HESS Opinions: Chemical transport modeling in subsurface hydrological systems – Space, time, and the "holy grail" of "upscaling"

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Abstract.

Extensive efforts over decades have focused on quantifying chemical transport in subsurface geological formations, from microfluidic laboratory cells to aquifer field scales. Outcomes of resulting models have remained largely unsatisfactory, however, largely because domain heterogeneity – characterized for example by porosity, hydraulic conductivity and geochemical properties – is present over multiple length scales, and "unresolved", practically unmeasurable heterogeneities and preferential pathways arise at virtually every scale. While *spatial* averaging approaches are effective when considering overall fluid flow, wherein pressure propagation is essentially instantaneous, purely *spatial* averaging approaches are far less effective for chemical transport essentially because well-mixed conditions do not prevail. We assert here that an explicit accounting of *temporal* information, under uncertainty, is an additional but *fundamental* component in an effective modeling formulation. As an outcome, we further assert that "upscaling" of chemical transport equations – in the sense of attempting to develop and apply chemical transport equations at large length scales, based on measurements and model parameter values obtained at significantly smaller length scales – can be considered an unattainable "holy grail". Rather, we maintain that it is necessary to formulate, calibrate and apply models using measurements at similar scales of interest.

Keywords: Preferential flow, anomalous transport, numerical modeling, measurements

1 Introduction

1.1 Background

There have been extensive efforts over the last ~60 years to model and otherwise quantify fluid flow and chemical (contaminant) transport in soils and subsurface geological formations, from millimeter-size, laboratory microfluidics cells to aquifer field scales extending to hundreds of meters and even tens of kilometers.

Soils and subsurface formations typically exhibit significant heterogeneity, in terms of domain characteristics such as porosity, hydraulic conductivity, structure, and biogeochemical properties (mineral and organic matter content). However, only more recently has it become broadly accepted that effects of heterogeneity over multiple length scales, with "unresolved", practically unmeasurable heterogeneities arising at every length scale from pore to field, cannot be simply "averaged out". Indeed, much research on flow and transport in porous media, dating since ~1950, has been based on the search for length scales at which one can define a "representative elementary volume", or otherwise-named "averaging volume", above which variability in fluid and chemical properties become constant. In this context, too, many varieties of homogenization, volume averaging, effective medium, and stochastic continuum theories have been developed in an extensive literature. These methods allowed formulation of continuum-scale, generally Eulerian, partial differential equations to quantify ("model") fluid flow and chemical transport, which were then applied in the soil and groundwater literature at length scales ranging from millimeters to full aquifers. While originally deterministic in character, a variety of stochastic formulations and Monte Carlo numerical simulation techniques, introduced from the 1980s, enabled analysis of uncertainties in input parameters such as hydraulic conductivity.

However, while analysis of fluid flow using these methods has proven relatively effective, modeling of chemical transport, and an accounting of associated (biogeo)chemical reactions in cases of reactive chemical species and/or host porous media, has revealed serious limitations. We discuss the reasons for this in the sections below. Briefly, the overarching reason for these successes and failures is that *spatial* averaging approaches are effective when considering overall fluid flow rates and quantities: pressure propagation is essentially instantaneous and the system is "well mixed" because mixing of water "parcels" is functionally irrelevant. However, purely *spatial* averaging approaches are far less effective for chemical transport, essentially because well-mixed conditions do not prevail, and spatial averaging is inadequate; here, an explicit, additional accounting of *temporal* effects is required.

The focus of the current contribution is on modeling conservative chemical transport in geological media. In terms of modeling, one can delineate two main types of scenarios: (i) *pore-scale modeling* in relatively small domains, with a detailed and specified pore structure, and (ii) *continuum-scale modeling* in porous media domains, that average pore space and solid phases at scales from laboratory flow cells to field-scale plots and aquifers. Case (i) requires, e.g., Navier-Stokes or Stokes equations solutions for the underlying flow field, coupled with solution of a local

72 (e.g. advection-*diffusion*) equation for transport, while case (ii) requires Darcy (or related) equation
73 solutions for the underlying flow field, coupled with solution of a governing transport equation for
74 chemical transport. Note*:* here and throughout, we shall use the terms *continuum level* and
75 *continuum scale* in reference to case (ii) scenarios, and *pore-scale* to refer to case (i) scenarios,
76 although we recognize that pore-scale Navier-Stokes and advection-diffusion equations, too, are
77 continuum partial differential equations.
78
79   **Disclaimer:** Here and throughout this contribution, the overview comments and references to
80 existing philosophies, methodologies and interpretations are written mostly in broad terms, with
81 only limited citations selected from the vast literature. This approach is taken with a clear
82 recognition and respect for the extensive body of literature that has driven our field forward over
83 the last decades, but with the express desire to avoid any risk of unintentionally alienating
84 colleagues and/or misrepresenting aspects of relevant studies. *As an Opinion contribution, and*
85 *with length considerations in mind, there is no attempt to provide an exhaustive listing and*
86 *description of relevant literature.*
87
88
89 **1.2 Assertions**
90
91 The pioneering paper of Gelhar and Axness (1983) focused on quantifying conservative chemical
92 transport at the continuum level. They expressed heterogeneity-induced chemical spreading in
93 terms of the (longitudinal) macrodispersion coefficient – as it appears in the classical
94 (macroscopically 1d) advection-dispersion equation – with knowledge of the variance and
95 correlation length of the log-hydraulic conductivity field and the mean, ensemble-averaged fluid
96 velocity. The conceptual approach embodied in Gelhar and Axness (1983) – and by many
97 researchers since then (as well as previously) – was founded on delineation of the *spatial*
98 *distribution* of the hydraulic conductivity, and application of an averaging method to yield a
99 governing transport equation with "effective parameters" that describes chemical transport at a
100 given length scale (e.g. Dagan, 1989; Gelhar, 1993; Dagan and Neuman, 1997).
101   In contrast, we assert here that *spatial* information, alone, is generally insufficient for
102 quantification of chemical transport phenomena. Rather, *temporal* information is an additional,
103 but fundamental, component in an effective modeling formulation. In the discussion below, we
104 shall justify this argument by a series of examples. We examine (i) *spatial* information on, e.g. the
105 hydraulic conductivity distribution at the continuum level, or distribution of the solid phase at the
106 pore-scale level; and (ii) *temporal* information on, e.g. contaminant (tracer, "particle") transport
107 mobility and retention in different regions of a domain. We thus define a type of "information
108 hierarchy", with different types of information required for different flow and chemical transport
109 problems of interest.
110   As an outcome of the above assertion and the discussion below, we further assert that
111 "upscaling" of chemical transport equations – development and application of chemical transport
112 equations at large (length) scales, with corresponding parameter values, based on measurements

113 and model parameter values obtained at significantly smaller length scales – can be considered an
114 unattainable "holy grail". Rather, we maintain that it is necessary to formulate and calibrate
115 models, and then apply them, over spatial scales with relatively similar orders of magnitude. This
116 does not exclude use of similar equation *formulations* at different spatial scales, but it does entail
117 use of different parameter values, at the relevant scale of interest, that cannot be determined *a*
118 *priori* or from purely spatial or flow-only measurements.
119
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1.3 Approach – Outline

While our focus is on chemical transport, knowledge of fluid flow and delineation of the velocity
field throughout the domain is a prerequisite. We therefore first discuss fluid flow as an intrinsic
element of the "information hierarchy". Specifically, we address how:

(1) Basic structural information on "conducting elements" in a system representing a porous
    and/or fractured geological domain can provide insight regarding overall fluid conduction
    in the domain, as a function of "conducting element" density. We emphasize that without
    direct simulation of fluid flow in such a system, this type of analysis does not delineate the
    actual flow field and velocity distributions throughout the domain.

(2) Spatial information on the hydraulic conductivity distribution at a continuum scale, or solid
    phase distribution at the pore scale, throughout the domain, can be used to *determine the*
    flow field. We then show that this is insufficient to define chemical transport.

(3) Temporal information on chemical species migration, which quantifies distributions of
    retention and release times (or rates) of chemicals by advective-dispersive-diffusive and/or
    chemical mechanisms, can be used to *determine the full spatial and temporal evolution of*
    a migrating chemical plume, either by solution of a transport equation or use of particle
    tracking on the velocity field.

We comment, parenthetically, that in conceptual-philosophical terms, this hierarchy and the
"limitations" of each level are in a sense analogous to representation of geometrical constructs in
multiple dimensions: in principle, one can represent, as a *projection*, a d-dimensional object in d–
1 dimensions. But of course, by its very nature, a *projection* does not capture all features of the
construct in its "full" dimension. To illustrate, an imaginary 1d curve can represent a 2d Möbius
strip, a 2d perspective drawing can represent a 3d cube, and a 3d construct can represent a 4d object
(where the 4th dimension might be time) — and yet, none of these d–1 dimensional representations
contains all features of the actual d-dimensional objects. Similarly, despite our frequent attempts
to the contrary, one cannot properly describe (2) only from (1), or (3) only from (2).

2 Fluid flow

Analysis of the geometry of structural elements in a domain can yield basic insights on fluid flow

153   patterns. This approach is used, for example, when examining fracture networks in essentially
154   impermeable host rock. As discussed below, however, full delineation of the underlying velocity
155   field ultimately requires solution of equations for fluid flow.
156   In this context, percolation theory (Stauffer and Aharony, 1994) is particularly useful in
157   determining, statistically, whether or not a domain with N "conducting elements" (e.g. fractures)
158   includes sufficient element density to form a connected pathway enabling fluid flow across the
159   domain. One can estimate, for example, the critical value, N_c, for which the domain is "just"
160   connected, as a function of fracture length distribution, or the critical average fracture length as a
161   function of N needed to reach domain connectivity (Berkowitz, 1995). Similarly, percolation
162   theory shows how the overall hydraulic conductivity of the domain scales as the number of
163   conducting elements, N, relative to the N_c critical number of conducting elements required for the
164   system to begin to conduct fluid. Percolation theory also addresses diffusivity scaling behavior of
165   chemical species. But, fundamentally, percolation is a statistical framework suitable for large
166   ("infinite") domains, and provides universal scaling behaviors with no coefficient of equality; see
167   e.g., Sahimi (2021) for detailed discussion.
168   Other approaches have been advanced to analyze domain connectivity, for example using
169   graph theory and concepts of identification of paths of least resistance in porous medium domains
170   (e.g. Rizzo and de Barros, 2017), or topological methods (e.g. Sanderson and Nixon, 2015). Like
171   percolation theory, such approaches provide useful information and "estimates" on the hydraulic
172   connectivity and flow field, and even on first arrival times of chemical species, without solving
173   equations for fluid flow and chemical transport. However, these methods do not provide full
174   delineation of the flow field and velocity distribution throughout a domain.
175   These considerations indicate that, in general, dynamic aspects of fluid flow are critical:
176   knowledge of pure geometry is not sufficient, and *we must actually solve for the flow field*, at either
177   the pore-scale or a continuum scale, to determine the velocity field and actual flow paths
178   throughout the domain. Delineation of a flow field and velocity distribution by solution of the
179   Navier-Stokes equations (or Stokes equation for small Reynolds numbers), or by solution of the
180   Darcy equation, may be considered rigorous, correct and effective. But in the process of solving
181   for the flow field, two *key* features arise, one more relevant to pore-scale analyses, and the other
182   more relevant to continuum-scale analysis, as detailed in Sect. 2.1 and Sect. 2.2, respectively.
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185 **2.1 Pore-scale flow field analysis**

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187 Why is knowledge only of the geometrical "static" structure (spatial distribution of solid phase)
188 insufficient to know the flow dynamics in a pore-scale domain? Consider the 2d domain shown in
189 Figure 1, containing sparsely and randomly distributed obstacles (porosity of 0.9). Figure 1 shows
190 solutions of the Navier-Stokes equations for two Reynolds number (Re) values. [Recall: Re $\equiv$
191 $\rho v L/\mu$, where ρ and μ are density and dynamic viscosity of the fluid, respectively, v is fluid
192 velocity, and L is a characteristic linear dimension. Here and throughout, the fluid is assumed to

193 have constant viscosity.] Andrade et al. (1999) showed clearly that well-defined preferential flow
194 channels at lower Re, while at higher Re, channeling is less intense and the streamline distribution
195 is more spatially homogeneous in the direction orthogonal to the main flow. The domain shown in
196 Fig. 1 is not intended to represent a natural geological domain, but rather to illustrate streamline
197 behavior in even relatively simple pore-scale geometries.

198   Figure 1 demonstrates that the streamlines in individual pores change because of the interplay
199 between inertial and viscous forces, given by Re. In other words, with a change in overall fluid
200 velocity or hydraulic gradient across the domain, the actual flow paths can be altered, together
201 with a change in overall and (spatially) local residence times of fluid molecules; the same factors
202 also govern chemical species, as addressed below. Of course, the significantly lower porosities
203 and more tortuous pore space configuration in natural, heterogeneous geological porous media
204 may affect the impact of inertial effects, especially at the pore scale, but the principle remains
205 relevant. [We note, too, parenthetically, that the behavior shown in Fig. 1 is relevant also to fluid
206 flow within fracture planes, wherein the obstacles represent contact areas and regions of variable
207 aperture.]

208   Clearly, then, except in highly idealized and simplified geometries, use of a purely analytical
209 solution to identify the full velocity field and streamline patterns at the pore scale is not feasible.
210 Moreover, the extent and changes in streamlines are not intuitively obvious without full numerical
211 solution of the governing flow equations, for any specific set of porous medium structures and
212 boundary conditions.

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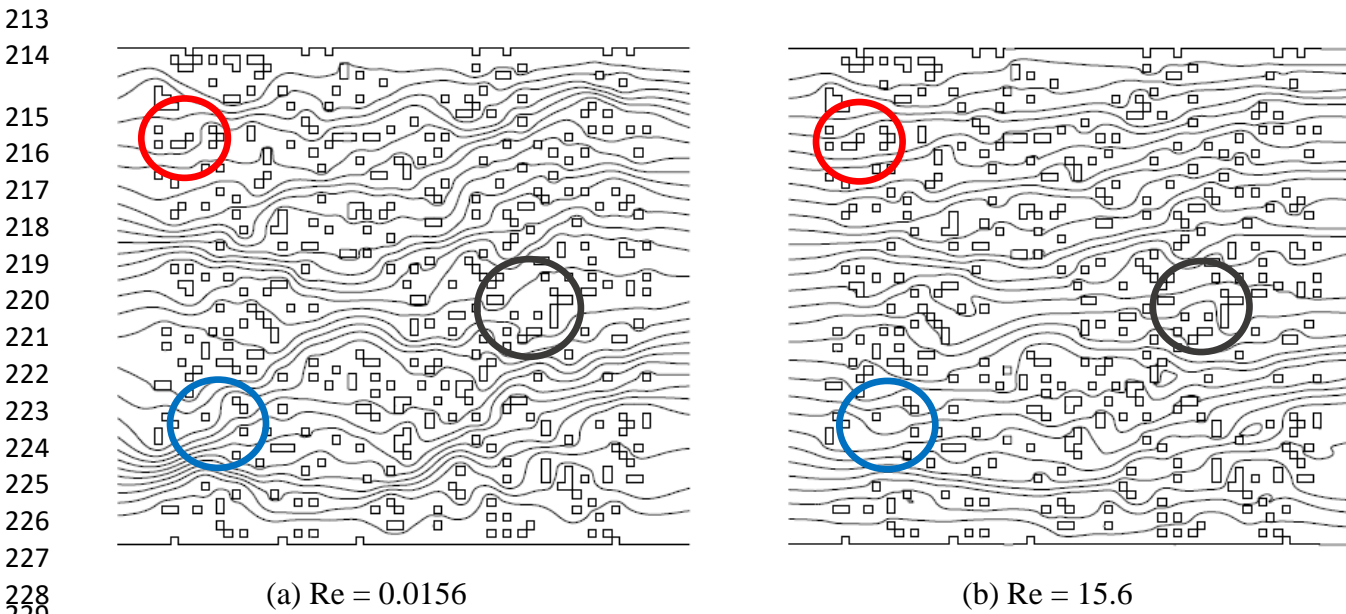
(a) Re = 0.0156   (b) Re = 15.6

Figure 1. 2d domain containing randomly distributed obstacles (squares and rectangles). Stream functions
for (a) Re = 0.0156 and (b) Re = 15.6 are shown with constant increments between consecutive streamlines
(from Andrade et al., 1999; Copyright, American Physical Society). The different patterns of preferential
pathways are clear and distinct. The three pairs of circles (red, blue, black) highlight three (of many) specific
locations where the streamlines are seen to change as a function of Re.

2.2 Continuum-scale flow field analysis

Considering now continuum-scale domains, but in analogy to the example shown in Sect. 2.1, we illustrate why knowledge only of the geometrical "static" structure is insufficient to know the flow dynamics, without solution of the Darcy equation. Here, the geometrical structure refers to the spatial distribution of the hydraulic conductivity, K.

Figure 2 represents a realization of a numerically-generated (statistically homogeneous, isotropic, Gaussian) hydraulic conductivity 2d domain. The Darcy equation solution for this domain yields values of hydraulic head throughout the domain; these are converted to local velocities, to enable delineation of the streamlines and preferential flow paths. The latter are highlighted by actually solving for chemical transport, by following the migration of "particles" representative of masses of dissolved chemical species injected along the inlet boundary of the flow domain; see Edery et al. (2014) for details. Of particular significance is that 99.9% of the injected particles travel in preferential pathways through a limited number of domain cells. We return to Figure 2 in Sect. 3.3.2, where we discuss a framework that effectively characterizes and quantifies chemical transport.

Unlike the pore-scale case shown in Sect. 2.1, at the Darcy/continuum scale, streamlines are not altered with changes in the overall hydraulic gradient, as long as laminar flow conditions are maintained. And yet, preferential flow paths are (possibly surprisingly) sparse and ramified, sampling only limited regions of a given heterogeneous domain, with the vast fraction of a migrating chemical species that interrogates the domain being even more limited. Significantly, except in highly idealized and simplified geometries delineation of these pathways is not intuitively obvious (e.g. by simple inspection of the hydraulic conductivity map in Fig. 2a) or definable from a priori analysis or tractable analytical solution. Rather, numerical solution of the governing flow equations is required, for any particular/specific set of porous medium structures and boundary conditions. [Note, too, that critical path analysis from percolation theory (discussed in Sect. 2) – again from purely "static" information without solution of the flow field – yields an incorrect interpretation, as shown in detail by Edery et al. (2014).]

We emphasize that the delineation of "preferential flow paths" is usually relevant only for study of chemical transport; if water *quantity*, alone, is the focus, then specific "flow paths" travelled by water molecules – and their advective and diffusive migration along and between streamlines, and into/out of less mobile regions – are of little practical interest. On the other hand, the movement of chemical species, which experience similar advective and diffusive transfers, must be monitored closely to be able to quantify overall migration through a domain. We return to consider patterns of chemical migration in Sect. 3. This argument, too, reinforces the assertion that delineation of actual chemical transport cannot be deduced purely from spatial information and solution for fluid flow, but must be treated by solution of a transport equation.

274   (a)   (b)

275   (c)

286   (d)

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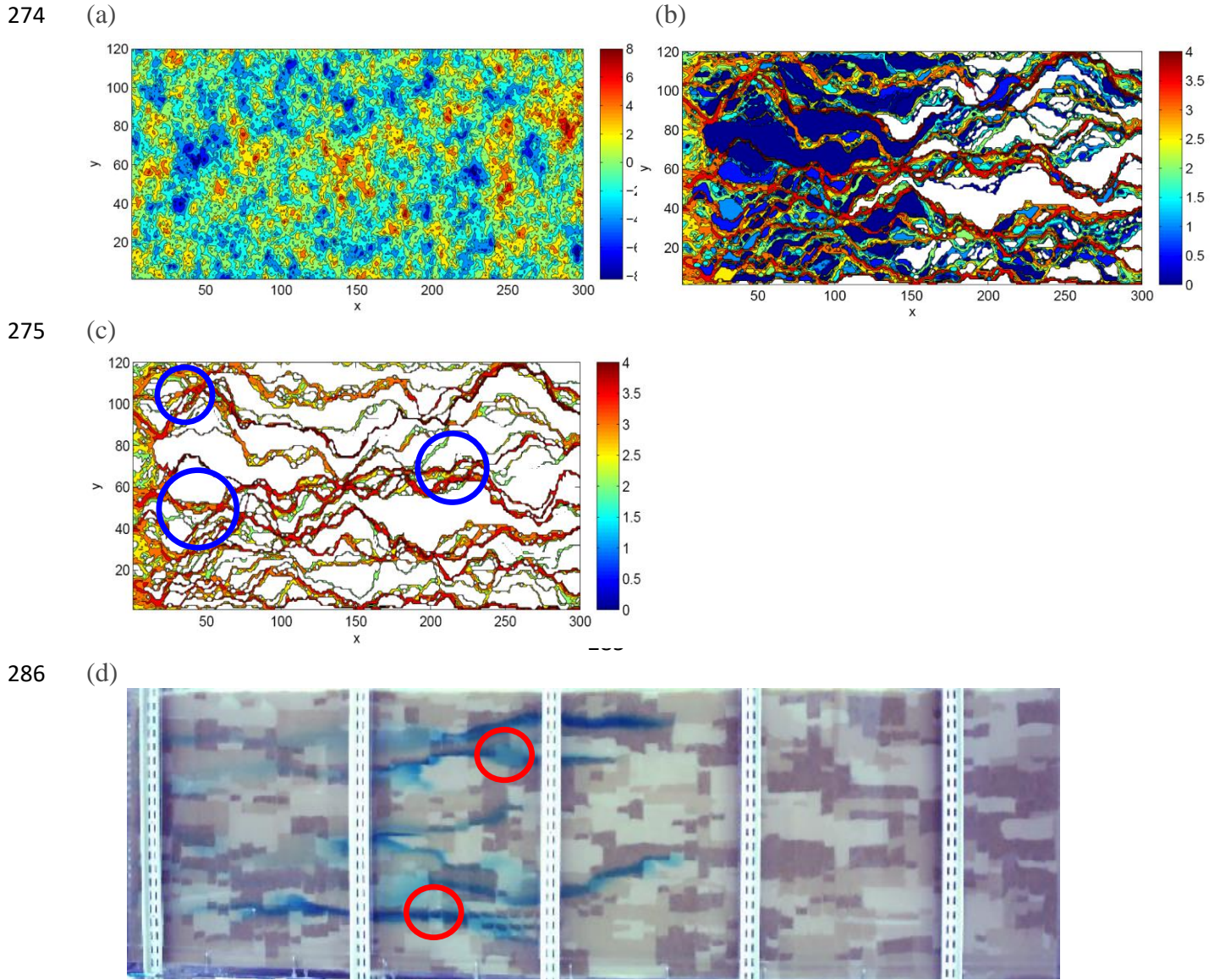
Figure 2. Maps of (a) hydraulic conductivity, K, distribution in a domain with 300×120 cells, (b) preferential pathways for fluid flow (and chemical transport), and (c) preferential pathways through cells that each contain a visitation of at least 0.1% of the total number of chemical species particles injected into the domain (flux-weighted, along the entire inlet boundary). Flow is from left to right. Note that the color bars are in $\ln(K)$ scale for Figure 2a, and $\log_{10}$ number of particles for Figures 2b,c (Edery et al., 2014; © with permission from the American Geophysical Union 2014). (d) Laboratory flow cell (dimensions 2.13 (length) × 0.65 (height) × 0.10 (width) m) with an exponentially correlated K structure, showing preferential pathways for blue dye injected near the inlet (flow is left to right); dark, medium, and light colored sands represent high, medium and low conductivity, respectively (Levy and Berkowitz, 2003; © with permission from Elsevier 2003). The circles shown in (c) and (d) highlight two (of many) regions in which the pathways are seen to contain lower K "bottlenecks".

It is significant, too, that fluid flow and chemical transport occur in preferential pathways that contain low conductivity sections (indicated by circles in Figs. 2c,d). How do we explain passage through low hydraulic conductivity "bottlenecks" within the preferential pathways, rather than

313   migration "only" through the highest conductivity patches?

314   To address this question, we first consider what happens in a 1d path. Consider two paths, each
315   containing a series of five porous medium elements or blocks, with distinct hydraulic conductivity
316   values, K_i. Consider Path 1, with a series hydraulic conductivity values of 3, 3, 3, 3, 3, and Path 2,
317   with values 6, 6, 1, 6, 6 (specific length/time units are irrelevant here). The value of $K = 1$
318   represents a clear "bottleneck" in an otherwise higher K path than that of Path 1. In a 1d series,
319   however, the overall hydraulic conductivity ($K_{overall}$) of the path is given by the harmonic mean of
320   the conductivities of the elements comprising the path: $K_{overall} = 5 / (\Sigma_{i=1,5} 1/K_i)$; significantly, in
321   the two cases here, both paths have $K_{overall} = 3$. So a "bottleneck" ($K=1$) can be "overcome" and
322   does not cause necessarily a potential pathway to be less "desirable" than a pathway without such
323   "bottlenecks". In other words, flow through pathways containing some low K regions should be
324   expected. Of course, in 2d and 3d systems, patterns of heterogeneity and pathway "selection" by
325   water/chemicals are significantly more "complicated", but the principle discussed here for 1d
326   systems still holds, in the sense that lower hydraulic conductivity ("bottleneck") elements can (and
327   do) exist in the preferential pathways (e.g. Margolin et al., 1998; Bianchi et al., 2011).

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329

330   **3 Chemical transport**

331

332   We now consider the next level of the "information hierarchy" outlined in Sect. 1.3. To quantify
333   the evolution of a migrating chemical plume, knowledge of the flow field is not generally
334   sufficient, and additional means to characterize and quantify the behavior are needed. Dynamic
335   aspects of chemical transport require us to think (also) in terms of *time*, not just *space* and physical
336   structure. Moreover, it is generally insufficient to determine the transport of the chemical plume
337   center of mass. Rather, in terms of water resource contamination and remediation, for example, it
338   is critical to characterize, respectively, the early and late arrival times at compliance or monitoring
339   regions downstream of the point, areal, or volumetric region in which the chemical species entered
340   the system.

341   As we show below, it becomes clear that there are dynamic aspects of chemical transport, over
342   and above the role of the flow field: *we must actually solve for chemical transport*, at either the
343   pore-scale or a continuum scale, to determine the spatial plume and/or temporal breakthrough
344   curve evolution of the migrating chemical plume. In *both* pore-scale and continuum-scale domains,
345   the *critical* control that arises is that of time, in addition to space. This is in sharp contrast to fluid
346   flow at pore and continuum scales, as shown in Sect. 2.1 and Sect. 2.2: pore-scale fluid flow
347   displays changing streamlines with changes in hydraulic gradient, while continuum-scale fluid
348   flow follows distinct but difficult to identify preferential flow paths essentially independent of the
349   hydraulic gradient.

350   We point out, too, that for both pore-scale and continuum-level scenarios, one can solve
351   explicitly a governing equation for transport. Alternatively, one can obtain an "equivalent"
352   solution by solving for "particle tracking" of transport along the calculated streamlines, in a
353   Lagrangian framework. In other words, particle tracking methods essentially represent an

alternative means to solve an (integro-)partial differential equation for chemical transport; such methods can be applied, too, when the precise partial differential equation is unknown or the subject of debate. We also note that solution of the relevant equations for fluid flow and chemical transport is sometimes achieved by (semi-)analytical methods, if the flow/transport system can be treated sufficiently simply (e.g. as macroscopically, section-averaged 1d flow and transport in a rectangular domain).

We first discuss principal features of pore-scale (Sect. 3.1) and continuum-scale (Sect. 3.2) chemical transport, and in Sect. 3.3, we focus on effective model formulations. We focus on conservative chemical species, and mention chemical reaction effects only peripherally. Note that other factors such as temporally/spatially changing fluid viscosity and surface tension, or mechanical and wetting properties of the solid phase, represent further complexities that are not considered here.

3.1 Pore-scale chemical transport analysis

To illustrate why knowledge only of the flow field is insufficient for full quantification of chemical transport, consider the three porous medium domains shown in Fig. 3. Each domains is comprised of pore-scale images of a natural rock, modified by enlarging the solid phase grains, to yield three different configurations: a statistically homogeneous system domain, a weakly correlated system, and a structured, strongly correlated system (see Nissan and Berkowitz (2019) for details). Fluid flow was determined by solution of the Navier-Stokes equations (Fig. 1a). Transport of a conservative chemical species was then simulated via a (Lagrangian) streamline particle tracking method, for an ensemble of particles that advance according to a Langevin equation. Transport behavior was determined for two values of macroscopic (domain average) Péclet number (Pe). [Recall; $Pe \equiv vL/D$, where v is fluid velocity, L is a characteristic linear dimension, and D is the coefficient of molecular diffusion.] Here, the macroscopic Pe is based on the mean particle velocity and mean particle displacement distance per transition (or "step").

Figure 3 shows that regardless of possible pore-scale streamline changes as a function of hydraulic gradient (recall Sect. 2.1, considering different values of Re), the choice of *macroscopic* Péclet number in a given domain plays a significant role in the evolution of the migrating chemical plume. In particular, the relative effects of advection and diffusion, which vary locally in space, are critical, as is the overall residence time in the domain. We stress here, and return to this key point in discussion below, that the spatially and in some cases temporally *local* changes in relative effects of advection and diffusion – characterized by the *local* Pe – dominate determination of the plume evolution. This can be understood from study of Fig. 3, for two choices of macroscopic Pe values in each of the three heterogeneity configurations; the different patterns of longitudinal and transverse spreading are observed clearly.

The behavior shown in Fig. 3 is essentially well-known from extensive simulations and experiments appearing in the literature. This behavior is described here to stress the importance of

394 *temporal* effects, and to point out that information only of the advective velocity field – as
395 discussed in Sect. 2.1 and Sect. 2.2 – is not sufficient to "predict" chemical transport.

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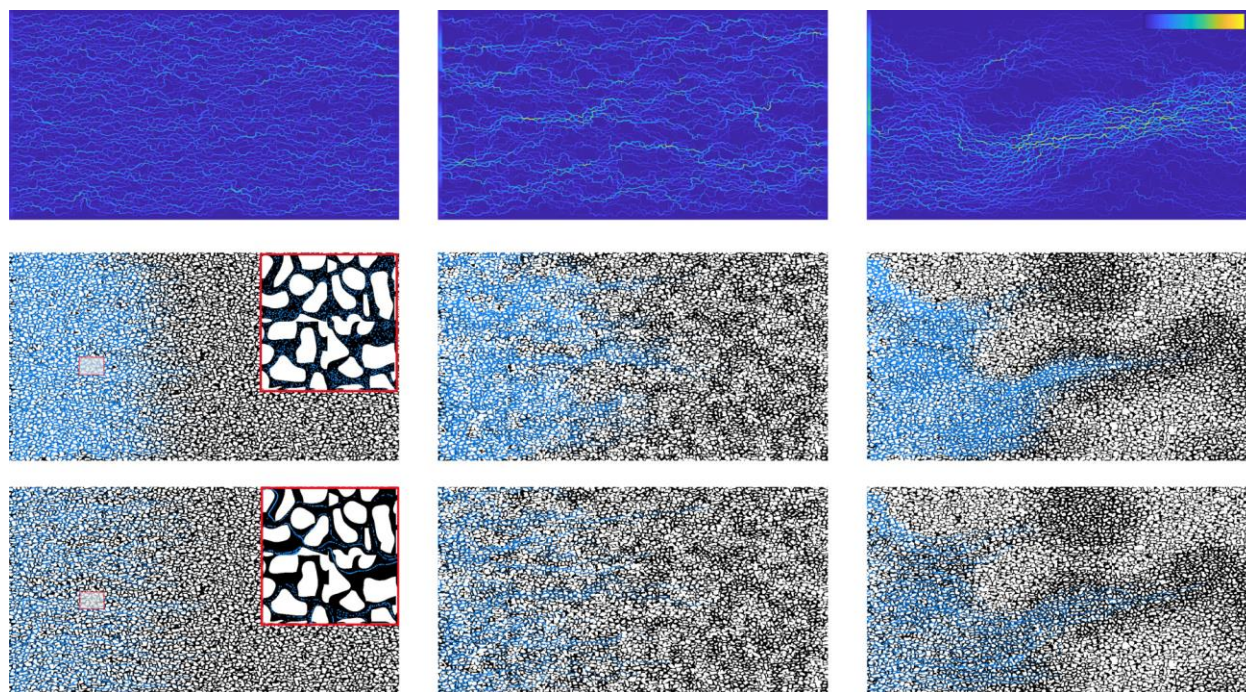
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Figure 3. Fluid velocities and chemical migration in three porous media configurations (from left to right):
homogeneous system, randomly heterogeneous system, and structured heterogeneous system. The upper
row shows the (normalized) velocity field for the three configurations; the color bar represents relative
velocity, with dark blue being lowest. The middle and lower rows show, respectively, numerically-
simulated particle tracking patterns of an inert chemical species (blue dots) at Pe = 1 (middle row) and Pe
= 100 (lower row) for the three configurations (white color indicates solid phase; black color indicates
liquid phase). Each system has overall dimensions of 8 cm (length) × 6 cm (height). Note: The particles
plumes are shown at 10% of the final time of each simulation; absolute travel times differ among the plots.
The insets in the left side plots of the middle and lower rows show the pore-scale chemical species
distributions; note the more diffuse pattern for Pe = 1 (from Nissan and Berkowitz, 2019; © with permission
from American Physical Society 2019).

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3.2 Continuum-scale chemical transport analysis

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414 The aspects discussed in Sect. 3.1 are relevant, analogous and applicable essentially also to
415 chemical transport at the continuum scale. Consider the two laboratory experiments shown in Fig.
416 4 and Fig. 5. Each flow cell was filled with a different clean, sieved sand configuration; see Levy
417 and Berkowitz (2003) for details. Figure 4 shows a uniform ("homogeneous") packing of clean
418 sand, while Fig. 5 shows a coarse sand containing a randomly heterogeneous arrangement of
419 rectangular inclusions consisting of a fine sand. The flow cells, fully saturated with water, enabled
420 macroscopically (section-averaged) 1d, steady-state flow, with a mean gradient parallel to the
421 horizontal axis of the cell. As seen in the two figures, neutrally-buoyant, inert red dye was injected
422 at seven (Fig. 4) and five (Fig. 5) points near the inlet side, to illustrate the spatiotemporal evolution

423   of the chemical plumes.
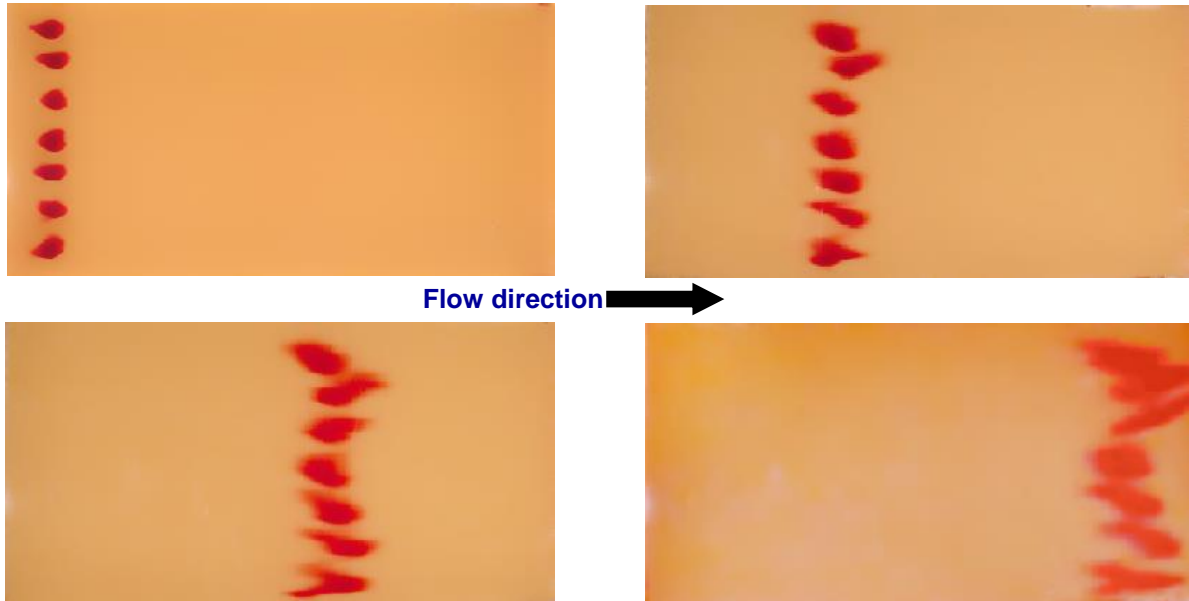
Figure 4. Photographs of dye transport in a flow cell (dimensions 0.86 (length) × 0.45 (height) × 0.10 (width) m) containing a uniform packing of quartz sand (average grain diameter 0.532 mm), under a constant flow rate with Pe >1, at four times (Levy and Berkowitz, 2003; © with permission from Elsevier 2003).
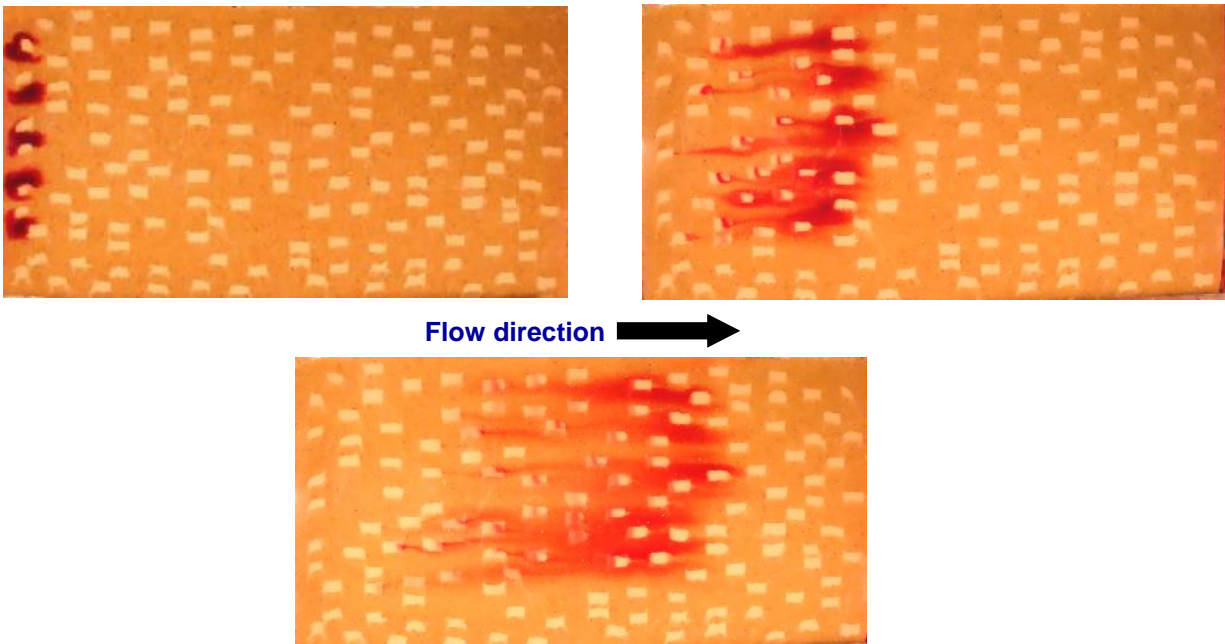
Figure 5. Photographs of dye transport in a flow cell (dimensions 0.86 (length) × 0.45 (height) × 0.10 (width) m) containing a randomly heterogeneous packing of quartz sand, under a constant flow rate with

470 Pe >1, at three times. The rectangular inclusions comprise sand with an average grain diameter ~0.5×
471 smaller, and hydraulic conductivity ~3× lower, than the surrounding sand matrix (Levy and Berkowitz,
472 2003; © with permission from Elsevier 2003).
473
474 Most notably, in both Fig. 4 and Fig. 5: (i) each of the plumes has a different, unique pattern,
475 which continues over the duration of the plume migration; and (ii) none of the plumes is
476 "elliptical", as expected in classical Fickian transport theory and embodied in solutions of the
477 classical advection-dispersion equation (ADE). Indeed, vertical averaging of each plume shown in
478 Fig. 4 and Fig. 5, at each time, does not yield Gaussian (normally distributed) concentration
479 profiles, but rather asymmetrical, "heavy-tailed" profiles.
480 At this juncture, note that here and below we use the terms "non-Fickian", or "anomalous" –
481 others sometimes use the terms "pre-asymptotic" or "pre-ergodic" – to denote any chemical
482 transport behavior that differs from that described by the classical ADE or similar type of
483 continuum-scale formulation. Typically, though, non-Fickian transport is characterized by early
484 and or late arrival times of migrating chemical species to some control or measurement plane/point,
485 relative to those resulting from solution of the ADE. The ADE applies to so-called Fickian
486 behavior, in the sense that it accounts for mechanical dispersion as a macroscopic form of Fick's
487 law; mechanical dispersion arises as an "effective" (or "average") quantity that describes local
488 fluctuations around the average (advective) fluid velocity. Thus, in this formulation, a pulse of
489 chemical introduced into a macroscopically 1d, uniform velocity, for example, leads to temporal
490 and spatial concentration distributions that are equivalent to a normal (Gaussian) distribution.
491 It is in this context that the term "homogeneous" packing used above is placed in quotation
492 marks, to indicate that in natural geological media, "homogeneity" does not really exist. Any
493 natural geological sample of porous medium contains multiple scales of heterogeneity; and at each
494 particular scale of measurement, "unresolved" heterogeneities that are essentially unmeasurable
495 are present. And thus, as seen in Fig. 4 for example, the overall transport pattern even in an
496 "homogeneous" system can be non-Fickian (anomalous). *We therefore emphasize that because*
497 *natural heterogeneity in geological formations occurs over a broad range of scales, "normal"*
498 *(Fickian) transport tends to be the "anomaly", whereas "anomalous" (non-Fickian) transport is*
499 *ubiquitous, and should be considered "normal".*
500 Moreover, as noted in Sect. 2.2, streamlines are not altered with changes in the overall
501 hydraulic gradient, at the continuum (Darcy) scale, as long as laminar flow conditions are
502 maintained, because increasing the hydraulic gradient increases the fluid velocity along the
503 existing, "predefined" streamlines by the same factor. However, the character of chemical
504 transport can be altered, as the change in residence time in the domain affects the relative effects
505 of advection and diffusion space. And in domains with heterogeneous distributions of hydraulic
506 conductivity, the local Pe (Sect. 3.1) can vary more strongly, too.
507 Thus, we argue that patterns of chemical transport cannot be fully determined from information
508 only on the velocity field; solution of an appropriate continuum-scale transport equation cannot be
509 avoided. In conclusion, then, and with particular reference to the (conceptually and theoretically
510 beautiful) classical ADE – and to "conventional" conceptual understanding and quantitative

511 description of chemical transport – we suggest that one must separate mathematical convenience
512 and wishful thinking from the reality of experiments: there is a definitive need for more powerful
513 formulations of transport equations. In this context, one is reminded of the quotation by the
514 biologist Thomas Henry Huxley: "The great tragedy of science—the slaying of a beautiful theory
515 by an ugly fact." (*President's Address to the British Association for the Advancement of Science,*
516 *Liverpool Meeting, 14 Sep 1870*).
517
518

3.3 Modeling chemical transport, and the myth that "fewer parameters is always better"

521 So how *do* we effectively model chemical transport?
522 As noted at the outset of Sect. 2, solution of the Navier-Stokes or Darcy equations to determine
523 the full *flow* field and velocity distribution in a given porous medium domain has been proven
524 correct and effective in most applications, and is well-accepted in the literature. However,
525 modeling of chemical transport is more contentious, the reasons for which we expand upon below.
526 We argue here that modeling of chemical species transport requires us to think in terms of *time*,
527 not just *space*. To assist the reader to enter this frame of thinking, and to sharpen our
528 conceptualization, we provide two examples to illustrate aspects of time and space in the context
529 of chemical transport dynamics:

(1) The classical example of the brachistochrone (ancient Greek: "shortest time"), or path of
   fastest descent, is the curve that would carry an idealized point-like body, starting at rest
   and moving along the curve, without friction, under constant gravity, to a given end point
   in the shortest time. Somewhat non-intuitively, the path that leads to the shortest travel
   time is not a straight line, but, rather, a special curve that is longer than a straight line (a
   cycloid), as demonstrated by Johann Bernoulli in 1697 (see:
   http://old.nationalcurvebank.org//brach/brach.htm).

(2) What error can be introduced when "averaging" in terms of space? Consider the case of
   driving a total distance of 100 km, by first traveling 50 km at 1 km h^{-1}, and then traveling
   50 km at 99 km h^{-1}. If we average the speed in terms of space (distance), then we traveled
   two segments of 50 km at two speeds, so the average speed is $(1 + 99) / 2 = 50$ km h^{-1}. In
   this framework, the total time to travel the 100 km "should" only have been 2 h. However,
   in terms of *time*, the travel time is actually 50.5 h.

543 These simple examples help to emphasize the errors introduced by traditional conceptual
544 thinking, wherein the effects of *spatial* transport and domain heterogeneity are quantified only on
545 the basis of spatial characteristics. It is worth recalling, too, Einstein's quantitative treatment of
546 Brownian motion (Einstein, 1905). Prior to his analysis, researchers applied – with puzzlement –
547 a time-dependent velocity, *v*, to quantify experimental measurements. Einstein (1905) instead
548 examined a recursion relation and expansion that led to a diffusion equation whose solution
549 showed, for the first time, that the root mean squared displacement of particles undergoing
550 Brownian motion is proportional to $\sqrt{t}$, and not to *vt* as had been assumed traditionally. An

astounding conceptual breakthrough over a century ago, this nature of diffusive motion is now "common knowledge".

In this same framework of focusing on *time*, the examples shown in Fig. 4 and Fig. 5 emphasize that for chemical transport, we must recognize the critical role of "*rare events*". These rare events involve chemical species – migrating "particles" or "packets" – that are held up or retained while traveling through or in/out of lower velocity regions in the porous domain over various periods of time. Such events can have a dominant impact on overall transport patterns, at both pore and continuum scales. In this context, one must exercise caution with simple averaging of "small velocity fluctuations" and effects of molecular diffusion. Rather, small-scale heterogeneities in both space and time do not necessarily "average out" or become insignificant at larger scales; rather, the effects of "rare events" (e.g. temporary trapping of even small amounts of chemical species via diffusion into and out of low velocity regions) and fluctuations can propagate and become magnified, *within and across* length scales from pore to aquifer.

Armed with these thoughts, we suggest that modeling chemical transport has been debated in the literature for at least three reasons:

1. The desire to work with spatial averaging approaches and equations: The research community was (and still is) split over the need to recognize and incorporate, *explicitly*, influences of temporal mechanisms caused largely by spatial heterogeneity (as characterized by the domain hydraulic conductivity), when formulating "effective" (or "averaged") equations. And even when recognized, debate remains as to appropriate mathematical formulation.

2. The lack of data: At least part of the difficulty in developing appropriate models is the lack of availability of high-resolution laboratory data and field measurements against which chemical transport models can be tested. Indeed, many elaborate theoretical developments have been advanced over the decades, with accompanying, analytical and numerical solutions — and yet, remarkably, comparative studies against actual laboratory data remain limited, and tests with field measurements are even sparser (see also Sect. 4 for further discussion of this point).

3. The choice of approach to, and purpose of, chemical transport modeling: Two overarching approaches to quantifying chemical transport can be defined, focusing on (i) quantification of "effective", "overall" chemical transport behavior without requiring high-resolution discretization and numerical solution of the domain, and, alternatively, (ii) high-resolution hydrogeological delineation and then intensive numerical simulation on highly discretized grids. We address approaches (i) and (ii) individually, below, in the context also of points (1) and (2).

The debate in the literature between "effective" and high-resolution hydrogeological modeling, as well as various preconceptions and misconceptions discussed below and in Sect. 4, lead naturally to consideration of the (often incorrectly invoked) argument that "fewer model parameters is better".

We first discuss briefly aspects of high-resolution hydrogeological modeling in Sect. 3.3.1,

591 and then focus on "effective" transport equation modeling in Sect. 3.3.2. We emphasize that the
592 latter approach is applicable to both small- and large-scale domains. The former approach is
593 generally intended for large- (field-)scale systems, although it is in some sense often applied for
594 detailed pore-scale modeling; this approach is not particularly contentious, per se, but is hampered
595 by the complexity and cost associated with the demand for highly detailed hydrogeological
596 information. Therefore, research work remains heavily invested in "effective" transport equation
597 modeling.
598
599
600 **3.3.1 High-resolution domain delineation and modeling**
601
602 Efforts to resolve large-scale aquifer systems, to delineate the hydraulic conductivity distribution
603 at increasingly higher resolutions, began in earnest in the 1990s. Analysis of field sites emphasized
604 relatively high-resolution discretization of domain structure (e.g. blocks of the order of 10 m^3 at
605 the field scale (Eggleston and Rojstaczer, 1998); $200 \times 200 \times 1$ m^3 at large regional scales (Maples
606 et al. 2019)). These efforts, first focusing on determining the fluid flow field, and subsequently on
607 delineating pathways for chemical transport, began largely because of dissatisfaction with results
608 of application of 1d, 2d, 3d forms of an "effective" (averaged) ADE (see further discussion in Sect.
609 3.3.2). Acquiring high-resolution measurements of structural (e.g. mineralogy, porosity) and
610 hydrological properties (e.g. hydraulic conductivity) was made more feasible in recent years by
611 advances in hydrogeophysics, and as well as by advances in computational capabilities that enable
612 incorporation of this information in finely-discretized meshes, and numerical solution for fluid
613 flow and chemical transport.
614   In these highly resolved, high-resolution gridded domains, the flow field can be determined
615 from solution of Darcy's law. Chemical transport is then simulated either by use of streamline
616 particle tracking methods, by accounting for advection and diffusion in a Lagrangian framework,
617 or via solution of a local, mesh element continuum-scale transport equation. For chemical
618 transport, use of an advection-*diffusion* equation might appear preferable – given that it requires
619 no estimate for the local dispersivity – but some researchers apply an advection-*dispersion*
620 equation, which necessitates use of mesh-scale dispersivity values that are either assumed or
621 estimated from local measurements. The latter case assumes mesh-scale transport to be fully
622 Fickian (recall Sect. 3.2). More recently, alternative formulations of a governing transport equation
623 that incorporates broad temporal effects can also be used in this type of modeling approach; see,
624 e.g. Hansen and Berkowitz (2020) for incorporation of a continuous time random walk method
625 (discussed in Sect. 3.3.2). [Parenthetically, we note that "analogous", high-resolution
626 measurements are made at the pore-scale – in mm to decimeter rock core samples – as a basis for
627 computationally-intensive modeling of fluid flow and chemical transport at these scales. Similar
628 to the evolution of this approach for field-scale studies, high-resolution measurements advanced
629 from use of 2d rock micrographs to advanced micro-computed tomography protocols (e.g. Thovert
630 and Adler, 2011; Bijeljic et al., 2013; recall Sect. 2.1).]

631   This approach is attractive in terms of the ability to "reproduce" detailed heterogeneous
632 hydraulic conductivity structures, and can provide useful "overall assessments" of fluid flow and
633 chemical transport pathways, and migration of a chemical plume. Moreover, solutions for fluid
634 flow and chemical transport can be considered "exact", at least at the scale at which the domain is
635 discretized; they can thus also capture at least some aspects of non-Fickian transport. But even at
636 this type of spatial resolution, the ability to effectively quantify actual chemical transport, even
637 relative to the limited available field measurements, remains a question of debate; the research
638 community, as well as practicing engineers, still often prefer to analyze chemical transport in a
639 domain by use of relatively simple (often 1d, section-averaged) model formulations.

640   Finally, we point out that in the context of efforts to obtain increasing amounts of structural
641 and hydrological information at a given field site, due consideration should also be given to the
642 "worth" of data. Thus – for example – in an effort to quantify fluid flow or conservative chemical
643 transport in an aquifer, do we really need "full", detailed knowledge of the system (e.g. porosity,
644 hydraulic conductivity) at every point in the formation? Possibly non-intuitively, the adage "more
645 data is better" is often not true, and model incorporation of statistical uncertainty can offer equally
646 satisfactory solutions with less costly, less measurement- and computationally-intensive, detail
647 (e.g. Dai et al., 2016).

648
649

650 **3.3.2 "Effective" characterization and modeling**

651

652 At least since the 1960's, the research community has focused enormous efforts on formulation of
653 "averaged", or "effective" (often macroscopically, section-averaged 1d) transport equations to
654 quantify chemical transport, without requiring high-resolution discretization and computationally-
655 intensive numerical solution of the domain. The now "classical" ADE was advanced as the
656 governing partial differential equation; see also further discussion on "effective scales of interest",
657 in the context of "upscaling" (Sect. 4). Recall that as discussed in Sect. 3.2, the ADE assumes
658 Fickian transport behavior, in the sense that mechanical dispersion – which is defined as an average
659 quantity to describe local fluctuations around the average (advective) fluid velocity – is treated
660 macroscopically by Fick's law. The classical ADE then specifies coefficients of longitudinal and
661 transverse dispersivity, which by definition are constants.

662   Solutions of the ADE were compared against conservative tracer experiments in laboratory
663 columns (generally 10-100 cm) to produce breakthrough curves of concentration vs. time, at a set
664 outlet distance; but even from the outset, the applicability of the ADE was questioned by some
665 researchers (e.g. Aronofsky and Heller, 1957; Scheidegger, 1959). Subsequent flow cell
666 experiments demonstrated, for example, that the dispersivity constants are not actually constant,
667 and change with length scale – even over tens of centimeters – to achieve even *approximate* fits to
668 the measurements (e.g. Silliman and Simpson, 1987). Moreover, solutions of the ADE appear
669 inadequate when compared to transport in laboratory flow cells with distinct regions of different
670 hydraulic conductivities (e.g. Maina et al., 2018). In a sense, then, it can be considered somewhat

surprising that this form of the ADE was subsequently assumed to apply, over several decades, in a rather sweeping fashion for a wide range of hydrogeological scenarios and length scales. Detailed discussions of these aspects appear in, e.g. Berkowitz et al. (2006, 2016). [Parenthetically, we stress again here that if one has complete information at the pore-scale, then solution of the Navier-Stokes and advection-*diffusion* equations within the pore space can capture the true chemical transport behavior, i.e. purely spatial information is sufficient to describe chemical transport. But at continuum scales, time and unresolved heterogeneities became critical, and an "averaged" equation like the ADE with a "macrodispersion" concept is problematic.]

To move beyond the ADE, and the definitive need for effective transport equations that quantify non-Fickian, as well as Fickian, transport (recall Figs. 4 and 5), we consider an alternative approach. The idea is to account for the temporal distribution that affects chemical migration, in addition to the spatial distribution, at a broad continuum level, and employ a transport equation in the spirit of a "general purpose" ADE. This approach necessarily leads to transport behaviors that are more general than those indicated by a "general ADE", i.e. in the context of an overall, averaged 1d transport scenario for example.

To explain this approach, we refer to the continuous time random walk (CTRW) framework, which is particularly broad and general (Berkowitz et al., 2006). Significantly, and conveniently, it turns out that special, or limit, cases of a general CTRW formulation lead to other well-known formulations that can also quantify various types of non-Fickian transport, as explained in, e.g., Dentz and Berkowitz (2003) and Berkowitz et al. (2006). These "subsets" include mobile-immobile (e.g, Feehley et al., 2000), multirate mass transfer (e.g. Haggerty and Gorelick, 1995; Harvey and Gorelick, 1995; Carrera et al., 1998), and time-fractional derivative formulations (e.g. Barkai et al., 2000; Schumer et al., 2003; Metzler and Klafter, 2004). Indeed, in spite of references to these model formulations as being "different", they are closely related, with clear mathematical correspondence. Each formulation has advantages, depending on the domain, problem and objectives of model use; but model selection must first be justified physically, and it is inappropriate, for example, to apply a mobile-immobile (two domain) model to interpret chemical transport in a "uniform, homogeneous" porous medium when it displays non-Fickian transport behavior (recall Fig. 4).

Here, we describe only briefly the principle and basic aspects of the CTRW formulation; detailed explanations and developments are available elsewhere (e.g. Berkowitz et al., 2006).

To introduce "temporal thinking" in the context of non-Fickian transport, we begin by mentioning the analogy between a classical random walk (RW) – which leads to Fick's law – and the CTRW. A classical random walk is given in Eq. 1:

$$P_{n+1}(\ell) = \sum_{\ell'} p(\ell, \ell') P_n(\ell') \tag{1}$$

where $p(\ell, \ell')$ represents the probability of a random walker ("particle") advancing from location ℓ' to ℓ, $P_n(\ell')$ denotes the probability of a particle being located at ℓ' at (fixed) time step n, and $P_{n+1}(\ell)$ denotes the probability of the particle then being located at ℓ at step n+1. With this

711   formulation in mind, Einstein (1905) and Smoluchowski (1906a,b) demonstrated that for *n*
712   sufficiently large and a sufficient number of particles undergoing purely (statistically) random
713   movements *in space*, the spatial evolution of the particle distribution is equivalent to the solution
714   of the (Fickian) diffusion equation. This elegant discovery demonstrated that a partial differential
715   equation and its solution can be represented by following, numerically, the statistical movement
716   of particles (i.e. particle tracking) following a random walk. Remarkably, random walk
717   formulations are "generic" in the sense that they can be applied in a broad range of phenomena in
718   physics, chemistry, mathematics, and life sciences; here, they describe naturally migration of
719   chemical species (dissolved "particles" or "packets") in water-saturated porous media.
720   Generalizing the partial differential equation to include transport by advection, solution of the
721   ADE under various boundary conditions can then be determined by an appropriate random walk
722   method.
723   The simple random walk given in Eq. 1 can be generalized by accounting for time, replacing
724   the particle transition (or iteration) counter *n* by a time distribution. The generalized formalism in
725   Eq. 2, with the joint distribution $\psi(\mathbf{s}, t)$, called "continuous time random walk" and applied to
726   transport, was first introduced by Scher and Lax (1973):

728    $$R_{n+1}(\mathbf{s}, t) = \sum_{s'} \int_0^t \psi(\mathbf{s} - \mathbf{s}', t - t') R_n(\mathbf{s}', t') dt' \qquad (2)$$

730   where $R_{n+1}(\mathbf{s}, t)$ is the probability per time for a particle to just arrive at site **s** at time *t* after *n*+1
731   steps and $\psi(\mathbf{s}, t)$ is the probability rate for a displacement from location **s′** to time **s** with a difference
732   of arrival times of *t-t′*. It is clear that $\psi(\mathbf{s}, t)$ is the generalization of $p(\ell, \ell')$ in Eq. 1, and that the
733   particle steps can each now take place at different times. Indeed, it is precisely this explicit
734   accounting of a distribution of temporal contributions to particle transport, not just spatial
735   contributions, that offers the ability to effectively quantify transport behaviors as expressed by,
736   e.g. heavy-tailed, non-Fickian particle arrival times.
737   To where does the generalization in Eq. 2 lead us? In a mindset similar to that of Brownian
738   motion, and Einstein's 1905 breakthrough mentioned above at the outset of Sect. 3.3, a puzzle
739   arose about seven decades later for researchers attempting to interpret observations of electron
740   transit times in disordered semiconductors. The electron mobility (defined as velocity per unit
741   electric field), which was considered an intrinsic property of the material, was found to depend on
742   variables that changed the duration of the experiment, such as sample length or electric field. Scher
743   and Montroll (1975), considering Eq. 2, discovered that the mean displacement $\overline{\ell}$ of the electron
744   packet does not advance as $\overline{\ell} = vt$, but rather as $\overline{\ell} \sim t^\beta$.
745   In the context of chemical transport in geological formations, the behavior $\overline{\ell} \sim t^\beta$ can be
746   attributed to a wide distribution of transition times in naturally disordered geological media. In the
747   CTRW formulation, the transition time distribution is characterized by a power law of the form
748    $\psi(t) \sim t^{-1-\beta}$ for $t \to \infty$ and $0 < \beta < 2$; significantly, the resulting transport behavior is Fickian for
749    $\beta > 2$. At large times, for this $\psi(t)$ dependence, the mean displacement $\overline{\ell}(t)$ and standard deviation

$\overline{\sigma}(t)$ of the migrating chemical plume $c(\mathbf{s}, t)$ scale as $\overline{\ell}(t) \sim t^\beta$ and $\overline{\sigma}(t) \sim t^\beta$ for $t \to \infty$, $0 < \beta < 1$ (Schlesinger, 1974). Moreover, for $t \to \infty$ with $1 < \beta < 2$, the plume scales as $\overline{\ell}(t) \sim t$ and $\overline{\sigma}(t) \sim t^{(3-\beta)/2}$. These behaviors are notably different than that of Fickian transport models, for which (from the central limit theorem), $\overline{\ell}(t) \sim t$ and $\overline{\sigma}(t) \sim t^{1/2}$.

With the concepts described here, and using the generally applicable decoupled form $\psi(\mathbf{s}, t) = p(\mathbf{s})\psi(t)$, where $p(\mathbf{s})$ is the probability distribution of the transition lengths and $\psi(t)$ is the probability rate for a transition time t between sites, Eq. 2 can be developed into an (integro-)partial differential equation. Thus, the ADE given by

$$\frac{\partial c(\mathbf{s},t)}{\partial t} = -[\mathbf{v}(\mathbf{s}) \cdot \nabla c(\mathbf{s}, t) - \mathbf{D}(\mathbf{s}) : \nabla^2 c(\mathbf{s}, t)] \tag{3}$$

where $c(\mathbf{s}, t)$ is the concentration at location $\mathbf{s}$ and time t, $\mathbf{v}(\mathbf{s})$ is the velocity field and $\mathbf{D}(\mathbf{s})$ is the dispersion tensor, is replaced by the more general CTRW transport equation:

$$\frac{\partial c(\mathbf{s},t)}{\partial t} = -\int_0^t M(t - t')\left[\mathbf{v}_\psi \cdot \nabla c(\mathbf{s}, t') - \mathbf{D}_\psi : \nabla\nabla c(\mathbf{s}, t')\right] dt' \tag{4}$$

where $\mathbf{v}_\psi$ and $\mathbf{D}_\psi$ are generalized particle velocity and dispersion, respectively, and $M(t)$ is a temporal memory function based on $\psi(t)$.

The strength of this type of formulation is that it effectively quantifies (non-Fickian) early arrivals and late time tailing of migrating chemical species, and the spatial evolution of chemical plumes in heterogeneous media. For example, recalling the scenario in Fig. 2, wherein 99.9% of the inflowing particles traverse the preferential pathways seen in Fig. 2c, detailed numerical simulations indicate that concentration breakthrough curves exhibit significant, non-Fickian, long-time tails (Edery et al., 2014). Choice of an appropriate power-law form of $\psi(t)$ was then shown to capture this behavior; moreover, a functional form defining the value of the power-law exponent β in $\psi(t)$ was identified, based on statistics of the hydraulic conductivity and particle interrogation of the domain (Edery et al., 2014).

Equation (4) is essentially an ADE weighted by a temporal memory. When $\psi(t)$ is an exponential function (or power law but for $\beta \geq 2$), $M(t) \to \delta(t)$ and we recover Fickian transport described by the ADE; thus, the ADE assumes, implicitly, that particle transition times are distributed exponentially. But with a power law form $\psi(t) \sim t^{-1-\beta}$ for $0 < \beta < 2$, the transport is non-Fickian. A wide range of functional forms of $\psi(t)$ can be chosen, including, e.g. truncated power law forms that allow evolution to Fickian transport at large times or travel distances (e.g. Dentz et al., 2004), as well as Pareto (e.g. Hansen and Berkowitz, 2014) and curved (or inverse gamma; e.g. Nissan and Berkowitz, 2019) temporal distributions. Other, generally simpler, choices of $\psi(t)$ or $M(t)$ lead to mobile-immobile, multirate mass transfer, and time-fractional derivative formulations, as mentioned above. We note, too, that the elegant result derived by Gelhar and Axness (1983) and others, discussed in Sect. 1.2, is valid only at an asymptotic limit, wherein transport is Fickian and there is no residual non-Fickian memory in thbe plume advance.

789 A plethora of related studies have examined a range of perspectives and applications that
790 explore CTRW formulations. These studies address, for example, numerical simulations (e.g. Le
791 Borgne et al., 2008; Berkowitz and Scher, 2010; Hansen, 2020; Kang et al., 2014; Rhodes et al.,
792 2008; Edery, 2021), fractured formations (e.g. Geiger et al., 2010; Wang and Cardenas, 2017),
793 stream transport (e.g. Boano et al., 2007), and laboratory measurements at difference scales (e.g.
794 Le Borgne and Gouze, 2008; Major et al., 2011). Other studies have explored space-fractional
795 differential equations (e.g. Benson et al., 2000; Wang and Barkai, 2020).

796 Each of these power law forms of course requires one or more parameters – at least β – and in
797 some cases, other parameters that define, e.g. a transition time from non-Fickian to Fickian
798 transport (Berkowitz et al., 2006; Hansen and Berkowitz, 2014; Nissan et al., 2017). These
799 parameters have physical meaning, and are not purely empirical; perspectives on "numbers of
800 parameters" associated with all models are discussed in Sect. 3.3.3. The question of how model
801 parameter values are determined is addressed in Sect. 4.1.

802 The efficacy of formulations that incorporate, whether explicitly or implicitly, some type of
803 power-law characterization of temporal aspects of chemical transport, is now generally recognized
804 in the literature. Indeed, applications of mobile-immobile, multirate mass transfer, time-fractional
805 advection-dispersion, and general CTRW formulations have been applied quite extensively and
806 successfully. In particular, solutions of Eq. 4 and related variants have interpreted a wide range of
807 chemical transport scenarios: (i) pore-scale to meter scale laboratory experiments, field studies,
808 and numerical simulations, in (ii) porous, fractured, and fractured porous domains, (iii) accounting
809 for constant and time-dependent velocity fields, and (iv) for both conservative and reactive
810 chemical transport scenarios. Solutions to address some of these scenarios are more easily obtained
811 by use of particle tracking methods that incorporate the same considerations and power-law form
812 of $\psi(t)$, as embedded in Eq. 4.

813 Like the ADE, Eq. 3, the formulation given in Eq. 4 represents a continuum-level mechanistic
814 model (as derived in, e.g., Berkowitz et al. 2002), in the sense that both equations contain clear
815 advective and dispersive contributions. The occurrence of a broad distribution of transition times,
816 fundamental to CTRW and related approaches, emanates from a variety of physical controls.
817 Discussion in the literature about the need for "mechanistic models" often uses the term rather
818 loosely: "mechanistic" transport model equations are based on fundamental laws of physics, with
819 constant parameters that have physical meaning (e.g. hydraulic conductivity, diffusivity, sorption),
820 and thus offer process understanding. But to quantify the spatiotemporal evolution of a migrating
821 chemical plume, additional parameters are needed. Because of the nature of geological materials,
822 a transport equation should of course capture the relevant physical mechanisms that influence the
823 transport, as well as chemical mechanisms if the species is reactive; but to do so, we must *also*
824 capture the uncertain characterization of hydrogeological properties due to the reality of
825 unresolved, unmeasurable heterogeneities at any length scale of interest. Thus, we suggest that a
826 *mechanistic-stochastic equation formulation* such as given in Eq. 4 is required. Such an equation
827 (i) incorporates a probability density function to account for temporal transitions that cannot be
828 determined only from spatial information, (ii) describes known transport mechanisms with

829 physically meaningful parameters, and (iii) accounts for unknown (and unknowable) information.
830   We note here, too, that other stochastic continuum averaging methods have been proposed in
831 the literature, in the same context of efforts to formulate a "general", "effective" transport equation
832 at a specific scale of interest (see further discussion on "effective" equations and "upscaling" in
833 Sect. 4). In many cases, though, sophisticated stochastic averaging and homogenization
834 approaches have led to transport formulations that are essentially intractable, in terms of solution,
835 and/or have remained at the level of hypothesis without being tested successfully against actual
836 data.
837
838

3.3.3 Are fewer parameters always better? (Answer: No!)

841   The term "modeling" is used in many contexts and with differing intents. However, in the
842 literature dealing with chemical transport in subsurface hydrological systems, there are frequent
843 but often misguided "arguments" regarding "which model is better", with a major point of some
844 authors being the claim that "fewer parameters is always best". Not always. Indeed, some models
845 involve more parameters than others, but if these parameters have physical meaning and are needed
846 as factors to quantify key mechanisms, then "more parameters" is not a "weakness". We
847 emphasize, too, that when weighing use of *any* specific model, "better" also depends, at least in
848 part, on what the modeling effort is addressing. Clearly – regardless of the number of parameters
849 – a "back-of-the-envelope" calculation using a simple model is sufficient if, for example, one
850 requires only an order of magnitude estimate of the center-of-mass velocity of a migrating
851 contaminant plume, or in other words, no need for artillery to swat a mosquito. [In this context,
852 quoting Albert Einstein regarding his simplification of physics into general relativity: "Everything
853 should be made as simple as possible, but not simpler."]
854   Considering chemical transport in subsurface geological formations, and the aim of
855 quantifying (modeling) the evolution of a migrating chemical plume in both space and time, we
856 return to focus on the ADE- and CTRW-based formulations discussed in Sect. 3.3.2. As noted in
857 the preceding sections, CTRW and related formulations can describe transport behaviors
858 effectively. Most significantly, the seminal work of Scher and Montroll (1975) showed that the β
859 exponent *must* be included because the mean displacement is not linear with time (i.e. the mean
860 displacement $\overline{\ell}$ of the electron packet does not advance as $\overline{\ell} = vt$, but rather as $\overline{\ell} \sim t^{\beta}$). Similarly,
861 a corresponding parameter, relative to an ADE formulation invoking Fickian transport, is
862 unavoidable when transport is non-Fickian.
863   It should be recognized that quantitative model information criteria, or model selection criteria,
864 can be used to assess and compare various model formulations that are applied to diverse scenarios
865 (such as fluid flow, chemical transport) in subsurface geological formations. These information
866 criteria include AIC (Akaike, 1974), AICc (Hurvich and Tsai, 1989), and KIC (Kashyap, 1982)
867 measures, as well as the Bayesian (or Schwarz) BIC (Schwarz, 1978). They are formulated to rank
868 models, or assign (probabilistic) posterior weights to various models in a multimodel comparative

869 framework, and therefore focus on model parameter estimates and the associated estimation
870 uncertainty. As such, these information criteria discriminate among various models according to
871 (i) the ability to reproduce system behavior, and (ii) the structural complexity and number of
872 parameters. Discussion of theoretical and applied features of these criteria is given elsewhere (e.g.
873 Ye et al., 2008). Using such measures specifically in the context of the ADE and CTRW
874 formulations, with an accounting also of chemical reactions, it was shown that while solution of
875 an ADE can fit measurements from some locations quite closely, the CTRW formulation offers
876 significantly improved predictive capabilities when examined against an entire experimental data
877 set (Ciriello et al., 2015). In addition, focusing on the most sensitive observations associated with
878 the CTRW model provides a stronger basis for model prediction, relative to the most sensitive
879 observations corresponding to the ADE model.

880   To conclude this section: Notwithstanding the above arguments, some readers might continue
881 to argue that the approach discussed here – viz., the need for time considerations as well as space
882 such as embodied in the CTRW framework and related formulations – is "inelegant" because it
883 requires more parameters relative to the classical ADE. In response, the reader is encouraged to
884 recall the words of Albert Einstein following criticism that his theory of gravitation was "far more
885 complex" than Newton's. His response was simply: "If you are out to describe the truth, leave
886 elegance to the tailor".

887
888

889 **4 The holy grail of upscaling, and myths about "a priori" parameter determination**

890

891 We begin by defining the term "upscaling" in the context of the discussion here on chemical
892 transport. As defined in the Introduction, Sect. 1.2, we use the term "upscaling" to describe the
893 effort to develop and apply chemical transport equations at large length scales, and identify
894 corresponding model parameter values, based on measurements and parameter values obtained at
895 significantly smaller length scales.

896   We attempt "upscaling" in the hope of developing governing equations for chemical transport
897 at larger and larger scales, from pore, to core, to plot, and to field length scales. Clearly, then,
898 "upscaling" is relevant to the modeling approach discussed in Sect. 3.3.2 – which focuses on use
899 of "averaged", or "effective" (often 1d, or section-averaged) transport equations – and not to the
900 high-resolution domain delineation and modeling approach of Sect. 3.3.1.

901   However, in light of the discussion in Sect. 2 and Sect. 3, we argue that "upscaling" of chemical
902 transport equations is very much an unattainable holy grail. Particularly in light of recognizing
903 temporal effects, in addition to spatial characterization, we maintain that it is necessary to
904 formulate and calibrate models, and then apply them, at similar measurement scales of interest. Of
905 course, similar equation *formulations* can be applied at different spatial scales. But parameter
906 values for transport equations cannot generally be determined a priori or from purely spatial or
907 flow-only measurements; *measurements with a temporal "component", at the relevant length*
908 *scale of interest, are required.*

909   In Sect. 4.1, we briefly discuss aspects of model calibration. This leads naturally to our
910   discussion of upscaling in Sect. 4.2.
911
912

913   **4.1 Parameter determination and model calibration**

914

915   First, it is prudent to offer some words about the need for parameter estimation, or model
916   calibration. Unless one is dealing with first principles calculations of a physical process such as
917   molecular diffusion in a perfectly homogeneous domain, *a priori* determination of model
918   parameters – for *any* model equation formulation – requires calibration against actual experimental
919   measurements. In some limited cases, detailed numerical simulations can be used at small (pore)
920   scales, e.g. using an advection-*diffusion* equation together with solution of the Navier-Stokes
921   equations to first determine the precise flow field in the pore space; but this also necessitates
922   detailed measurements of the pore structure such as obtained by computed tomography
923   measurements (e.g. Bijeljic et al., 2013). Indeed, then, at any realistic problem or scale of interest,
924   *all* chemical transport models require calibration.
925   This fundamental tenet should be clear and well-recognized, yet the literature contains all-too-
926   frequent – and both misguided and misleading – "criticism" of various model formulations,
927   claiming that "parameters are empirical because they are estimated by calibration (fitting) to
928   experiments"; additional "criticisms" follow, for example, that such as a model is therefore not
929   "universal", and/or "it therefore has no predictive capability". We address these latter "criticisms"
930   in Sect. 4.2. Parameters are *not* "empirical" simply because their values are determined by
931   matching to an experiment. Moreover, it should be recognized that application even of the classical
932   ADE at various column and larger scales requires estimates – obtained by calibration – of
933   dispersivity coefficients; and for high-resolution domain delineation and modeling as discussed in
934   Sect. 3.3.1, calibrated "block-scale" dispersivities are needed. [Note: If dispersivities are not
935   actually determined for a specific experiment, but selected from on the literature for "typical"
936   values of dispersivity, there is still a reliance on calibration from previous "similar" studies.]
937   Moreover, with reference to the desire for model parameters that represent fundamental, *spatial*
938   hydrogeological properties of the domain, note that even the classical ADE dispersivity parameter
939   is not uniquely identified with such properties; rather, it varies even in a given domain as a function
940   of chemical plume travel distance or time.
941   With regard to model "universality", recall that, for example, percolation theory (discussed at
942   the beginning of Sect. 2) offers "universal" exponents in scaling relationships. But even for this
943   type of convenient and useful, statistical model, such scaling relationships, too, can only advance
944   from "scaling" (e.g. $A \sim B$) to a full "equation" (e.g. $A = kB$) by calibration of a coefficient of
945   equality (k) against actual measurements. So even in "simple" models, model calibration cannot
946   be avoided.
947   To address "empiricism" – here enters the question of whether parameters of a particular model
948   (in this case, equations for chemical transport) have a physical meaning. As discussed in Sect.

3.3.2, a *mechanistic-stochastic equation formulation* such as given in Eq. 4 incorporates a probability density function to describe known transport mechanisms in a stochastic sense; but stochastic does not mean "unphysical", and the parameters as given in, e.g., particular functional forms of $M(t)$ or $\psi(t)$ are indeed physically meaningful. For example, the key β exponent characterizing the power law behavior can be linked directly to the statistics of the hydraulic conductivity field (Edery et al., 2014), or, in a fracture network, be determined from the velocity distribution in fracture segments (Berkowitz and Scher, 1998), which is related directly to physical properties of the domain. Similarly, corresponding parameters appearing in "subset" formulations to quantify non-Fickian transport – e.g. mobile-immobile, multirate mass transfer, and time-fractional derivative formulations – can be understood to have physical meaning (e.g. Haggerty and Gorelick, 1995; Harvey and Gorelick, 1995; Carrera et al., 1998; Dentz and Berkowitz, 2003; Berkowitz et al., 2006). These parameters, too, of course require determination by model calibration to experimental data, or where appropriate to results of numerical simulations, just as for ADE and any other model formulation.

4.2 Upscaling, the scale of interest, and predictive capabilities

Upscaling of *fluid flow* "works" because at the Darcy scale – which is the "practical" scale for most applications – flow paths and streamlines do not change with increasing gradient, as long as a transition to turbulent flow is not reached. The equation formulation remains valid, and the fluid residence time in a domain is irrelevant because self-diffusion of water does not affect overall fluid fluxes.

For chemical transport, though, the situation is totally different. Why? Because "upscaling" entails some kind of "coupled" averaging or parameterization in both space *and* time, and it is far from clear how, if at all, this can be achieved. Moreover, small-scale concentration fluctuations do not necessarily "average out", but instead propagate from local to larger spatial scales. To illustrate another aspect of the complexity, the Péclet number (Pe) in heterogeneous media, with preferential pathways, varies locally in space (recall Fig. 3 and the discussion in Sect. 3.1). Averaging to obtain a macroscale ("upscaled") Pe must address the relative, locally varying effects of advection and diffusion in space, as well as the overall residence time in the domain; after all, it is these effects that dominate determination of the plume evolution. Thus, upscaling requires spatial averaging, but (at least an) *implicit* temporal averaging must also be included. It can be argued that no single, effective Pe can be defined for the entire domain; whether or not it is possible, and how, it is possible to average local Pe values to achieve a single, meaningful domain-scale Pe remains an open question. And whether we like it or not, even with complete information on the spatial (local) Pe distribution, the impact on the overall transport pattern evolution cannot be determined without actually solving for transport in the domain.

For chemically reactive species, the transport situation becomes even more complex, because the local residence time, not just the local Pe, must be taken into consideration. Moreover, when

989 precipitation or dissolution processes are present, the velocity field will change locally, introducing
990 additional local temporal and spatial variability. And when sorption is present but tapers off – for
991 example, when the cation exchange capacity is met – even the diffusion coefficient itself changes.
992 These factors further complicate attempts to upscale. [In this context, too, it should be noted that
993 for chemically-reactive systems, it is well-known that there is often a significant lack of
994 correspondence between laboratory and field-based estimates of geochemical reaction rates and
995 rates of rock weathering, with field-scale estimates – often based on macroscopically Fickian,
996 ADE-like transport formulations – being generally significantly smaller (e.g. White and Brantley,
997 2003).]

998 Thus, we suggest that focusing efforts on attempting to develop upscaling methodologies for
999 chemical transport, based on any transport equation formulation, appears to be doomed largely to
1000 failure – as evidenced, too, by decades of research publications. Rather, we argue that because of
1001 the subtle effects of temporal mechanisms, and their close coupling to spatial mechanisms, use of
1002 an "effective", or "averaged" continuum-level equation to describe chemical transport requires
1003 calibration of a suitable model at the appropriate scale of interest, with model parameter values
1004 calibrated at essentially the same scale. The model can then be applied to examine transport
1005 behaviors over spatial scales with relatively similar orders of magnitude.

1006 We emphasize, though, that as stated at the outset of Sect. 4, we do argue that similar
1007 (continuum-level) transport equation *formulations* can be applied at different spatial scales, as long
1008 as they are mechanistically correct, with a *temporal* component, and the parameter values are based
1009 on *measurements at the relevant length scale of interest.*

1010 Now, in the context of the above arguments regarding "upscaling" and model application, we
1011 return to the ideas presented in Sect. 3.3.2 and consideration of model formulations that account
1012 for both spatial and temporal effects. We first mention use of the ADE. As pointed out in Sect. 3.2
1013 and extensive literature, the "constant" (as required by the ADE formulation) "intrinsic"
1014 dispersivity parameter changes significantly even over relatively small increases in length scales
1015 (e.g. 10's of cm's; Silliman and Simpson, 1987) – and therefore also over time scales. It therefore
1016 makes no real sense to attempt to define an "upscaled" dispersivity parameter for larger scales.
1017 Even in the framework of high-resolution domain delineation and modeling, discussed in Sect.
1018 3.3.1 – which is not "upscaling" as defined here – the question remains as to what dispersivity
1019 values are relevant for field-scale aquifer "blocks" of the order of 100 to 1000's of m^3.

1020 In contrast, CTRW and related transport formulations with explicit accounting of time effects,
1021 as outlined in Sect. 3.3.2, can be applied meaningfully to interpret real measurements and transport
1022 behavior at "all" scales. We *can* use the same equation formulation at different scales, with
1023 different but relevant parameters at each scale. We emphasize, too, that we do not argue for "hard"
1024 length scales: in principle, e.g., an appropriate CTRW-based model calibrated at 20 cm will be
1025 applicable to 100 cm scales, and a model calibrated on a 100 m scale data set can be applicable at
1026 a kilometer scale (e.g. Berkowitz and Scher, 1998, 2009; Rhodes et al., 2008; Geiger et al., 2010;
1027 Edery, 2021). The point, though, is that it makes no sense to calibrate at a centimeter scale and
1028 then expect to somehow "upscale" parameters to apply the same model at a kilometer scale. [Note:

1029   As an aside, over very large field-length and field-time scales, we point out that homogenization
1030 effects of molecular diffusion *may* become more significant, lessening impacts of some
1031 preferential pathways.] Similarly, a CTRW-based approach can be applied over a range of *time*
1032 scales, because the power law accounting for temporal effects can be as broad as needed. In these
1033 cases, temporal effects are critical, because at the continuum (Darcy) scale, streamlines do not
1034 change but residence times do. Specifically, for example, a model formulation with a fixed set of
1035 parameters can interpret transport measurements in the same domain, but acquired under different
1036 hydraulic gradients or fluid velocities, and thus domain residence times (Berkowitz and Scher,
1037 2009). Indeed, because of the temporal accounting, CTRW has been applied successfully over
1038 scales from pores (e.g. Bijeljic et al., 2013) to kilometers (e.g. Goeppert et al., 2020), with
1039 parameter calibration at the relevant scale of interest. In principle then, a calibrated model shown
1040 to be meaningful over one region of a porous medium or geological formation can offer at least a
1041 reasonable estimate of transport behavior elsewhere in the medium/formation, at a similar
1042 length/time scale, and as long as the medium/formation can be expected to have reasonably similar
1043 hydrogeological structure and properties.

1044   Finally, another critical aspect must be pointed out with regard to *continuum-scale* transport
1045 models as outlined in Sect. 3.2. The preceding discussion leads to the stated need and desire – at
1046 least in principle – to achieve model "prediction". This term appears often, but it is often used
1047 incorrectly. Fitting a model solution to data is of course not "prediction". On one hand, using
1048 specific experiments and data sets, models can be used to *characterize* transport behavior, e.g., is
1049 transport Fickian or non-Fickian?, or, is a migrating chemical plume compact or elongated and
1050 ramified?, which is of fundamental importance. But if *prediction* is the ultimate goal (recognizing
1051 that addressing *prediction uncertainty* is yet another consideration), then we require multiple data
1052 sets from the same porous medium or geological formation, in the sense that we need
1053 measurements over a range of length scales, and/or over a range of time scales (i.e. same distance,
1054 different flow rates). An intended model can then be calibrated against one part of the data set; the
1055 calibrated model is then applied "as is" and the resulting solution, a "prediction", is compared
1056 against other "previously unknown" measurements. At the laboratory scale, such a protocol is
1057 feasible, but rarely executed. Rather, the literature generally reports fits of transport equation
1058 solutions *at specific scales* – individual data sets at a given length scale – and not over a range of
1059 scales, so that no real testing of "upscaling" or "prediction" is achieved. Thus, even at laboratory
1060 scales, true "predictive capability" of a model is rarely examined or reported. [Note: A similar
1061 approach to "prediction" can be done in a purely numerical/computational study, using "ground
1062 truth simulations" that are *assumed* correct (e.g. Darcy flow calculations and then streamline
1063 particle tracking for chemical transport in a highly-resolved domain; recall Sect. 3.3.1), and then
1064 comparing solutions from a continuum (partial differential equation) model solution. But it should
1065 be recognized that results from *assumed* simulation methods are often unsatisfactory when
1066 compared against experimental measurements and field observations.]

1067   And at the field scale, the situation is even less satisfying; large-scale field tests for chemical
1068 transport are difficult and expensive to execute, so that systematic data sets that enable testing of

model "prediction" – as well as even initial calibration of a transport model – are essentially non-existent. Moreover, while larger-scale structural features can be identified in principle via non-invasive geophysical methods, higher resolution sampling and measurements of hydraulic conductivity and geochemical parameters are necessarily highly limited. As a result, oft-used, non-unique interpolation of sparse concentration measurements is employed to yield (ideally 3d) contour maps of hydrogeological parameters and actual chemical concentrations; but interpolation will unrealistically smooth and dampen existing ramified and irregular preferential pathways (recall Fig. 2). Thus, notwithstanding the extensive research efforts reported in the literature, truly comparative studies using field measurements – to genuinely test proposed "upscaling" methodologies – are essentially non-existent (e.g. Berkowitz et al., 2016). In this context, then, we note that criticism in the literature that a given continuum model "demonstrates no predictive capability" is in fact not generally based on its assessment relative to sufficiently resolved, representative, and real data sets. Finally, it is important to recognize that models are most commonly tested against 1d, section-averaged concentration breakthrough curves, which can be (i) measured directly in laboratory column experiments, (ii) estimated or derived in 2d/3d laboratory flow cells by averaging over control planes, or (iii) estimated from limited monitoring well measurements (single or multi-level sampling with depth) at a fixed number of locations. The latter case, in particular, requires extensive interpolation and/or assumption of a large-scale, essentially 1d and uniform, macroscopic flow field. Moreover, chemical transport model discrimination often requires breakthrough curves that extend over the late time tailing, which are particularly difficult to determine in field conditions, due both to interruptions or lack of practicality in well monitoring at long times, and to detection limits of measurement methods. While reliance on such 1d (section averaged, over some control plane) breakthrough curves may not be ideal, it is often the *reality* in terms of feasible data acquisition. As a direct consequence, model selection, model parameter fits, and model calibration results may each (and all) be non-unique and lead to confusing or conflicting conclusions. It is therefore critical that we at least select from mechanistic-stochastic models based on fundamental laws of physics, with parameters that have physical meaning, as discussed in Sect. 3.3.2, rather than from models invoking purely statistical distributions or assumptions known to be incorrect.

5 Concluding remarks

The ideas, arguments and perspectives offered here represent an effort to somehow summarize and synthesize an understanding of existing approaches and methods proposed to quantify conservative chemical transport in subsurface hydrological systems. The literature on this subject is vast, extending over decades, and measurements and observations of chemical transport range from pore-scale microfluidic laboratory cells to aquifer field scales. A similarly broad range of model formulations has been proposed to quantify and interpret these measurements/observations. And yet, outcomes of these efforts are often largely unsatisfactory.

We contend that modeling obstacles arise largely because domain heterogeneity – in terms of porosity, hydraulic conductivity, and geochemical properties – is present over multiple length scales, so that "unresolved", practically unmeasurable heterogeneities and preferential pathways arise at every length scale. Moreover, while *spatial* averaging approaches are effective when considering overall fluid flow – wherein pressure propagation is essentially instantaneous and the system is "well mixed" – purely *spatial* averaging approaches are far less effective for chemical transport, essentially because well-mixed conditions do not prevail. We assert here that an explicit accounting of *temporal* information, under uncertainty, is an additional – but *fundamental* – component in an effective modeling formulation. As a consequence, we argue that for continuum-scale analysis, mechanistic-stochastic models such as those outlined in Sect. 3.2 must be invoked to account explicitly for both "additional" temporal effects and unresolved heterogeneity. Clearly, no single model is "best" for all situations and objectives, but any selected model must be physically relevant and justified.

We further assert, as an outcome of these arguments, that "upscaling" of chemical transport equations – in the sense of attempting to develop and apply chemical transport equations at large length scales based on measurements and model parameter values obtained at significantly smaller length scales – is very much an unattainable holy grail. Rather, because probabilistic considerations required to account for small-scale fluctuations do not necessarily "average out" – and can propagate from local to larger spatial scales – we maintain that it is necessary to formulate and calibrate models, and then apply them, over spatial scales with similar orders of magnitude.

In all of our efforts to reasonably model chemical transport in subsurface hydrological systems, we should recognize and accept the objective of advancing our science by integrating theory, computational techniques, laboratory experiments and field measurement, with the aim of extracting broadly applicable insights and establishing practical, functional tools. In this context, as a close colleague and mentor said to me many, many years ago, "remember, this is hydrology, with very real problems to address…we're not doing string theory".

We have included many points for discussion and open thought. Understandably, the reader may not agree with all arguments and conclusions raised here, but scholarly debate is critical: it is hoped that this contribution will stimulate further discussion, assist in ordering classification of the (often confusing) terminologies and considerations, and identify the most relevant, real questions for analysis, implementation and future research.

We hope that the above thoughts and illustrations (i) encourage careful consideration prior to data collection, whether from field measurements, laboratory experiments, and/or numerical simulations, (ii) assist in experimental design and subsequent analysis, and, even more significantly, (iii) influence the research agenda for the field by challenging researchers to ask and address appropriately formulated questions. In terms of "modeling" efforts: recall the statement by Manfred Eigen (Nobel prize chemistry, 1967): "A theory has only the alternative of being right or wrong. A model has a third possibility: it may be right, but irrelevant."

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