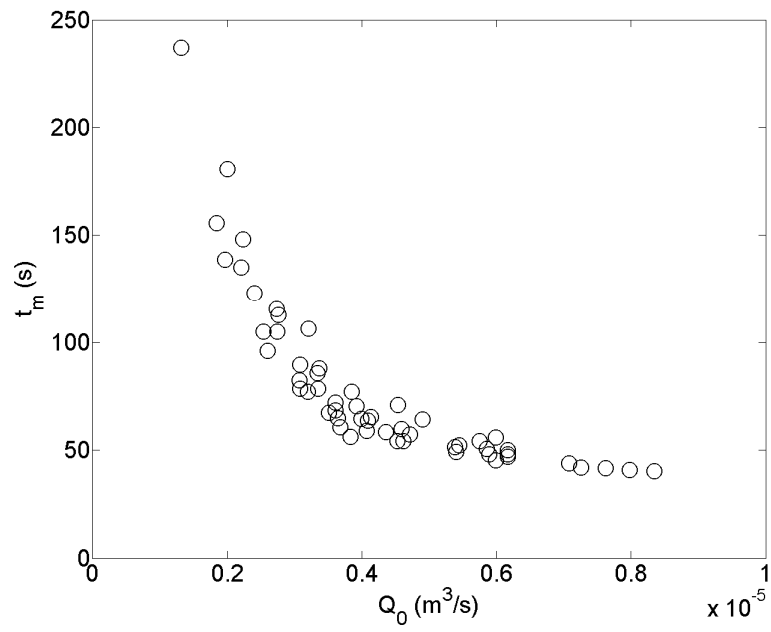
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712 **Figure 3. Average resistance to flow versus injection flow rate  $Q_0$  ( $\text{m}^3/\text{s}$ ). The circles represent the experimental values, the**  
 713 **straight line represents the resistance to flow evaluated by equation (31).**



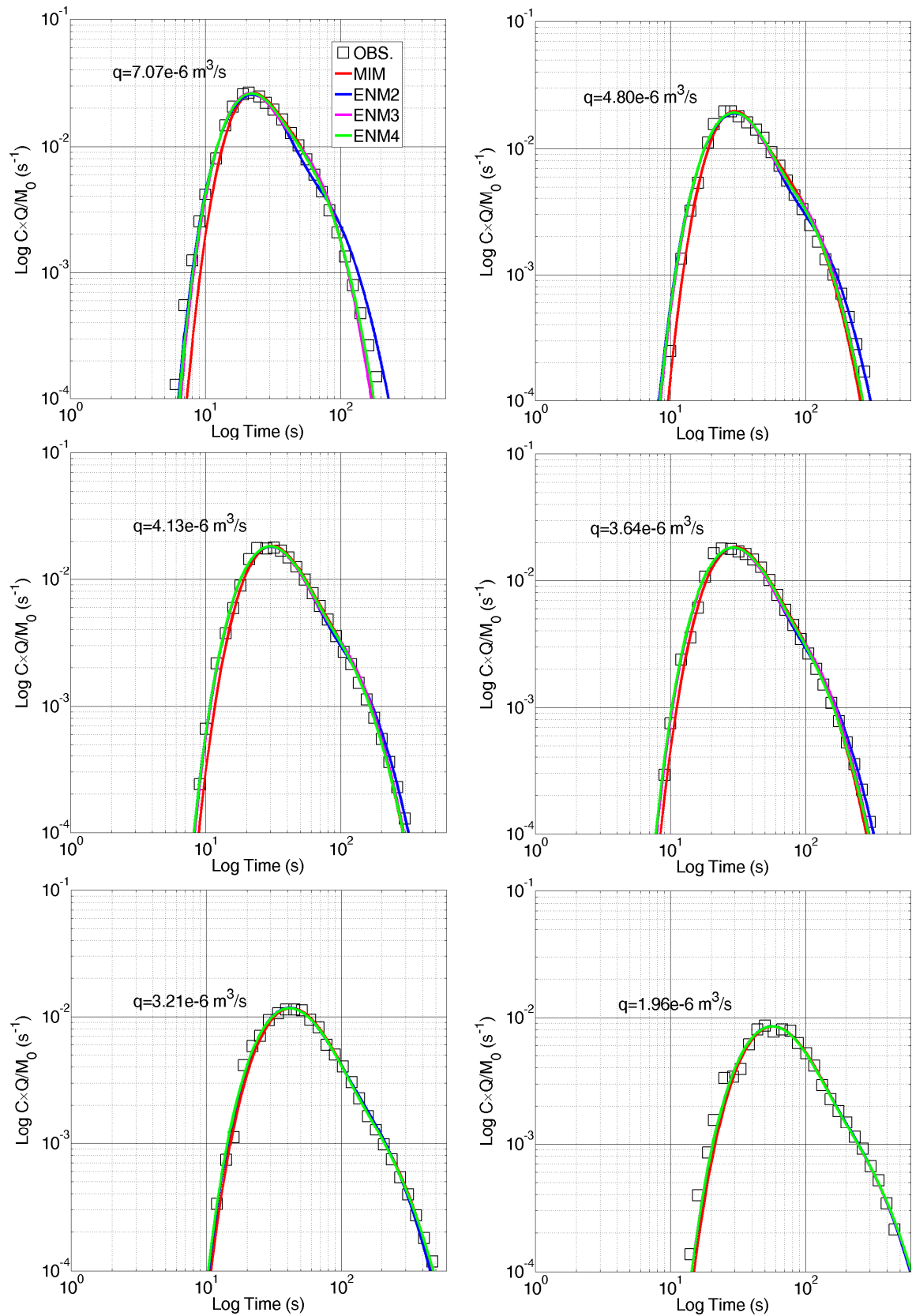
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715 **Figure 4. Probability of water distribution evaluated for main path  $P_Q$  versus injection flow rate  $Q_0$  ( $\text{m}^3/\text{s}$ ).**

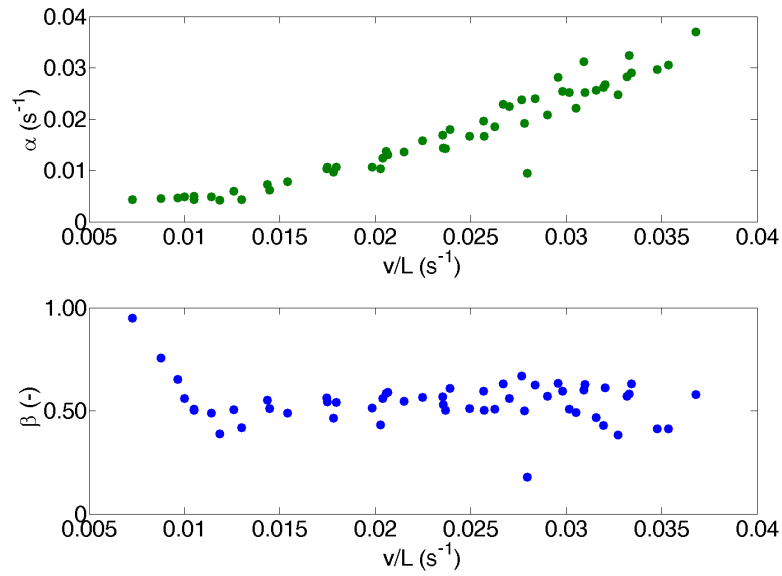


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717 **Figure 5. Mean travel time  $t_m$  (s) versus injection flow rate  $Q_0$  ( $\text{m}^3/\text{s}$ ).**



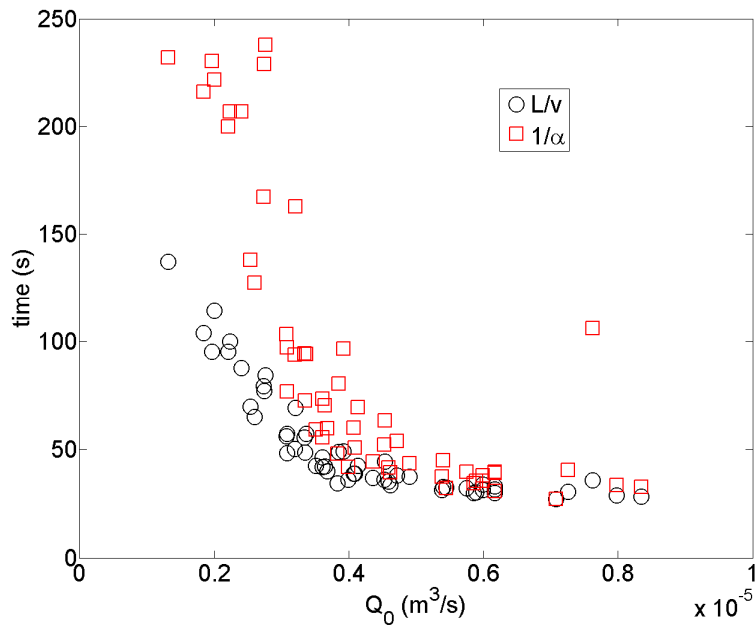
**Figure 6. Fitting of breakthrough curves at different injection flow rates using each of the four models (MIM, ENM1, ENM2, ENM3).**



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**Figure 7. Immobile – mobile ratio ( $\beta$ ) as function of normalized velocity  $v/L$  ( $s^{-1}$ ) for MIM model. An outlier is evidenced for  $v/L=0,028 s^{-1}$**



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**Figure 8. Transport time ( $L/v$ ) (reciprocal of normalized velocity) and exchange time ( $1/\alpha$ ) (reciprocal of the exchange term) as function of injection flow rate  $Q_0$  ( $m^3/s$ ) for mobile - immobile model MIM.**



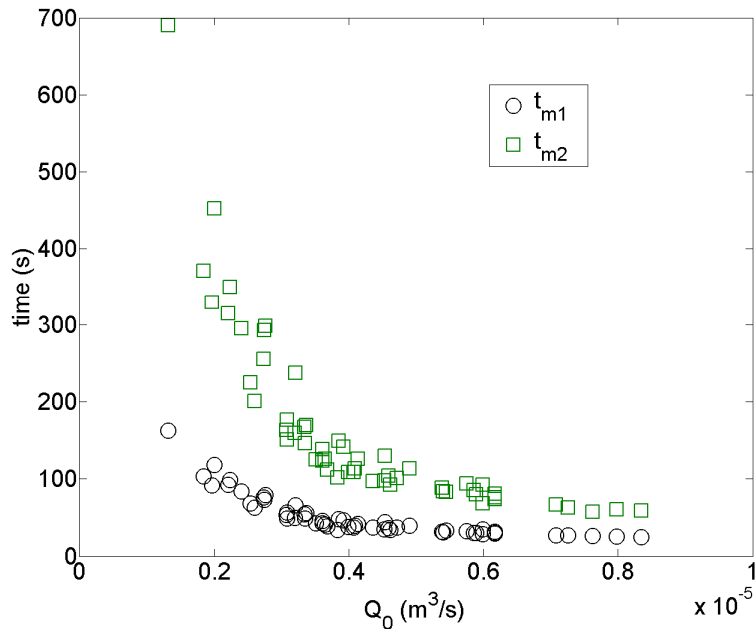


Figure 9. Travel time for main path  $t_{m1}$  (s) and travel time for secondary path  $t_{m2}$  (s) for ENM4 as function of injection flow rate  $Q_0$  ( $m^3/s$ ).

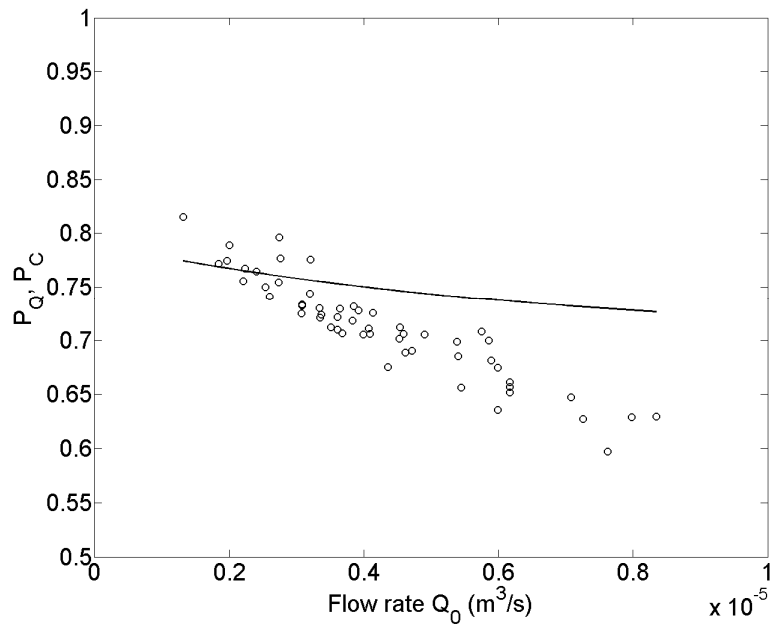


Figure 10. Comparison between the Probability of water distribution  $P_Q$  evaluated as the square brackets term in Equation (29) (straight line) and the probability of particle transition  $P_C(P_Q)$  for ENM3 (circle) varying the injection flow rate  $Q_0$  ( $m^3/s$ ).

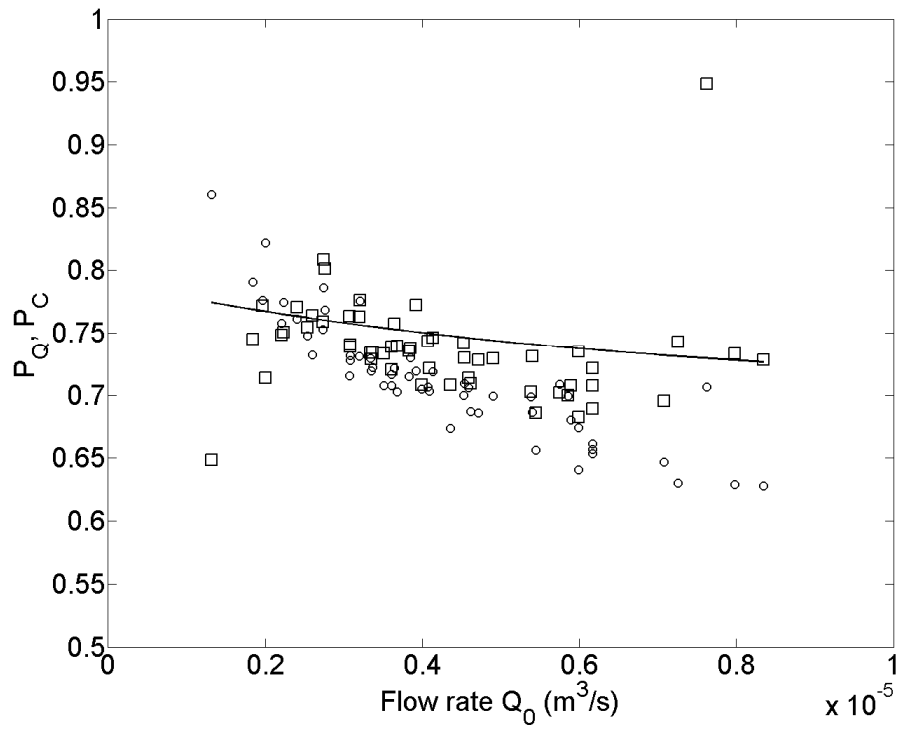


Figure 11. Comparison between the Probability of water distribution  $P_Q$  evaluated by the flow model (straight line) and the probability of particle transition  $P_c$  (square) and  $P_Q$  (circle) for ENM4 varying the injection flow rate  $Q_0$  ( $\text{m}^3/\text{s}$ ).

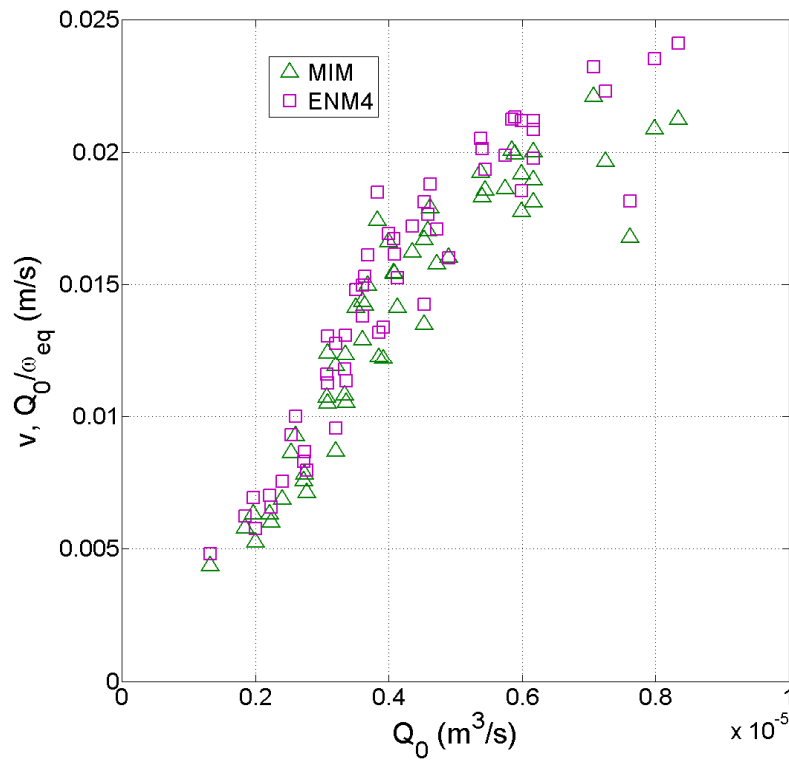


Figure 12. velocity  $v$  ( $\text{m/s}$ ) as function of the injection flow rate  $Q_0$  ( $\text{m}^3/\text{s}$ ) for MIM and ENM4 models. Note that for MIM model the  $v$  is determined assuming the length of medium equal to the length of main path ( $L = 0.601$  m). Instead for the ENM4 model the velocity is determined dividing  $Q_0$  for the equivalent area  $\omega_{eq}$ .

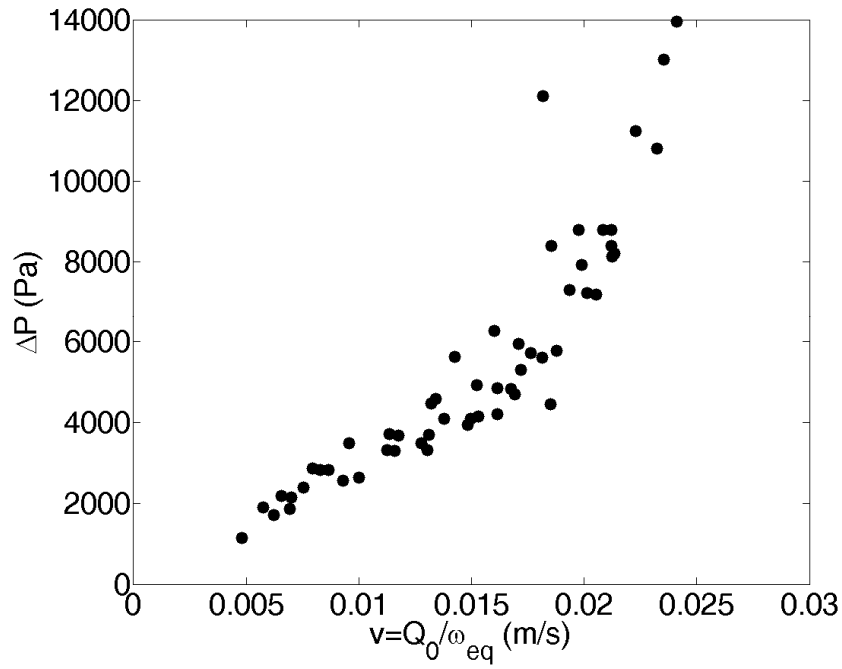


Figure 13. difference of pressure  $\Delta P$  (Pa) as function of velocity  $v$  (m/s) for ENM4. The velocity is determined dividing  $Q_0$  for the equivalent area  $\omega_{eq}$ .

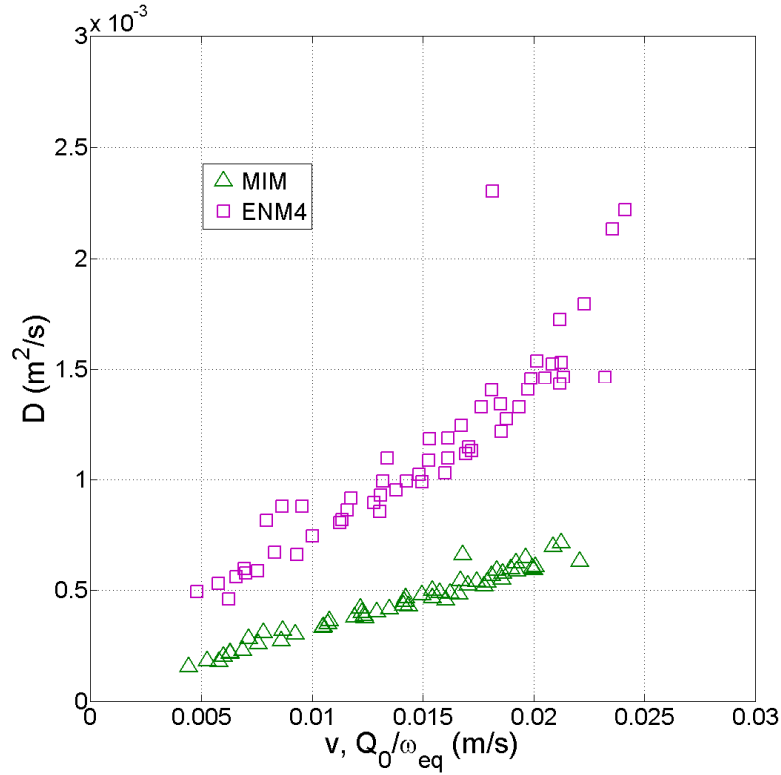


Figure 14. Dispersion  $D$  ( $m^2/s$ ) as function of velocity for MIM and ENM4 models. Note that for MIM model  $D$  is determined assuming the length of the medium equal to the length of the main path ( $l=0.601$  m). Instead for ENM4 model  $D$  is determined as  $D=Q_0 \cdot \alpha_l / \omega_{eq}$ .