Debates - Stochastic Subsurface Hydrology from Theory to Practice: Why stochastic modeling has not yet permeated into practitioners?

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Highlights

- Process modeling and upscaling are keys to understanding flow and transport in porous media
- Proper knowledge of the geological architecture is a must for hydrogeological modeling, either deterministic or stochastic
- Reactive transport is still a challenge for stochastic modeling, but completely unrealistic for deterministic ones in field applications
- Stochastic modelers are one of the reasons non-deterministic models have not yet permeated in industry: We keep fighting about equations!

Key Words: Stochastic modeling, upscaling, non-Fickian transport, reactive transport, field applications

1. Introduction

Stochastic hydrogeology has been a topic in WRR and other journals for over 40 years. Arguably, the topic reached its maturity more than a decade ago. In parallel, numerical modeling has become routine in hydrogeological studies. In spite of this, non-deterministic models have not reached practitioners. In this debate paper we want to stress the limitations of stochastic modeling when applied to real applications, comment on the reasons why stochastic models fail to become an attractive alternative for practitioners, and suggest tips that may improve our ability to produce transferable non-deterministic models.

Spatial variability and uncertainty

Heterogeneity is a fundamental property that must be accounted for when studying natural processes. One approach is to consider groundwater parameters as regionalized variables, or spatial random functions (SRFs) based on the principles stated by Matheron (1965). An SRF, $Z(\boldsymbol{x}, \omega)$, is a function of space whose outcome is non-deterministic. For any number of points $(\boldsymbol{x_1}, \ldots, \boldsymbol{x_n})$, $Z(\boldsymbol{x_1}, \omega) \ldots Z(\boldsymbol{x_n}, \omega)$ are non-independent random variables and all the body of statistics based on Kolmogorov's axioms apply. On the other hand, fixing $\omega = \omega_0$, we get one realization of the random field, a single space function, and all the body of calculus applies. The collection of all the space functions for the different ω values is called the ensemble.

A fundamental question arises: Why use random functions to represent a deterministic reality? The answer is uncertainty, arising from incomplete information regarding the true hydrological and biogeochemical processes occurring over a wide range of temporal and spatial scales. In this context, the best we hope for is to have a few (potentially noisy) measurements, characteristic of some (unknown) support volume, and maybe some indications about general trends. As reality is uncertain, we model any given parameter by a SRF, and reality becomes just one of the infinite possible realizations. The first problem is how to get the statistics of the ensemble (statistical space) from one single realization (physical

space). This is possible only if some type of stationarity prevails and the ergodic hypothesis is invoked. Ergodicity implies that all states of the ensemble are available in each realization, a premise that can never be validated rigorously, as just a single realization is available.

The stochastic equations

By using a stochastic approach, the variables that appear in the classical equations used in hydrogeology become random, and the groundwater flow and solute transport equations become stochastic partial differential equations (s-PDE). Boundary and initial conditions may or may not be treated as SRFs. Several stochastic methods are available, such as:

- Perturbation methods: consist of expanding the dependent variable in an asymptotic sequence and to derive individual PDE's for each term in the expansion. By solving them, low order approximations of the solution are obtained. Closure analysis becomes critical. An alternative is to directly write the PDEs satisfied by moments (i.e., moment equations).
- Monte Carlo methods: involve generating equally-likely realizations of all parameters. Each run becomes a deterministic model and stochasticity stems from the ensemble. The output allows reconstructing the multivariate distribution of the dependent variable. These intensively CPU demanding methods are routinely used in complex problems.
- PDF-based methods: to directly find the full conditional pdf or cdf of the dependent variable. So far this method has only been applied to very simple configurations.

Importantly, structural uncertainty is not considered in these approaches which typically assume that the structure of the governing PDE for the state variable is fully known.

2. Deterministic vs. stochastic approaches and scaling

It is nothing but a modeler's choice

When modeling a site, choosing a deterministic or a stochastic approach is just a modeler's choice. Deterministic approaches are based on viewing parameters as constant in pre-specified zones, implying that the main features controlling flow and transport can be explicitly identified. Nonetheless, this does not imply neglecting the importance of heterogeneity, as deterministic parameter calibration incorporates uncertainty quantification. The main problem arises at the conceptualization stage, since data rarely suffice for unequivocal definition of zonation, since zone boundaries are fuzzy even if at all existing.

Instead, stochastic approaches are motivated by recognizing both the importance of spatial variability and the impossibility of fully and precisely describing the statistical characterization of hydraulic parameters in full. Thus, the need for simplifying assumptions, such as log-conductivity being fully characterized by two-point statistics (e.g., being multinormal, bimodal or defined as a suite of indicator functions), or else using reconstruction methods based on a combination of data and a priori defined spatial shapes (e.g., multiple point geostatistics).

The problem of scales

We consider spatial variability at four different scales: pore, local, formation, and regional. Early and most successful results in stochastic hydrogeology correspond to the regional scale, such as the derivation of effective hydraulic conductivity [*Matheron*, 1967; *Gutjahr et al.*, 1978] or that of macrodispersion [*Gelhar and Axness*, 1983] as a function of some statistical parameters of hydraulic conductivity, K. While effective K values are still used routinely in numerical models, the concept of macrodispersion was rapidly challenged, once it was clear that solute transport was always non-ergodic [*Kitanidis*, 1988]. This is actually a key point. If macrodispersion is invoked, deterministic transport models would suffice (no need for stochastic models). This could be of interest in large-basin water resources management problems, or in long-range pollution, where local scale variations should be smoothed out on purpose to avoid the possibility of somebody asking: What happens in my back yard?

95 At the formation scale, flow and transport are of a three-dimensional nature. Most problems
96 of interest in hydrogeology occur at this scale, and it is where stochastic models might find
97 their niche. Examples would be flow in the vicinity of a well, or solute transport near the
98 source, that can only be properly resolved if heterogeneity is fully accounted for and, more, if
99 models are properly conditioned to geological data. Loosely quoting Prof. Andre Journel from
100 Stanford University in a talk given in 1992: "…if I ever find myself crossing paths with
101 somebody using unconditional realizations, I will cross the street".

102 The local scale is the one used to define the governing equations used in most hydrogeological
103 models. The real applications are mostly limited to laboratory experiments. Thus, this scale is
104 more appropriate for research efforts rather than actual field problems. Finally, the pore scale
105 has traditionally been ignored in hydrogeology. Lately there have been significant advances in
106 the field of micro-CT imaging, allowing the study of flow and transport in pore networks with
107 resolutions down to microns.

108 The question is then how and up (or better down) to what size we need to take our models
109 and whether there is a clear gain in using stochastic descriptions of reality. The answers are
110 still unclear. The unresolved issues are process dependent and therefore in the sequel we
111 clearly separate those of flow, conservative transport, and reactive transport.

112

113 **3. Groundwater flow: Process description, unresolved issues, and model choices**

114 Several unresolved issues can be considered here:

115 (1) Hydrogeology includes the word "geology". Practitioners are perfectly aware, and
116 hydrogeology reports routinely start with a thorough geological description. Yet, some
117 stochastic hydrogeologists disregard this point as in "I will not allow data to contradict my
118 beautiful mathematical theory". Considerable efforts have been devoted to generate process-
119 based or pattern-based geological descriptions. Conditioning on hard geological data is a must,

120 but certainly not enough. Direct reconstruction methods oversmooth the shape of facies
121 interphases, with significant implications in transport. Soft data, either geophysical data or
122 prior descriptions of geological patterns, should be incorporated with care, as there is the
123 danger of conditioning "too much". We contend that the need for conditioning the model on
124 the best available geological description is known by practitioners and thus widely used in
125 deterministic modeling; yet, we routinely build our stochastic models based on simplistic
126 geometrical depictions and hope that the SRF framework will be smart enough to take over. As
127 a consequence, practitioners have the impression that deterministic models, if uncertainty is
128 properly evaluated, can outperform stochastic models in terms of robustness [see the
129 unambiguous discussion by *Pool et al.*, 2015].
130 (2) Flow at the local scale is satisfactorily modeled using Darcy's law. At the formation
131 scale Darcy's law is just hypothesized, without proof.
132 (3) Hydraulic conductivity is a macroscopic quantity derived rigorously from the
133 dissipation of viscous forces. Yet, in practice K is mostly derived from hydraulic tests (thus
134 representative of some undefined support volume) or indirectly obtained from empirical
135 formulae (too local to become representative), without considering the pore network
136 geometry [except for recent advances in pore scale simulations, *Pereira Nunes et al.*, 2016] .
137 (4) Storage coefficient (S) is a rigorous quantity, derived theoretically in terms of specific
138 weight of water, aquifer thickness, porosity, and compressibility of water and the mineral
139 skeleton. Nevertheless, it is seldom computed this way. When S is derived from the
140 interpretation of pumping tests, the results have very little to do with the actual value.
141 Variations in S are never properly characterized (we will emphasize this point later) and at
142 most they are hypothesized or estimated from weak correlations with other parameters.
143 (5) In unsaturated flow, water retention curves or relative permeability functions are
144 mostly empirical and therefore they are site specific and dependent on window resolution.

(6) Not all are bad news. Upscaling of hydraulic conductivity is a well resolved problem, with a number of analytical and numerical methods available. While local K values are highly uncertain and may span a wide range of orders of magnitude even in seemingly homogeneous aquifers, upscaled K values are less variable and less uncertain due to the averaging process.

The issue then is whether we feel comfortable advocating for stochastic modeling in flow problems. Practitioners might think that such models should only be used if large data sets of piezometric head and hydraulic parameters are available. Actually it is quite the opposite; they are best suited for when information is minimal and we must rely on our technical knowledge, which we can introduce in the model as priors (which become model hypotheses).

Following this idea, we stress the paradox of model reconstruction. Let us assume a simple 2D model where transmissivity $T(\boldsymbol{x})$ is spatially variable (with a given mean and variance, σ^2_{lnT}) and storage coefficient S is constant in space. We then perform a series of hydraulic tests and interpret them using hydraulic tomography. It is immediately observed that the $T_{est}(\boldsymbol{x})$ values (*est* indicating estimated values) are spatially variable with the same mean but a much smaller variance than that of $T(\boldsymbol{x})$ ($\sigma^2_{lnT_{est}} \ll \sigma^2_{lnT}$). On the other hand S_{est} becomes spatially variable and provides information about connectivity, a term that lacks a formal definition but that intuitively informs about the continuity and directionality in the natural arrangement of geological facies or bodies. Detecting the location of conducting features, implies the need to condition the model on all available geological information (hard or soft), without having to impose a very high variance variogram in unconditional realizations, or else deterministically delineate the highly conductive interconnected features. Moreover, the small value of $\sigma^2_{lnT_{est}}$ may lead to the wrong conclusion that the medium is quite homogeneous and there is no need to account for heterogeneity.

169 Another point of discrepancy is the usefulness of models. In the words of *Gupta and Nearing*
170 [2014] we are "…more interested in the specific value of models to developing understanding
171 about the dynamics/behavior of a system, and less so in their use for prediction at a specific
172 time and place". While the authors of this paper fully support this statement, we believe most
173 practitioners, local authorities and policy makers would definitely be against it. They want
174 answers, given in quantitative terms and with full certainty. Is this a reason why practitioners
175 rely on deterministic models? Most probably they think that whatever comes out from models
176 is the closest to the truth they can get. Yet, they probably do not realize that whenever they
177 ask for risk assessments they are actually adopting a stochastic vision of the problem. We
178 should blame ourselves for not being able to convey such a message.

179 Finally, when analyzing subsurface flow at different scales we find that the same formal
180 equation is applicable provided we accurately upscale heads, parameters, and boundary
181 conditions. This has resulted in a large number of numerical codes capable of solving the flow
182 equation using a bunch of well-stablished numerical methods. Actually, the same codes can be
183 used for deterministic or stochastic models for the direct problem, and some commercial
184 codes can actually handle the inverse problem also in both cases. CPU time may or may not be
185 an issue, but technically there are no major differences.

186

187 **4. Conservative transport: Upscaled equations and model choices**

188 In conservative transport the situation is radically different than for flow. As discussed later,
189 there is a strong division in the community regarding the governing equations that should be
190 used, and on the most appropriate numerical methods to solve them.

191 As the variable of interest in transport is solute concentration, it seems adequate to use an
192 Eulerian approach, with traditional numerical methods (e.g., finite differences or finite
193 elements). This does not work. An alternative is the use of Lagrangian methods that track the

movement of mass. The circle is closed if particles are used to estimate concentrations, leading to Eulerian-Lagrangian methods. All of this is well-known, but it relies on assuming we know with certainty the proper governing equation. And here it seems we cannot bring the community to agreement, causing an infinite sense of confusion that would definitely prevent practitioners from using any of the developed theories. That is, no matter what they do, half of the scientists will claim they are not using the proper equation or numerical method, so why not use the simplest equation even if everybody agrees it does not work?

A starting point would be to agree on the equation valid at the pore scale, and then perform upscaling. And this is already controversial. With a pore network description at the micrometer scale, one might reconstruct particle trajectories by solving the Stokes equation, to compute the velocity field, and allow for advection and diffusion. But a particle is not a molecule, so we cannot blindly apply the solutions of molecular diffusion to particles without formal upscaling.

Coupling advection and diffusion in a medium composed of voids and solids gives rise to hydrodynamic dispersion. If this follows Fick's law, the governing equation of transport is the advection-dispersion (ADE). But dispersion is governed by variations in groundwater velocity at all scales (in time and space). Upscaling flow leads to a reduction in the variance of upscaled velocities, and therefore the need for block-dispersion parameters [*Rubin et al.*, 1999] to properly reproduce solute dispersion (the limit is macrodispersion in a constant velocity model), still assuming that the ADE is valid at some local scale. However, this last statement is controversial. Many authors argue that the ADE does not hold at any scale. Others invoke that the ADE properly fits experimental data [*Ginn et al.*, 2013].

An example of the discussion of the proper transport equation to use was provided in the 2015 AGU Chapman conference, which devoted one session to discuss whether a local ADE with sufficient data is enough to model the MADE site and another one to present the performance of alternative equations. An example of the former is that of *Salamon et al.* [2007], who

219 considered that the ADE is valid at the meter scale; even in such a small field with a high
220 density of data, the problem could not be considered deterministic, as simulations in equally
221 probable conductivity maps provided substantially different results (Figure 1). It is clear that
222 while all realizations could capture the presence of tailing in the spatial distribution, none of
223 them could provide a good description of the observed front edge of the plume, which exhibits
224 an uncharacteristic flat profile.

225

226 Figure 1

227

228 We must keep in mind that at the MADE site most authors have only tried to reproduce the
229 integrated mass along the flow direction, rather than the full 3D spatial distribution of point
230 concentrations. The bad quality of the fits obtained from simulations based on the ADE and
231 upscaled parameters have been associated to either the sampling strategy or to the presence
232 of rate-limited transfer processes. The latter is supported by two direct evidences: (1) Vacuum
233 extractions at 0.5 bar and 5 bars showed that bromide was not distributed uniformly in the
234 local pore space, the latter extracts containing about 3 times the concentration of the former;
235 (2) observation of aquifer outcrops reveal the presence of high permeable interconnected
236 structures at the sub-meter scale sandwiched between low-permeability units.

237 Interestingly, it turns out that by simply adding a single-rate mass transfer term into the local
238 ADE, the simulated front edge of the plume significantly improves (Figure 2). There is a
239 rationale for this; even if the ADE were valid at some undefined small scale, there is no reason
240 why Fick's law would hold at some intermediate scale. Actually, it has been shown that
241 transport is always non-Fickian, so that the expression "anomalous transport" is misleading. In
242 the last two decades, efforts have been devoted to writing alternative and phenomenological
243 transport equations. There are three main alternatives, whether the form of the equation is

244 borrowed from the field of physics (resulting in a Continuous Time Random Walk –CTRW-
245 model), mathematics (leading to a fractional ADE –fADE- model) or that of chemistry (single-
246 rate or multi-rate mass transfer –SRMT/MRMT- models).

247

248 Figure 2

249

250 Despite being heavily contested, all non-Fickian models share a good characteristic: they do
251 work! Such models work well in reproducing integrated observables, such as breakthrough
252 curves displaying realistic tailing, negative asymmetrical spatial concentration profiles, or
253 concentration build-up in pump-and-treat remediation efforts after pumping ceases [*de Barros*
254 *et al.,* 2013]. Yet, so far, all parameters models are difficult, if at all possible, to correlate with
255 physical parameters describing heterogeneity, although it is clear that they should heavily
256 depend on medium architecture [*Zhang et al.*, 2013; *Bianchi and Zheng*, 2016].

257 Going back to the MADE site, let us assume that transport is controlled by diffusion from low
258 permeable areas. *Fernàndez-Garcia and Sanchez-Vila* [2015] showed that when the memory
259 function follows a power law distribution, the effective coefficient of a time-dependent single-
260 rate mass transfer model (t-SRMT) scales with the inverse of time. This nicely fits (without
261 calibration) the compilation of SRMT coefficients from *Haggerty et al.* [2004], presented in
262 Figure 3 together with the estimated time-representative mass transfer coefficients reported
263 by *Guan et al.* (2008) for the MADE site, showing that they do not follow the trend. This may
264 have two different interpretations: (1) that the estimated parameters were affected by subgrid
265 heterogeneity not included in the upscaled model, or (2) that the behavior of the ensemble
266 does not preclude that of any given specific site. In fact, Figure 4 shows that the coefficients
267 reported by *Guan et al.* [2008] follow the t-SRMT associated with a double rate mass transfer
268 model, questioning the common use of power law memory functions.

Figure 3

Figure 4

In summary, the model to be used is a modeler's personal choice. All non-Fickian models are equally adequate to reproduce observations, and are equivalent under restrictive conditions. Yet, there are limitations. Most applications use a reduction in the number of dimensions, as they aim at fitting global observables. Therefore, it is not possible to match local concentration maps with non-Fickian models, and we should be very careful when calibrating parameters from point measurements. Altogether there seem to be strong reasons why practitioners feel uneasy about using non-Fickian models and keep relying on the ADE, even though it is known to provide inadequate answers.

5. Reactive transport: Process description, observables, and model choices

For most reactions, the equations and the corresponding rates are well-known and can be found in the literature, even in textbooks, based on data from batch experiments. When advection gets into the picture, mapping reactions is challenging, as the transport of reactants and products are controlled by aquifer heterogeneity. The question is whether incorporating additional source terms to account for reactions will result in proper equations for transport of reactive species. In general, the answer is no. Reactions take place at the molecular scale, driven by local chemical imbalances that might be a consequence of transport processes.

Upscaling becomes a real challenge for reactive transport. The question is, can we use the rates derived from batch experiments in a real field model? Obviously not. Let us consider the simple reactive problem of annihilation, where at any given point in space two substances X

and Y cannot coexist, as whenever they get in contact an instantaneous irreversible reaction takes place ($X + Y \rightarrow \emptyset$). The amount of reaction q taking place at any point and time is

$$q\left(\boldsymbol{x}, t^{k+1}\right) = \min\left(X\left(\boldsymbol{x}, t^{k}\right), Y\left(\boldsymbol{x}, t^{k}\right)\right). \quad (1)$$

Notice that we are adopting here a simple explicit scheme just for the purpose of illustration (most probably it would be the worst numerical scheme to use in any real application). The transport equation for X (we could also write the one for Y) is

$$\frac{dX}{dt} = L(X) - r, \quad (2)$$

where $L(\cdot)$ stands for any transport operator. If we were solving the reactive problem in some coarse mesh, the total reaction Q at time t in one element V of the mesh would be

$$Q\left(t^{k+1}\right) = \int_V \min\left(X\left(\boldsymbol{x}, t^{k}\right), Y\left(\boldsymbol{x}, t^{k}\right)\right) dV. \quad (3)$$

In (3), X, Y are the point concentrations that can never be estimated with certainty, and so the need to map some smoothed version of the concentrations $\bar{X}$, $\bar{Y}$ using any of the transport equations already discussed. Now, it turns out that in volume V, $\bar{X}$, $\bar{Y}$ can coexist, and that

$$Q\left(t^{k+1}\right) \neq \int_V \min\left(\bar{X}\left(\boldsymbol{x}, t^{k}\right), \bar{Y}\left(\boldsymbol{x}, t^{k}\right)\right) dV. \quad (4)$$

If transport was conservative, we could write an upscaled equation for $\bar{X}$ as already presented, but since reaction will take place, the governing equation would look like

$$\frac{d\bar{X}}{dt} = L^*(\bar{X}) - q^*, \quad (5)$$

where L^* could represent any operator including a non-Fickian dispersive term, selected by the modeler. But then, what is q^*? It turns out that the actual expression for q^* depends on grid size and on the transport model used. The most significant point to make here is that now $\bar{X}$, $\bar{Y}$ are observable quantities, that is, amenable of being measured.

As a consequence, the approach relying on setting up a domain discretization and adopting a strategy based on defining flow, assuming a model for the conservative transport equation and producing forward simulations of reactive transport at that scale is bound to fail. The reason is that variability in concentrations at the local (sub-grid) scale is the reaction driver, while models provide some averaged concentrations at the grid scale. At this point we still do not know how to properly upscale the parameters controlling reactions. Efforts based on volume averaging theory provide a correct setup [*Porta et al.*, 2013; *Wood and Valdes-Parada*, 2013], but this has not been adapted to real field problems and require averaging over large volumes as compared to the characteristic length scale of heterogeneity.

Direct upscaling is typically challenged in real field applications by the presence of hydraulically connected features [*Trinchero et al.*, 2008: *Pedretti et al.,* 2014], often exceeding the size of the model representative volume. The spatial distribution of highly permeable persistent geological bodies that concentrate solutes in connected channels controls not only the arrival of toxic concentrations and its subsequent risk to human life or ecosystems [*Henri et al.*, 2015; *Fiori et al.*, 2015] but also the occurrence of biochemical reactions [*Rubol et al.*, 2014; *Sanchez-Vila et al.*, 2013], as they provide most of the nutrients that are vital to ecological systems. The representation of connected features in stochastic theories is still a major challenge.

6. Discussion: Do stochastic models represent somehow reality? Can we do better?

We start by stating that deterministic models do not represent reality at all. The reason is the combination of unsampled natural heterogeneity and scenario uncertainty. This is a point to convey to practitioners [see the lucid discussion of *Renard*, 2007]. So, despite all problems and limitations, only stochastic models have a chance of providing the answers needed for proper groundwater management efforts. We must make a clear effort to explain why all answers

must be provided in probabilistic terms, incorporating the concept of acceptable risk defined as the probability of any system to unsatisfactorily meet the demands in space or time.

In this section we address the issue of numerical methods applied to solve the different equations proposed in this text in order to provide the best tools to be used in stochastic reactive transport models, further discussing pros and cons. Codes that can handle multiple species and chemical reactions are typically based on Eulerian numerical methods. A major challenge is the description of natural hydro-bio-chemical heterogeneities at the proper scale [e.g., *Rubol et al.*, 2014; *Cirpka and Valocchi*, 2007].

To illustrate the problem, let us consider a precipitation problem involving the mixing of two different waters carrying in solution two aqueous species, A and B, in instantaneous local equilibrium with a solid mineral M, and driven by the chemical reversible reaction $A + B \leftrightarrow M$. *De Simoni et al.* [2005] demonstrated that the reaction rate given by the local ADE-based model can be decomposed into the product of two terms;

$$r(x,t) = f_{ch}(u)\, f_{mix}(u), \tag{6}$$

where $f_{ch}(u) = 2K_p\left(u^2 + 4K_p\right)^{-3/2}$ is driven by chemistry and $f_{mix}(u) = \nabla^t u\, D\, \nabla u$ expresses how the two waters mix. Here, u is the conservative component defined by subtraction of the concentrations of reactants, $u = [A] - [B]$, K_p is the constant of equilibrium, and D the dispersion coefficient. Considering that the aquifer is homogeneous, initially in chemical equilibrium, and that a water with a characteristic chemical signature Δu_0 is continuously injected through an infinite source line perpendicular to the flow direction, the solution of the transport problem is

$$u(x,t) = u_0 + \Delta u_0\, erfc\left(\frac{x - vt}{\sqrt{4Dt}}\right). \tag{7}$$

Assuming that $u_0 + \Delta u_0 \ll K_p$, and integrating (7) in space and time we obtain that the total amount of mineral precipitated is proportional to the square root of D and given by

$$R(t) = \int_0^t \int_{-\infty}^{+\infty} r(x,t')dxdt' = \Delta u_0^2 \, f_{ch}(u_0)(8\pi)^{-1/2} \, D^{1/2} \, t^{-1/2}. \quad (8)$$

This implies that small errors in the estimation of the dispersion coefficient may drastically affect the estimation of the total amount of reaction, depending on the problem at hand. A large body of literature includes variations in the expression of f_{mix} to analyze scalar dissipation rates in conservative [*Le Borgne et al.*, 2010] and non-conservative tracers [*Engdahl et al.*, 2013], a concept directly related to measurements of entropy.

The most important disadvantage of Eulerian methods is that the inherent truncation errors involved in the space and time discretization typically induce artificial oscillations and numerical dispersion. The latter results in an overestimation of the total amount of reaction, and it is known to depend on two characteristic numbers, Grid-Courant ($Cu = \frac{v\,\Delta t}{\Delta x}$), and Grid-Peclet ($Pe = \frac{v\,\Delta x}{D}$), where Δx and Δt denote the spatial and temporal discretization, and v is the flow velocity. The dependence of the numerical dispersion on these dimensionless numbers relies on the chosen discretization scheme. In general, one can state that the relative error caused by numerical dispersion is

$$\epsilon_c = \frac{D_{num}}{D} - 1 = f(Cu, Pe) - 1, \quad (9)$$

where D_{num} is the dispersion coefficient exhibited by the computer simulation and D is the true value. For a wide range of schemes this can be explicitly written as [*Peaceman*, 1977]

$$f(Cu, Pe) = Pe\left(\left(\frac{1}{2} - \alpha\right) + Cu\left(w - \frac{1}{2}\right)\right), \quad (10)$$

where α is the spatial weighting factor for the advective flux and w is the temporal weighting factor (explicit, implicit or Crank-Nicholson). Combining (8) and (9) leads to an expression for the relative error in the total amount of reaction induced by the chemical system

$$\epsilon_R = \frac{R_{num}}{R} - 1 = \frac{\sqrt{D_{num}}}{\sqrt{D}} - 1 = \sqrt{f(Cu, Pe)} - 1. \quad (11)$$

Figure 5 shows the behavior of ϵ_R as a function of Pe and Cu for an implicit approximation scheme with upstream weighting (α=0 and w=1), a popular scheme among reactive transport codes. Results suggest that Pe < 1 leads to very small relative errors (ϵ_R < 1%).

Figure 5

The question is then what Pe is typically used in stochastic modeling? A rough estimation can be done: When heterogeneity is explicitly described by high-resolution conductivity maps, cell longitudinal and transverse dispersivities are taken as proportional to the element size, e.g., α_L≈0.1 Δx and α_T≈0.01 Δx. This is supported by stochastic theories and the review of tracer data performed by *Gelhar et al.* [1992]. This means that for a standard discretization method the corresponding Grid-Peclet numbers range between 10 and 100, which leads to a more than 100% relative error. For instance, at the Cape Code site the evolution of the spatial moments of Bromide led to $\alpha_L/\alpha_T \approx 60$, yielding a P_e value of transverse dispersivity over 600. Thus, the overestimation of the total reaction becomes even worse when chemical reactions are controlled by transverse dispersivity, a common situation in contaminant transport [e.g., *Cirpka et al.*, 2015]. No wonder that a lot of research has been devoted in recent years to overcome this problem by developing new numerical methods.

Particle tracking methods constitute attractive numerical techniques but they have only recently been applied to reactive transport modeling [*Tartakovsky et al.*, 2007]. They are based on tracking a large number of particles injected into the system to simulate the evolution of a plume and moved by explicit expressions that try to represent the underlying processes. Since the method is meshless, truncation errors and artificial dispersion are negligible. The method can efficiently and effortlessly incorporate non-Fickian transport [*Zhang and Benson*, 2008] or multiple porosity systems [*Benson and Meerschaert*, 2009; *Henri and Fernàndez-Garcia*, 2015].

However, the method is not free of disadvantages. The main one is the need for reconstructing concentrations (actually activities) from particles. This step is theoretically free of numerical errors only for an infinite number of particles. In real applications, with a limited number of particles injected, kernel-based approaches largely minimize reconstruction errors [*Fernàndez-Garcia and Sanchez-Vila*, 2011; *Siirila-Woodburn et al.*, 2015]. Since the propagation of the latter with time is unknown, Eulerian-Lagrangian formulations that estimate concentrations as the simulation progresses cannot be assessed. Thus, pure Lagrangian formulations based only on particle interactions seem best suited to simulate reactive transport [*Rahbalaram et al.*, 2015; *Paster et al.*, 2014]. However, they are limited in the type of reactions they can handle efficiently: Linear sorption, first-order decay, and reaction chains.

For non-linear reactions, where transport of all particles cannot be decoupled, efficient search algorithms based on computational geometry are then a must [*Paster et al.*, 2014]. Examples are the bimolecular reaction [*Ding et al.*, 2013] and Michaelis-Menten enzyme kinetics [*Ding and Benson*, 2015]. Some unresolved issues are: (1) There is no formal particle upscaling process; (2) the methods assume that transport and reactions are uncoupled. *Henri and Fernàndez-Garcia* [2014] have shown that network reactions can substantially affect particle advection and dispersion.

In sum, stochastic reactive transport modeling can best represent reality but suffer from numerical problems stemming from the need to deal with large grid-Pe numbers. Some of these issues can be solved using Lagrangian approaches, but at the expense of other non-trivial numerical problems. In contrast, deterministic models with zonal parameterization can substantially reduce Pe by using large effective dispersivity values, but are forced to face structural and conceptual problems due to the emergence of macroscopic processes such as incomplete mixing. The lack of understanding of these processes in real applications tends to overpredict the actual reaction rates, seriously questioning the use of these models.

7. Outlook and final discussion

Hydrogeological modeling is the best way to integrate all available information in a site. Moreover, it is required in any professional report. Models should embed natural heterogeneity, but information is never sufficient. We contend that the only way to deal with modern hydrogeology problems is by relying on stochastic modeling, being the mathematically correct way to address the degree of uncertainty in the outcome of any study. As a corollary of this statement, all results should be given in statistical terms (pdfs or expected values plus some quantification of the prediction error). The driving processes, and thus the PDEs to adopt in any modeling effort are scale-dependent. Also, hydraulic parameters embedded in the equations depend on scale, but also in the interpretation method used to obtain them.

Geological architecture is critical; any model that hopes to resemble reality must incorporate as detailed geology as possible. Geology controls the location of high/low conductivity areas and the presence of conducting connected features. This is known by practitioners and so profusely used in deterministic modeling, but most times it is neglected in stochastic models; so, the general impression is that deterministic models provide the most robust results.

When analyzing flow problems, deterministic and stochastic methods are mature, and numerical codes for forward and inverse problems exist. It is time that we start (or keep) teaching stochastic modeling and advocate for its use, allowing a (most probably slow) permeation of the ideas among practitioners.

The situation is quite different for problems involving solute transport. There is a strong disagreement in the community regarding the governing effective equations that should be used, being controversial and sometimes misunderstood. The ADE may be valid at some local scale, but cannot reproduce most of the observations at larger scales. Alternatives consider the use of the proper upscaled equations and the set of parameters that are valid at some

459 degree of discretization. But what is the meaning of the word “valid” here? Upscaled models
460 only work in an ensemble sense; that is, they cannot be used to model point concentrations,
461 but only integrated observables. That is, they cannot estimate intra-block variability, or how
462 this is transferred to predictions. It is important that we acknowledge this fact and use models
463 cleverly, without trying to ask them to give answers they cannot provide.

464 This effect is even more relevant for reactive transport. Most reactions are driven by variations
465 in the chemical signature at the local scale, so they cannot be directly addressed in upscaled
466 models. Thus, there is a need to provide proper physically upscaled equations and parameters
467 that can answer questions regarding reaction rates and quantities observed in real field
468 applications. Several efforts have been pursued in this direction, but mostly in unconditional
469 synthetic fields, without any proof that they would also hold at the field scale.

470 Deterministic models do not represent reality at all. They just provide the modeler’s best
471 guess. This is sometimes enough to provide overall mass balance and to analyze simple
472 scenarios. Anything else needs an approach that properly incorporates heterogeneity and
473 uncertainty. So, despite of all the problems, limitations, and negative comments given in this
474 text, we contend that only stochastic models have any chance of providing the answers
475 needed for proper groundwater management. We must convey to managers and stakeholders
476 the message that all hydrogeological answers must be provided in statistical terms,
477 incorporating the concept of acceptable risk defined as the probability of any system to
478 unsatisfactorily meet a potential demand.

479

480 **8. Postscript: Comments on the other papers in the debate**

481 We appreciate the opportunity of providing comments on the other three papers in the
482 debate. We enjoyed reading the paper of Cirpka and Valocchi (2016) that actually addresses
483 very similar topics that this one, in particular in blaming stochastic theoreticians for restraining

484 the use of non-deterministic models by practitioners. They further consider that stochastic
485 hydrogeologists have been mostly dealing with questions that have very little relevance in
486 practice. It seems that the gap between scientists and practitioners is continuously widening.
487 We think it is even worse, as some of the former actually despise the idea of providing answers
488 to practical problems. Two points to highlight are that model choice is critical and that
489 conditioning is key. These are also main points in our text, and so there is little we can
490 comment upon. Last, we agree with the authors that the evaluation of uncertainty should be a
491 primary target of stochastic analysis.

492 We read with interest the contribution of Fiori et al. (2016), focusing on the relevance and
493 interest of further pursuing theoretical developments in stochastic subsurface hydrology. The
494 authors base their approach on the sequence of heterogeneity statistical characterization
495 (achieved by field investigation), followed by the solution of the flow and transport equations.
496 We fully agree with them that we need data and that the community has developed new and
497 promising methods to get them. But the question still remains regarding the spatial resolution,
498 data support window, and how these data can be used as input into models. This is another
499 message to convey to practitioners: data is not error free, it is scale-dependent, and
500 interpretation methods are not innocuous, but rather transfer our own view of processes. Our
501 main point of disagreement is that we claim that full aquifer characterization goes beyond
502 statistical descriptions only and should be conditioned on actual data.

503 We also appreciate the interesting contribution of Fogg and Zhang (2016). We share a similar
504 message which points out that spatial distribution of hydraulic parameters must account for
505 transport and deposition processes, rather than rely on simple statistical descriptions (e.g.
506 based on variance or integral scales). We also agree that most efforts in stochastic
507 contaminant hydrology are restricted to small plumes in clastic sedimentary systems at the
508 10^2-10^3 m scale. This means that present stochastic methods may not be directly applicable
509 and must therefore be adapted for modeling complex geologic environments such as

crystalline rocks (covering one third of the Earth's surface), carbonates (strongly present in Europe), or evaporates (characteristic of dry regions). The authors further argue that regional scale groundwater quality management is likely the biggest challenge in stochastic hydrogeology. Several points are worth emphasizing in this respect. The complexity at the regional scale renders the geologic description most important, and hypothesis such as stationarity and ergodicity unfeasible. Fortunately, observables tend to be integrated measures, thus with moderate uncertainty as compared to point values.

As a final statement, we want to stress the need to educate students on stochastic modeling, as well as the need to convey the message to practitioners, stakeholders and politicians that using deterministic modeling is something they cannot afford, as it would mean providing incomplete and misleading answers. Instead, all results should be given in probabilistic terms, rather than providing a single value with a zero probability of being correct. The increasing interest in asking results to be provided in terms of risk evaluations is on our side.

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656

657 Figure captions

658 Figure 1: Longitudinal integrated mass distribution profiles measured at the MADE site of the
659 tritium plume and different Monte Carlo realizations considering that the local ADE is valid
660 at the metric scale [modified from *Salamon et al.*, 2007]. All simulations display
661 (insufficient) tailing, and there is a strong variability between individual realizations.

662 Figure 2: Best fit of the integrated mass profiles at the MADE site at time t=328 day by
663 assuming a single-rate mass transfer model with a mass transfer coefficient α_f=0.0033 d^{-1}
664 and a field capacity (rate of immobile vs. mobile porosity) β=7.

665 Figure 3: Compilation of the review data presented by *Haggerty et al.* [2004] for single-rate
666 mass transfer coefficients estimated for a number of experiments worldwide, adding the
667 estimations of *Guan et al.* [2008] for the MADE site. The latter values do not follow the
668 general trend described by the inverse of residence time.

669 Figure 4: Estimation of mass transfer coefficients reported by Guan et al. [2008] and best fit
670 obtained from the t-SRMT model assuming two mass transfer rates acting simultaneously.

671 Figure 5: Relative error of the total amount of reaction as a function of grid-P_e and grid-C_u for
672 an Eulerian implicit approximation scheme with upstream weighting (α=0 and w=1).

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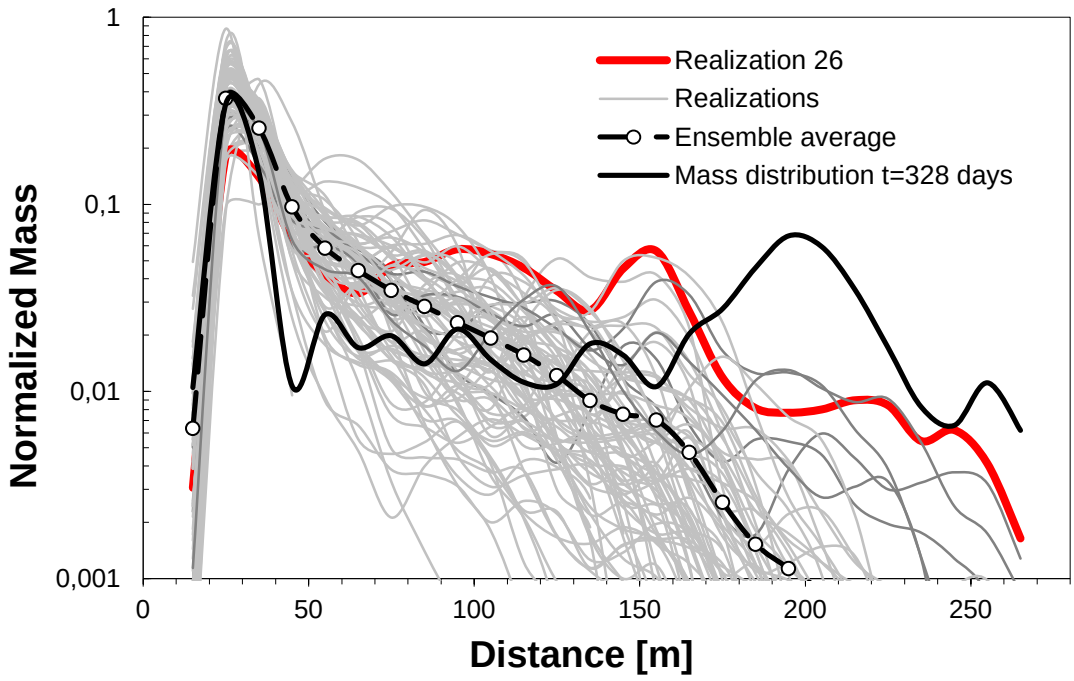

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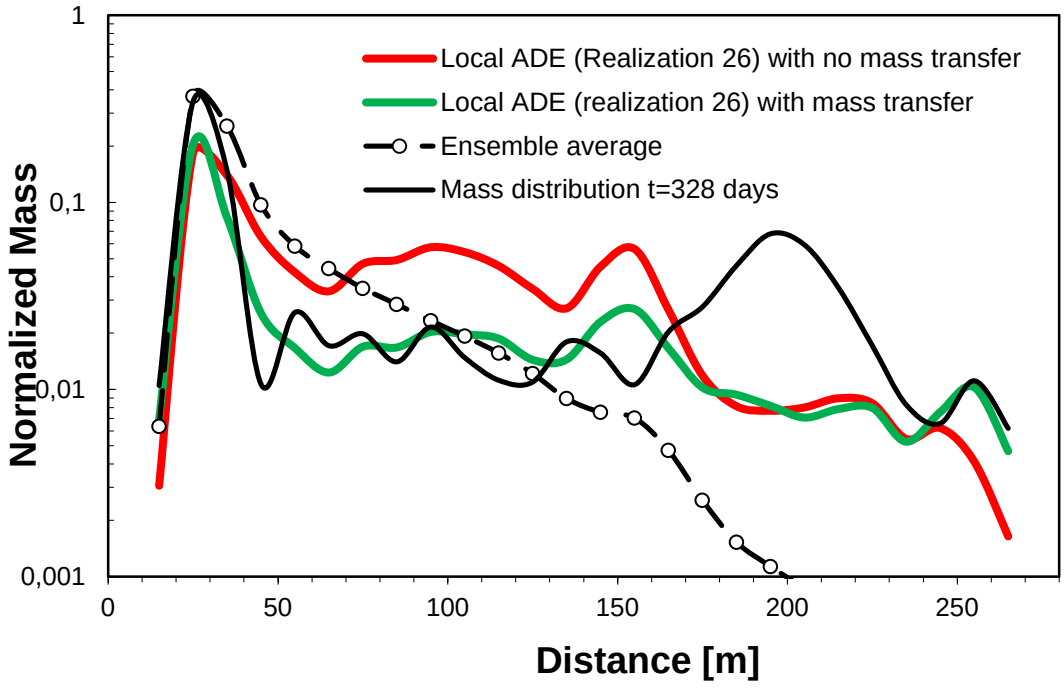

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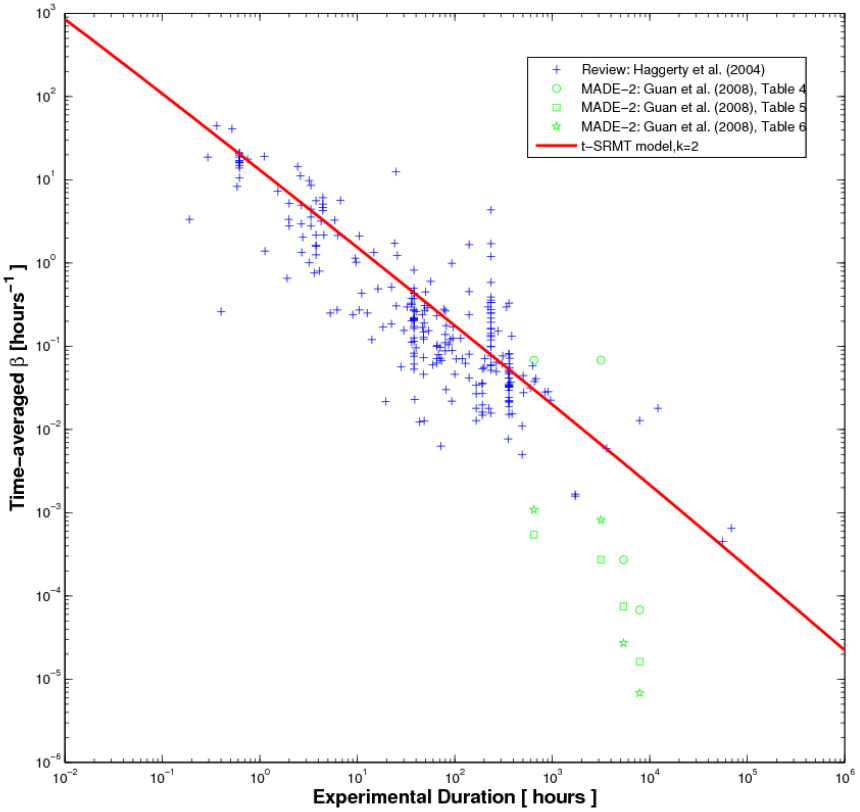

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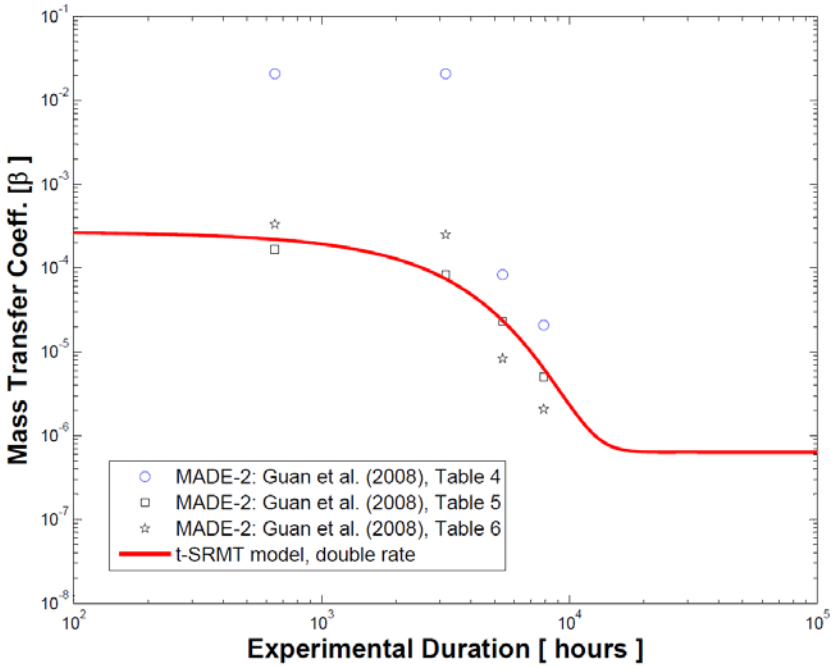

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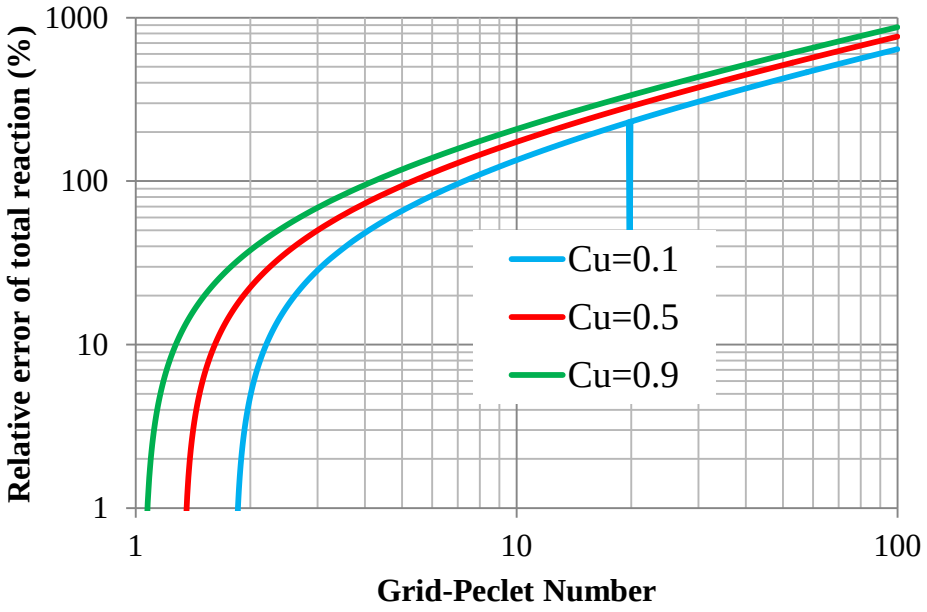

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