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Tristan Babey, Jean-Raynald de Dreuzy, Alain Rapaport, Alejandro Rojas-Palma. Inherent relevance of MRMT models to concentration variance and mixing-induced reactivity. *Advances in Water Resources*, 2017, 110, pp.291-298. 10.1016/j.advwatres.2017.09.024 . insu-01609279

**HAL Id: insu-01609279**

**<https://insu.hal.science/insu-01609279>**

Submitted on 3 Oct 2017

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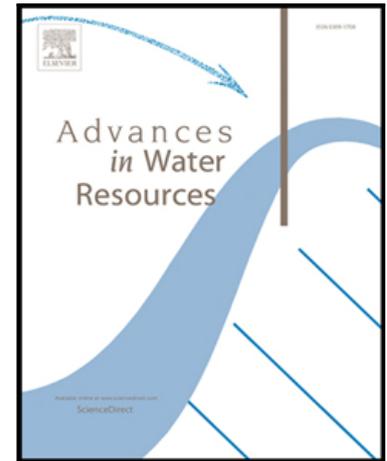
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## Accepted Manuscript

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PII: S0309-1708(17)30366-4  
DOI: [10.1016/j.advwatres.2017.09.024](https://doi.org/10.1016/j.advwatres.2017.09.024)  
Reference: ADWR 2958



To appear in: *Advances in Water Resources*

Received date: 10 April 2017  
Revised date: 21 July 2017  
Accepted date: 27 September 2017

Please cite this article as: Tristan Babey, Jean-Raynald de Dreuzy, Alain Rapaport, Alejandro Rojas-Palma, Inherent relevance of MRMT models to concentration variance and mixing-induced reactivity, *Advances in Water Resources* (2017), doi: [10.1016/j.advwatres.2017.09.024](https://doi.org/10.1016/j.advwatres.2017.09.024)

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**1 Highlights**

- 2 • Generic models of concentration variability in diffusion-dominated porosities.
- 3 • Mobile/immobile models like MRMT are relevant for concentration mean and variance.
- 4 • Combinations of porosities in MRMT inherently conserve concentration variance.
- 5 • Equivalent MRMT models approximate well homogeneous and heterogeneous reactivities.
- 6 • Equivalent MRMT should be of the same minimal dimension as the input/output system.

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# Inherent relevance of MRMT models to concentration variance and mixing-induced reactivity

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## Abstract

Several anomalous transport approaches have been developed to model the interaction between fast advectively-dominated transport in well-connected porosity and fracture structures and slow diffusively-dominated transport in poorly-connected or low-permeability ones. Among them, the Multi-Rate Mass Transfer approach (MRMT) represents the anomalous dispersion along the main flow paths (mobile zone) induced by a large distribution of first-order exchanges with immobile zones. Even though MRMTs have been developed for conservative transport processes in the mobile zone, we demonstrate that they also conserve the variance of the concentration distribution in the immobile zones, and, hence, pertain to mixing induced reactivity. This property is established whatever the organization of the immobile zones and whatever the injection and sampling conditions in the mobile zone. It inherently derives from the symmetry properties of the diffusion operator in the immobile zones, but cannot be directly extended to heterogeneous dispersive processes in the mobile zone.

*Keywords:* Anomalous transport, Reactive transport, Multi-Rate Mass Transfer models, Heterogeneous geological media

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## Highlights

1. Generic models of concentration variability in diffusion-dominated porosities.
2. Mobile/immobile models like MRMT are relevant for concentration mean and variance.
3. Combinations of porosities in MRMT inherently conserve concentration variance.
4. Equivalent MRMT models approximate well homogeneous and heterogeneous reactivities.
5. Equivalent MRMT should be of the same minimal dimension as the input/output system.

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## 36 1. Introduction

37 Dispersion in geological media derives from simple advective and diffusive processes in complex  
38 porous and fracture structures [Gelhar and Axness, 1983]. Solutes are delayed by trapping in  
39 poorly connected porosity structures and dispersed by exchanges with fast transport in localized  
40 channels. Such structures are found as intragranular clay particles [Scheibe et al., 2013], stagnant  
41 zones in carbonates [Bijeljic et al., 2013], poorly connected fracture clusters [Davy et al., 2010],  
42 hydraulic dead ends in fractures [Park et al., 2003] or incomplete dissolution patterns [Luquot  
43 et al., 2014]. Diffusion and trapping are significant and may induce non-Fickian anomalously slow  
44 and highly-dispersed transport [Bouchaud and Georges, 1990; Dentz and Berkowitz, 2003; Havlin  
45 and Ben-Avraham, 1987]. Anomalous transport has been reported both in porous and in fractured  
46 media at multiple scales from laboratory experiments [Soler-Sagarra et al., 2016; Zinn et al., 2004;  
47 Knorr et al., 2016], advanced analysis of microtomography images [Gjetvaj et al., 2015; Gouze  
48 et al., 2008], field experiments [Greskowiak et al., 2011; Le Borgne and Gouze, 2008] and numerical  
49 simulations [de Dreuzy and Carrera, 2016; Fernandez-Garcia et al., 2009; Lichtner and Kang, 2007;  
50 Roubinet et al., 2013; Willmann et al., 2010].

51 Several conceptual frameworks have been developed to model anomalous transport [Benson et al.,  
52 2000; Berkowitz et al., 2006; de Dreuzy and Carrera, 2016; Neuman and Tartakovsky, 2009].  
53 Among them, the mobile-immobile Multi-Rate Mass Transfer models (MRMT) [Carrera et al.,  
54 1998; Haggerty and Gorelick, 1995] does not only propose efficient characterization and upscaling  
55 methodologies [Willmann et al., 2008; Babey et al., 2015; Rapaport et al., 2017] but also a natural  
56 bridge to equivalent concentration distributions, which relevance can be assessed to model reac-  
57 tive transport [Donado et al., 2009; Henri and Fernandez-Garcia, 2015; Sanchez-Vila et al., 2010;  
58 Soler-Sagarra et al., 2016]. Synthetic experiments have shown that MRMT models provide close  
59 approximations of bulk reactivity even in non-linear equilibrium and kinetically-controlled cases  
60 [Babey et al., 2016]. This has been linked to the empirical observation that MRMT models do  
61 not only conserve mass by construction but also the porosity weighted integral of concentrations  
62 squared [de Dreuzy et al., 2013], which is directly linked to mixing-induced reactivity through the  
63 scalar dissipation rate [Le Borgne et al., 2010].

64 While the conservation of the porosity weighted integral of concentrations squared has so far been  
65 reported from numerical experiments in a couple of specific cases, we provide here the full demon-

66 stration of its conservation. This property is inherent to the formalism of the mobile/immobile  
 67 models (including MRMT) providing the model to be minimal. It derives from the conservation of  
 68 mass in the mobile zone and from the expression of the immobile concentrations as the direct dif-  
 69 ference between immobile and mobile concentrations. It does not require any additional condition.  
 70 The demonstration applies to any type of diffusively-dominated porosity structure exchanging with  
 71 advectively-dominated transport identified with the so-called mobile zones. We shortly discuss the  
 72 implications on the general relevance of MRMT models to chemical transport.

## 73 2. Dynamics of concentrations in mobile/immobile models

74 In this section, we recall the general framework proposed by Babey et al. [2015] to model solute  
 75 transport resulting from the interactions between a mobile zone and a finite number of  $n$  immo-  
 76 bile zones. This framework identified as the Structured Interacting Continua (SINC) model was  
 77 introduced as an extension of the classic Multiple Interacting Continua (MINC) model [Pruess  
 78 and Narasimhan, 1985; Karimi-Fard et al., 2006]. Transport is dominated by advection along the  
 79 “mobile zone”, and solutes are exchanged by diffusion with and between the different “immobile  
 80 zones”. Immobile zones can display any connectivity patterns coming, for example, from the dis-  
 81 cretization of diffusion within dead-ends of fractures or pore clusters [Davy et al., 2010; Gouze  
 82 et al., 2008; Karimi-Fard and Durlofsky, 2016], alluvial architectures [Zhang et al., 2013, 2014],  
 83 heterogeneous porous media [Li et al., 2011; Tyukhova et al., 2015; Tyukhova and Willmann, 2016]  
 84 or multi-porosity reservoirs [Geiger et al., 2013]. The SINC model is formalized as:

$$\frac{\partial C}{\partial t} + \Phi^{-1}MC = BL(c_1) \quad (1)$$

85 where  $C$  is the column vector made up of the solute concentrations in the mobile and immobile  
 86 zones:

$$C = [ c_1(r, t) \quad \dots \quad c_{n+1}(r, t) ]^T. \quad (2)$$

87  $c_1(r, t)$  is the concentration in the mobile zone and  $c_i(r, t)$  with  $i = 2 \dots n+1$  are the concentrations  
 88 in the  $n$  immobile zones.  $L$  is the advective-dispersive transport operator in the mobile zone:

$$L(c_1) = -\frac{1}{\phi_1} \nabla \cdot (qc_1) + \nabla \cdot (D_m \nabla c_1) \quad (3)$$

89 where  $\phi_1$ ,  $q$  and  $D_m$  are the uniform porosity, Darcian flow and diffusion-dispersion tensor in the  
 90 mobile zone.  $B$  is the restriction vector to the mobile zone:

$$B = [ 1 \ 0 \ \dots \ 0 ]^T. \quad (4)$$

91  $\Phi$  is the porosity matrix of size  $(n + 1, n + 1)$  which diagonal coefficients are the porosities of the  
 92 different zones  $\phi_i$ :

$$\Phi = \text{diag} \left( [ \phi_1 \ \dots \ \phi_{n+1} ] \right). \quad (5)$$

93 Finally, the matrix  $M$  of size  $(n + 1, n + 1)$  is the operator describing the diffusive-like exchanges  
 94 between the different zones.  $M$  can be compared to a weighted adjacency matrix [Godsil and Royle,  
 95 2001] as its coefficients correspond to rates of mass exchanges. Because it expresses a diffusion  
 96 process,  $M$  is a symmetric M-matrix which rows sum to zero. Eq. 1 can be rewritten to highlight  
 97 the interactions between the concentrations of the different zones:

$$\frac{\partial C}{\partial t} - AC = BL(c_1) \quad (6)$$

98 where  $A$  is the interaction matrix that synthesizes porosity and diffusive mass exchange effects:

$$A = -\Phi^{-1}M. \quad (7)$$

99 Except in the specific case of uniform porosity,  $A$  is not symmetric.

100 MRMT models with a finite number of immobile zones can be expressed within the SINC framework  
 101 as the subset of models with only mobile-immobile connections, with the corresponding porosity  
 102 and mass exchange matrices  $\Phi$  and  $M$  given by:

$$\begin{aligned} \Phi &= \text{diag} \left( [ \phi_1 \ \dots \ \phi_{n+1} ] \right) \\ M(i, j) &= 0 \text{ for } i > 1, j > 1 \text{ and } i \neq j \\ M(i, 1) &= M(1, i) = -\phi_i \alpha_{i-1} \text{ for } i > 1 \\ M(i, i) &= - \sum_{j:j \neq i} M(i, j) \end{aligned} \quad (8)$$

103 where  $\alpha_i$  and  $\phi_i$  are the rates of exchanges and porosities of the MRMT model Haggerty and  
 104 Gorelick [1995].

### 105 3. Conservation of concentration variance by MRMT models

106 Babey et al. [2015] and Rapaport et al. [2017] have demonstrated that any mobile-immobile model  
 107 identified as SINC in the previous section, i.e. whatever the connectivity of its immobile zones,  
 108 is equivalent to a unique (up to the numbering of the immobile zones) MRMT model, proving  
 109 the original model to be minimal. Equivalence between SINC and MRMT is meant here as the  
 110 same number of immobile zones and the same partition of concentrations between the mobile and  
 111 immobile zones:

$$c_1(r, t) = \bar{c}_1(r, t) \quad (9)$$

$$\sum_{i=2}^{n+1} \phi_i c_i(r, t) = \sum_{i=2}^{\bar{n}+1} \bar{\phi}_i \bar{c}_i(r, t) \quad (10)$$

112 where  $c_i$ ,  $\phi_i$  and  $n$  are respectively the concentrations, porosities and total number of immobile  
 113 zones for SINC, and  $\bar{c}_i$ ,  $\bar{\phi}_i$  and  $\bar{n}$  are their counterparts for the equivalent MRMT model.

114 When the original SINC model is not minimal, the variance of concentration is not conserved as  
 115 shown by the counterexample of Appendix A1. The absence of minimality cannot be detected with  
 116 any straightforward criterion as it concerns the exchanges of the overall immobile structure with  
 117 the mobile zone. The example of Appendix A1 does not show any visual symmetry or redundant  
 118 structure although it is not minimal. Minimality of the system can however be tested by its  
 119 controllability and observability properties [Andréa-Novel and de Lara, 2013] (here observability is  
 120 equivalent to controllability because input and output are in the same mobile zone: see [Rapaport  
 121 et al., 2017]). A system is said controllable if, for all couple of state vectors ( $C^a$ ,  $C^b$ ), there exists a  
 122 finite time  $T \geq 0$  and a input concentration  $c_1^{in}(\cdot)$  defined on  $[0, T]$  such that, applying this input  
 123 function, the solution  $C(\cdot)$  with initial condition  $C(0) = C^a$  satisfies  $C(T) = C^b$ . Controllability  
 124 is checked by the algebraic condition that the controllability matrix given by

$$\mathcal{C} = [B, AB, \dots A^n B] \quad (11)$$

125 is full rank. The lack of minimality means that there is some redundancy in the SINC structure in  
 126 terms of exchange terms (see example in Appendix A1). When the original model is non minimal,  
 127 it is however possible to reduce the model to an equivalent minimal one ([Chen, 1999]), which can

128 be sought here as a SINC model with less immobile zones ( $\bar{n} < n$ ) before applying the algorithm  
 129 given in [Rapaport et al., 2017] to then obtain an equivalent MRMT model with  $\bar{n}$  immobile zones.

130 After recalling how MRMT models can be built from minimal SINC models, we show that MRMT  
 131 models inherently preserve the porosity weighted integral of the concentrations squared:

$$\sum_{i=1}^{n+1} \phi_i c_i^2 = \sum_{i=1}^{\bar{n}+1} \bar{\phi}_i \bar{c}_i^2 \quad (12)$$

132 or equivalently in algebraic form:

$$C^T \Phi C = \bar{C}^T \bar{\Phi} \bar{C} \quad (13)$$

133 with  $C$  and  $\Phi$  the concentration vector and diagonal porosity matrix for SINC, and  $\bar{C}$  and  $\bar{\Phi}$  their  
 134 counterparts for the equivalent MRMT model.

135 Assuming the identity of concentration partition (Eqs. 9-10), the equivalent MRMT model to a  
 136 SINC model writes:

$$\frac{\partial \bar{C}}{\partial t} - \bar{A} \bar{C} = BL(c_1) \quad (14)$$

137 where  $\bar{A}$  and  $\bar{C}$  are the interaction matrix and concentration vector for the equivalent MRMT  
 138 model:

$$\begin{cases} \bar{A} = R A R^{-1} \\ \bar{C} = R C \end{cases} \quad (15)$$

139 with  $R$  the transformation matrix from SINC to MRMT. Concentrations  $\bar{C}$  are qualified as semi-  
 140 local as they are still concentrations from the dimension point of view but are only combinations  
 141 of effective concentrations  $C$ .  $R$  derives from the diagonalization of the sub-matrix  $A_S = A(2 : n + 1, 2 : n + 1)$ , which describes exclusively the exchanges between the immobile zones, into  
 142  $\bar{A}_S = \bar{A}(2 : n + 1, 2 : n + 1)$ :

$$\bar{A}_S = R_S A_S R_S^{-1} \quad (16)$$

144 where  $R_S$  is the matrix composed of the eigenvectors of  $A_S$ . The eigenvalues of  $A_S$  (diagonal  
 145 coefficients of  $\bar{A}_S$ ) are the rates  $\alpha_i$  of the equivalent MRMT model (Eq. 8). To be representative

146 of a MRMT model,  $\bar{A}$  must have the same shape as  $A$  described by Eq. 7:

$$\bar{A} = -\bar{\Phi}^{-1}\bar{M} \quad (17)$$

147 where  $\bar{\Phi}$  and  $\bar{M}$  are the porosity and mass exchange matrices given by Eq. 8. Rapaport et al.  
148 [2017] have shown that this condition is fulfilled only if the pair  $(A, B)$  is controllable. The full  
149 transformation matrix  $R$  then writes:

$$R = \begin{bmatrix} 1 & 0 \\ 0 & -R_S \bar{A}_S^{-1} \text{diag}(R_S^{-1} A(2:n+1, 1)) \end{bmatrix}. \quad (18)$$

150  $R$  verifies the conservation of concentrations in the mobile zone (Eq. 9). By construction,  $R$  also  
151 ensures that any uniform concentration profile in SINC remains equally uniform in its equivalent  
152 MRMT:

$$\begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix} = R \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix}. \quad (19)$$

153 From this formulation of the equivalence between SINC and MRMT, we derive the expressions of  
154  $\bar{\Phi}$  and  $\bar{M}$  as functions of  $\Phi$  and  $M$  and of the transformation matrix  $R$ . To this end, we develop  
155 the expression of  $\bar{A}$  in Eq. 15 by introducing the definition of  $A$  (Eq. 7):

$$\bar{A} = -R\Phi^{-1}MR^{-1}, \quad (20)$$

156 and introduce the matrices  $T = R\Phi^{-1/2}$  and  $S = \Phi^{-1/2}M\Phi^{-1/2}$  such that

$$\begin{aligned} \bar{A} &= -TST^{-1} \\ &= -TT^T(T^{-1})^TST^{-1}. \end{aligned} \quad (21)$$

157 We note  $T_S$  and  $S_S$  the sub-matrices of  $T$  and  $S$  made up of their last  $n$  rows and columns. As  
158  $\bar{A}_S$  is diagonal,  $T_S$  diagonalizes the matrix  $S_S$ :

$$T_S S_S T_S^{-1} = R_S A_S R_S^{-1} = \bar{A}_S \quad (22)$$

159 and, because  $S_S$  is symmetric, and  $\bar{A}_S$  has distinct eigenvalues,  $T_S$  is of the form  $DU$  where  $D$  is  
160 a diagonal matrix and  $U$  is a unitary matrix.  $T_S T_S^T$  is in turn equal to a positive diagonal matrix

161  $D^2$ . Due to the structure of the matrix  $R$ , one has:

$$TT^T = \begin{bmatrix} 1/\phi_1 & 0 \\ 0 & T_S T_S^T \end{bmatrix}. \quad (23)$$

162 Because  $TT^T$  is positive and diagonal, and because  $(T^{-1})^T S T^{-1}$  is symmetric, they can be identified  
163 respectively to  $\bar{\Phi}^{-1}$  and  $\bar{M}$  of Eq. 17:

$$\bar{\Phi} = (TT^T)^{-1} = (R^{-1})^T \Phi R^{-1} \quad (24)$$

$$\bar{M} = (T^{-1})^T S T^{-1} = (R^{-1})^T M R^{-1}. \quad (25)$$

164 It should be noted that the transformations of porosities and mass exchange rates from SINC to  
165 MRMT are identical and directly derive from the change of basis of the concentrations given by  
166 Eqs. 15, 18 and 19. The conservation of the porosity weighted integral of concentrations squared  
167 of Eq. 13 derives from the consistency between the change of basis of concentrations and porosities  
168 (Eqs. 15 and 24):

$$\begin{aligned} \bar{C}^T \bar{\Phi} \bar{C} &= C^T R^T (R^{-1})^T \Phi R^{-1} R C \\ &= C^T \Phi C. \end{aligned} \quad (26)$$

169 As this conservation directly results from the construction of MRMT without any additional con-  
170 straint, it is an inherent property of MRMT models of finite dimension (i.e. having a finite number  
171 of immobile zones). It fundamentally derives from the symmetry of the exchange matrix  $M$  of  
172 the mobile-immobile model, a fundamental property of the diffusion operator, which conditions  
173 the orthogonality of the matrix  $T$ , a property essential to the demonstration. The conservation of  
174 the porosity weighted integral of concentrations squared can be extended to all porosity structures  
175 that are equivalent to the same MRMT, i.e. that have the same mobile concentrations (Appendix  
176 A2).

177 The same conservation of the porosity-weighted sum of concentrations squared can also be es-  
178 tablished for the uniform radial diffusion in the immobile zone whatever its dimension (1, 2 or  
179 3), where the equivalent MRMT derives from a separation of variables methodology [Haggerty  
180 and Gorelick, 1995; Carrera et al., 1998]. As the former demonstration requires the number of  
181 immobile zones to be finite, we provide for an alternative demonstration in Appendix A3. we

182 show that this conservation derives again from the symmetry of the diffusion operator. In fact,  
183 the orthogonality of the basis function of the diffusion equation in radially uniform media removes  
184 cross products between basis functions. Proper choice of eigenvector normalization also derives  
185 from the conservation of uniform concentration profiles as in Eq. 19.

#### 186 4. Discussion and conclusions

187 Eqs. 10 and 12 show that the first and second moments of the concentration distribution in  
188 the immobile zones are conserved in the passage from the porosity structure to its equivalent  
189 MRMT model. This result pertains to any organization of the immobile zones and any injection  
190 conditions. It is also valid whether the initial porosity organization is described by continuous or  
191 discrete formalisms, as long as injection and sampling are carried out exclusively in the mobile  
192 zone. This is typically the case in tracer tests where tracers are injected into and collected from  
193 the flowing/mobile zone.

194 As both the first and second moments of the concentration distribution in the immobile zones are  
195 conserved in MRMT, so is the concentration variance and, hence, the scalar dissipation rate that  
196 strongly conditions mixing-induced reactivity [Le Borgne et al., 2011]. In fact, the reaction rate can  
197 be expressed as the product of the scalar dissipation rate by a chemical term, which depends on the  
198 nature of the reaction [De Simoni et al., 2005, 2007; Rubin, 1983]. For advective-diffusive transport  
199 without solute flux across boundaries, the scalar dissipation rate is inversely proportional to half of  
200 the second moment of the concentration distribution [Le Borgne et al., 2010]. Larger concentration  
201 variances result in stronger mixing potential between higher and lower concentration values and  
202 promote homogeneous reactivity (reactivity in solution). By reducing concentration variances,  
203 diffusive processes induced by mobile-immobile mass exchanges thus promote reactivity and, by  
204 consequence, reduce further mixing and reaction potentials.

205 The scalar dissipation rate only differs from the reaction rate by a chemical term that derives from  
206 the nonlinearity of the reactivity in the reactant concentrations [De Simoni et al., 2005]. Numerical  
207 simulations have however shown that the influence of this chemical term remains limited for  
208 most immobile porosity structures and reaction types also extending to heterogeneous reactivity  
209 including sorption and precipitation/dissolution [Babey et al., 2016]. The relevance of MRMT  
210 to model reactive transport fundamentally comes from the representativity for the concentration

211 distribution of its mean and variance in diffusively-dominated conditions. Although concentration  
212 distributions are more complex than Gaussian, they do not differ much and lead to close approxi-  
213 mations. As diffusion further smoothens concentration profiles, approximations become even closer  
214 with time.

215 Use of Multi-Rate Mass Transfer models for reaction rate predictions benefits from the development  
216 of different numerical approaches proposed for extending classical advection dispersion schemes in  
217 the mobile zone to account for exchanges with immobile zones. Approaches have been proposed  
218 based either on Eulerian schemes [Silva et al., 2009] or Lagrangian schemes [Noettinger et al.,  
219 2016; Roubinet et al., 2013]. They may be used to assess the concentration distribution and the  
220 associated reactivity rate either in a postprocessing step when transport and reactivity can be  
221 fully decoupled [Donado et al., 2009; Willmann et al., 2010] or with classical sequential or global  
222 implicit coupling methods otherwise [de Dieuleveult et al., 2009; Steefel et al., 2005]. Concentration  
223 gradients necessary for computing local reactivity rates may be obtained directly with appropriate  
224 schemes [Beaudoin et al., 2017] or eventually derived from finite-differencing the concentration  
225 field.

226 While diffusive processes in poorly connected porosity structures smoothen concentration gradi-  
227 ents, dispersive processes modeled at the fundamental scale of the spatial and temporal variabilities  
228 of the velocity field will tend, on the contrary, to retain concentration differences [Le Borgne et al.,  
229 2011; de Dreuzy et al., 2012]. When diffusive and dispersive processes occur in the same domain  
230 like in strongly heterogeneous porous media [Delhomme, 1979], mixing eventually results from the  
231 interplay between the spatial and temporal fluctuations of the velocity field at the origin of dis-  
232 persion and the diffusive exchanges in the least pervious zones [de Dreuzy et al., 2012; Pool et al.,  
233 2015]. Multi-Rate Mass Transfer models inherently built for diffusive processes no longer hold to  
234 model dispersion [de Dreuzy and Carrera, 2016] and other dynamic analysis of the concentration  
235 field based for examples on lamellas deformed by the velocity fluctuations may be used to approx-  
236 imate the concentration field [Le Borgne et al., 2015]. Further research is thus needed to explore  
237 the overall effect of combined dispersion and exchanges with diffusive zones.

238 In the restrictive case where macroscopic dispersion is dominantly induced by exchanges between  
239 advective and diffusive zones, conservative tracer testing already contains most of the information

240 necessary to evaluate the physical control of reactivity. Simple breakthrough curves are sufficient  
241 to calibrate MRMT models and produce predictions of the immobile concentration distribution,  
242 and reactive transport can be approached by simply coupling MRMT models with the targeted  
243 reactive processes.

#### 244 **Acknowledgments**

245 The ANR is acknowledged for its funding through its project Soil $\mu$ 3D under the no. ANR-15-  
246 CE01-0006.

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## 247 Appendix A1: Controllability of diffusive porosity structures

248 In this example, we show how the lack of controllability and minimality precludes the conservation  
 249 of the concentration variance. We consider four zones with the porosities  $\phi_1 = 1$ ,  $\phi_2 = 1$ ,  $\phi_3 = 2$ ,  
 250  $\phi_4 = 3$  and the exchange coefficients (coefficients of the matrix  $M$  of Eq. 1)  $m_{12} = 1$ ,  $m_{13} = 2$ ,  
 251  $m_{14} = 3$ ,  $m_{23} = 3$ ,  $m_{24} = 3$ . The first zone is the mobile zone, the three other ones are immobile  
 252 zones. The sum of the concentrations squared weighted by the porosities is

$$\Sigma = C^t \Phi C = C_1^2 + C_2^2 + 2C_3^2 + 3C_4^2. \quad (27)$$

253 The PDE of Eq. 6 can be written at a given position along the mobile zone as an input-output  
 254 representation such as:

$$\frac{dC}{dt} = AC + BC_{in}, \quad C_{out} = B^T C \quad (28)$$

255 where  $C_{in}$ ,  $C_{out}$  are respectively the input and output concentrations. Only advection is considered  
 256 in the mobile zone. In the specific case considered  $A$  and  $B$  are given by:

$$A = \begin{bmatrix} -7 & 1 & 2 & 3 \\ 1 & -7 & 3 & 3 \\ 1 & \frac{3}{2} & -\frac{5}{2} & 0 \\ 1 & 1 & 0 & -2 \end{bmatrix}, \quad B = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (29)$$

257 At first look, this structure does not exhibit any special property or symmetry that could make  
 258 believe that the input-output system is non minimal. The pair  $(A, B)$  is however non controllable,  
 259 even though one can check that the sub-matrix  $A(2 : 4, 2 : 4)$  has distinct eigenvalues. It can be  
 260 shown that:

$$AB = \begin{bmatrix} -7 \\ 1 \\ 1 \\ 1 \end{bmatrix}, \quad A^2 B = \begin{bmatrix} 55 \\ -8 \\ -8 \\ -8 \end{bmatrix} = -B - 8AB \quad (30)$$

261 and that the rank of the matrix  $\mathcal{C}$  defined in Eq. (11) is 2, where it should be full ranked. Therefore,  
 262 the system admits a minimal representation of dimension only 2. The equivalent immobile zone

263 can be found by merging the immobile zones in one with a porosity

$$\bar{\phi} = \phi_2 + \phi_3 + \phi_4 = 6 \quad (31)$$

264 and an equivalent concentration

$$\bar{C} = \frac{\phi_2 C_2 + \phi_3 C_3 + \phi_4 C_4}{\bar{\phi}} = \frac{C_2 + 2C_3 + 3C_4}{6}. \quad (32)$$

265 One can check that  $(C_1, \bar{C})$  is solution of the differential system:

$$\frac{d}{dt} \begin{bmatrix} C_1 \\ \bar{C} \end{bmatrix} = \begin{bmatrix} -7 & 6 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} C_1 \\ \bar{C} \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \end{bmatrix} C_{in}, \quad C_{out} = C_1 \quad (33)$$

266 that provides an equivalent input-output system. The sum of the concentrations squared weighted  
267 by the porosities in the equivalent representation is:

$$\bar{\Sigma} = C_1^2 + \bar{\phi} \bar{C}^2 = C_1^2 + \frac{(C_2 + 2C_3 + 3C_4)^2}{6} \quad (34)$$

268 which differs from  $\Sigma$ , because here the original representation is not minimal.

269 Indeed, the matrix  $R$  given in Eq. 18 is in this example:

$$R = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad (35)$$

270 which fails to be a transformation matrix to MRMT. One has

$$R_S = \begin{bmatrix} 0.8626094 & -0.4492446 & -0.4133648 \\ -0.2886751 & -0.5773503 & -0.8660254 \\ -0.0600512 & -0.6918374 & 0.7518886 \end{bmatrix} \quad (36)$$

271 that diagonalizes the sub-matrix  $A_S$ :

$$R_S \begin{bmatrix} -7 & 3 & 3 \\ \frac{3}{2} & -\frac{5}{2} & 0 \\ 1 & 0 & -2 \end{bmatrix} R_S^{-1} = \begin{bmatrix} -8.2603986 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -2.2396014 \end{bmatrix} \quad (37)$$

272 but the vector

$$R_S^{-1}A(2 : 4, 1) = \begin{bmatrix} 0 \\ -1.7320508 \\ 0 \end{bmatrix} \quad (38)$$

273 has null entries. In [Rapaport et al., 2017], it is proved that for matrices of the form of Eq. (7)  
 274 the vector  $R_S^{-1}A(2 : n + 1, 1)$  has non-null entries exactly when the pair  $(A, B)$  is controllable.

275 One may argue that having the pair  $(A, B)$  non controllable is a very particular and rare case (as  
 276 the property of having a singular controllability matrix of Eq. (11) is non generic in the set of  
 277 matrices  $A$  of the form of Eq. (7)), but the distance to uncontrollability (see [Eising, 1984])

$$\tau(A, B) = \min_{\lambda \in \mathbb{C}} \sigma_n([A - \lambda I, B]) \quad (39)$$

278 (where  $\sigma_n([A - \lambda I, B])$  denotes the smallest singular value of the augmented matrix  $[A - \lambda I, B]$ )  
 279 gives a "measure" of how far the original model can be from a non-minimal representation (having  
 280 thus some entries of the vector  $R_S^{-1}A(2 : n + 1, 1)$  possibly close to 0). Moreover, it is shown  
 281 in [Rapaport et al., 2017] how to exploit the transformation to a MRMT structure for minimal  
 282 representations that are close to non-minimal ones to obtain reduced MRMT models of smaller  
 283 dimension.

284 **Appendix A2: Conservation of concentrations squared between equivalent SINC mod-**  
 285 **els**

286 We show that the conservation of concentrations squared can be generalized to all SINC models  
 287 that are equivalent in the sense of Haggerty and Gorelick [1995] (i.e. identity of the mobile  
 288 concentrations). Consider two equivalent SINC models given by their interaction matrices  $A$  and  
 289  $Z$ . Each of these two SINC admits an equivalent MRMT model given by Eq. 14. Being equivalent  
 290 (and the pairs  $(A, B)$  and  $(Z, B)$  being controllable), the two MRMT configurations are identical,  
 291 up to the numbering of the immobile zones. So there exist two transformation matrices  $R_A$  and  
 292  $R_Z$  from SINC to MRMT such that (Eq. 15):

$$R_A A R_A^{-1} = \bar{A} = R_Z Z R_Z^{-1}. \quad (40)$$

293 Eq. 26 implies the conservation of the porosity weighted integral of concentrations squared:

$$C_A^T \Phi_A C_A = \bar{C}^T \bar{\Phi} \bar{C} = C_Z^T \Phi_Z C_Z \quad (41)$$

294 where  $C_A$  and  $\Phi_A$  are respectively the concentration vector and the diagonal porosity matrix  
 295 associated with  $A$ , and  $C_Z$  and  $\Phi_Z$  are their counterparts for  $Z$ . The relationships between these  
 296 quantities can be further expressed through the transformation matrix  $R_{AZ}$  that transforms the  
 297 SINC model given by  $A$  into the SINC model given by  $Z$ :

$$\begin{cases} C_Z = R_{AZ} C_A \\ \Phi_Z = (R_{AZ}^{-1})^T \Phi_A R_{AZ}^{-1} \end{cases} \quad \text{with } R_{AZ} = R_Z^{-1} R_A. \quad (42)$$

298 **Appendix A3: Conservation of the weighted sum of concentrations squared in planar,**  
 299 **cylindrical and spherical inclusions**

300 The general equation for mobile-immobile models with diffusion into planar, cylindrical or spherical  
 301 continuous immobile inclusions writes [Haggerty and Gorelick, 1995]:

$$\frac{\partial c_m}{\partial t} + \beta \frac{\partial \langle c_{im} \rangle}{\partial t} = L(c_m) \quad (43)$$

302 where  $c_m$  is the mobile concentration,  $\langle c_{im} \rangle$  is the mean concentration in the immobile domain  
 303 and  $\beta$  is equal to the ratio of the immobile to mobile total porosities. The solution of the PDE in  
 304 the immobile domain is given by:

$$c_{im}(r, t) = \sum_{i=1}^{\infty} a_i \frac{f(\sqrt{\alpha_i} r)}{\|f(\sqrt{\alpha_i} r)\|^2} e^{-\alpha_i t} \quad (44)$$

305 with

$$a_i = \int_0^1 r^{n-1} c_{im}(r, 0) f(\sqrt{\alpha_i} r) dr \quad (45)$$

306 and

$$\|f(\sqrt{\alpha_i} r)\|^2 = \int_0^1 r^{n-1} f^2(\sqrt{\alpha_i} r) dr. \quad (46)$$

307 For the layered ( $n = 1$ ), cylindrical ( $n = 2$ ) and spherical ( $n = 3$ ) cases, the explicit functions  
 308 and square norm values for Eq. 44 are given in Table 1, and the values of MRMT rates  $\alpha_i$  and  
 309 porosities  $\bar{\phi}_i$  are given in Table 1 of [Haggerty and Gorelick, 1995].

$n$	1	2	3
$f(\cdot)$	$\cos(\cdot)$	$I_0(\cdot)$	$\sin(\cdot)$
$\ f(\sqrt{\alpha_i} r)\ ^2$	$\frac{1}{2}$	$\frac{1}{2} I_1^2(\sqrt{\alpha_i} r)$	$\frac{1}{2}$

Table 1: Functions and square norm values of Eq. 44 for  $n = 1, 2, 3$ .  $I_0$  and  $I_1$  are the zero-order and first-order modified Bessel functions of the first kind.

310 By construction,  $f$  forms an orthogonal set of functions whatever the dimension of the inclusion.  
 311 The orthogonality of the function  $f$  more generally derives from the theorem of Sturm-Liouville.  
 312 The Sturm-Liouville theorem states the existence and the orthogonality of the basis function

313 for second-order linear differential equations, but does not give their analytical expression. The  
 314 MRMT model can generally be expressed as:

$$\bar{c}_{im,i}(t) = \sum_{i=1}^{\infty} \bar{c}_{im,i}(t=0)e^{-\alpha_i t}. \quad (47)$$

315 The relations between the continuous solutions of Eqs. 43-44 and the MRMT model of Eq. 47  
 316 provide constrains on the  $\bar{\phi}_i$  and  $\bar{c}_{im}(t=0)$ :

$$\bar{\phi}_i \bar{c}_{im}(t=0) = \frac{a_i}{\|f(\sqrt{\alpha_i}r)\|^2} \int_0^1 nr^{n-1} f(\sqrt{\alpha_i}r) dr. \quad (48)$$

317 Complementary relations derive from the identity of concentrations in the mobile zone:

$$\int_0^1 c_{im}(r,t) nr^{n-1} dr = \sum_{i=1}^{\infty} \frac{a_i}{\|f(\sqrt{\alpha_i}r)\|^2} \int_0^1 nr^{n-1} f(\sqrt{\alpha_i}r) e^{-\alpha_i t} dr. \quad (49)$$

318 These equations should be valid whatever the initial conditions and especially for  $c_{im}(r,t=0) = 1$   
 319 which corresponds to  $\bar{c}_{im,i}(t=0) = 1$  for all immobile zones  $i$ , like in Eq. 19 and in the Appendix B  
 320 of [Haggerty and Gorelick, 1995]. In such a case the MRMT porosities  $\bar{\phi}_i$  can be straightforwardly  
 321 identified as:

$$\begin{aligned} \bar{\phi}_i &= \frac{1}{n \|f(\sqrt{\alpha_i}r)\|^2} \left( \int_0^1 nr^{n-1} f(\sqrt{\alpha_i}r) dr \right)^2 \\ &= \frac{1}{n} \frac{\left( \int_0^1 nr^{n-1} f(\sqrt{\alpha_i}r) dr \right)^2}{\int_0^1 r^{n-1} f^2(\sqrt{\alpha_i}r) dr} \end{aligned} \quad (50)$$

322 The initial MRMT concentrations are given by:

$$\bar{c}_{im,i}(t=0) = \frac{\int_0^1 nr^{n-1} f(\sqrt{\alpha_i}r) c_{im}(r,t=0) dr}{\int_0^1 nr^{n-1} f(\sqrt{\alpha_i}r) dr}. \quad (51)$$

323  $\bar{c}_{im,i}(t=0)$  is simply some normalized scalar product of the initial condition  $c_{im,i}(t=0)$  by  
 324 the basis function corresponding to  $\alpha_i$ . The sum of the concentrations squared weighted by the

325 porosities  $\Sigma$  for the continuous formulation of the solution writes:

$$\begin{aligned}
 \Sigma &= n \int_0^1 r^{n-1} c_{im}^2(r, t) dr \\
 &= n \sum_{i=1}^{\infty} \frac{a_i^2}{\|f(\sqrt{\alpha_i}r)\|^4} e^{-2\alpha_i t} \int_0^1 r^{n-1} f^2(\sqrt{\alpha_i}r) dr \\
 &= n \sum_{i=1}^{\infty} \frac{a_i^2}{\|f(\sqrt{\alpha_i}r)\|^2} e^{-2\alpha_i t}.
 \end{aligned} \tag{52}$$

326 The sum of the concentrations squared weighted by the porosities  $\bar{\Sigma}$  in the equivalent MRMT  
 327 writes:

$$\begin{aligned}
 \bar{\Sigma} &= \sum_{i=1}^{\infty} \bar{\phi}_i \bar{c}_{im,i}^2(t=0) e^{-2\alpha_i t} \\
 &= \sum_{i=1}^{\infty} \frac{\left( \int_0^1 n r^{n-1} f(\sqrt{\alpha_i}r) dr \right)^2}{n \int_0^1 r^{n-1} f^2(\sqrt{\alpha_i}r) dr} \frac{n^2 a_i^2}{\left( \int_0^1 n r^{n-1} f(\sqrt{\alpha_i}r) dr \right)^2} e^{-2\alpha_i t} \\
 &= n \sum_{i=1}^{\infty} \frac{a_i^2}{\|f(\sqrt{\alpha_i}r)\|^2} e^{-2\alpha_i t} \\
 &= \Sigma.
 \end{aligned} \tag{53}$$

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