# 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~~these efforts~~ have remained largely unsatisfactory, however, largely because domain heterogeneity – ~~(~~characterized for example by~~in terms of, e.g.~~ 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. ~~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 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 ~~is very much~~ an unattainable "holy grail". Rather, we maintain that it is necessary to formulate, calibrate and apply models using measurements at similar scales of interest~~, in both space and time~~.

**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 ~~layers~~ 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 ~~layers~~ and subsurface formations ~~can~~ 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~~recognition~~ 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"~~, has become broadly accepted only more recently~~. Indeed, much research on flow and transport in porous media, dating since ~~particularly from~~ ~1950 ~~1990, but also essentially to date~~, 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 ~~use of~~ 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~~quantification~~ 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~~remained largely unsatisfactory~~. We discuss the reasons for this~~, in detail,~~ 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: ~~, wherein~~ 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 (e.g. advection-*diffusion*) equation for transport, while case (ii) requires Darcy (or related) equation solutions for the underlying flow field, coupled with solution of a governing transport equation for chemical transport. *Note:* here and throughout, we shall use the terms "*continuum level*" and "*continuum scale*" in reference to case (ii) scenarios, and "*pore-scale*" to refer to case (i) scenarios, although we recognize that pore-scale Navier-Stokes and advection-diffusion equations, too, are continuum partial differential equations.

*Disclaimer:* Here and throughout this contribution, the overview comments and references to existing philosophies, methodologies and interpretations are written mostly in broad terms, with only limited citations selected from the vast literature. This approach is taken with a clear recognition and respect for the extensive body of literature that has driven our field forward over the last decades, but with the express desire to avoid any risk of unintentionally alienating colleagues and/or misrepresenting aspects of relevant studies. *As an Opinion contribution, and with length considerations in mind, there is no attempt to provide an exhaustive listing and description of relevant literature.*

**1.2 Assertions**

The pioneering paper of Gelhar and Axness (1983) focused on quantifying conservative chemical transport at the continuum level. They expressed heterogeneity-induced chemical spreading in terms of the (longitudinal) macrodispersion coefficient – as it appears in the classical (macroscopically 1d) advection-dispersion equation – with knowledge of the variance and correlation length of the log-hydraulic conductivity field and the mean, ensemble-averaged fluid velocity. The conceptual approach embodied in Gelhar and Axness (1983) – and by many researchers since then (as well as previously) – was founded on delineation of the *spatial distribution* of the hydraulic conductivity, and application of an averaging method to yield a governing transport equation with "effective parameters" that describes chemical transport at a given length scale (e.g. Dagan, 1989; Gelhar, 1993; Dagan and Neuman, 1997).

In contrast, we assert here that *spatial* information, *alone*, is generally *insufficient* for quantification of chemical transport phenomena. Rather, *temporal* information is an additional, but *fundamental*, component in an effective modeling formulation. In the discussion below, we shall justify this argument by a series of examples. We examine (i) *spatial* information on, e.g. the hydraulic conductivity distribution at the continuum level, or distribution of the solid phase at the pore-scale level; and (ii) *temporal* information on, e.g. contaminant (tracer, "particle") transport mobility and retention in different regions of a domain. We thus define a type of "information hierarchy", with different types of information required for different flow and chemical transport problems of interest.

As an outcome of the above assertion and the discussion below, we further assert that

114 "upscaling" of chemical transport equations – development and application of chemical transport
115 equations at large (length) scales, with corresponding parameter values, based on measurements
116 and model parameter values obtained at significantly smaller length scales – can be considered an
117 unattainable~~is very much a~~ "holy grail". Rather, we maintain that it is necessary to formulate and~~,~~
118 calibrate models, and then apply them~~models, using measurements~~ over spatial scales with
119 relatively similar orders of magnitude~~in both space and time~~. This does not exclude use of similar
120 equation *formulations* at different spatial scales, but it does entail use of different parameter values,
121 at the relevant scale of interest, that cannot be determined *a priori* or from purely spatial or flow-
122 only measurements.
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125 **1.3 Approach – Outline**
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127 While our focus is on chemical transport, knowledge of fluid flow and delineation of the velocity
128 field throughout the domain is a prerequisite. We therefore first discuss fluid flow as an intrinsic
129 element ~~aspect~~ 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 ~~(porous and/or fractured)~~ can provide ~~basic~~ insight
    regarding overall fluid conduction in the domain, as a function of "conducting element"
    density. We emphasize that without direct simulation of fluid flow ~~(as well as chemical
    transport)~~ in such a system, this type of analysis ~~is insufficient in terms of~~does not
    ~~defining~~delineate the actual flow field and velocity distributions throughout the domain.
(2) Spatial information on~~, in particular,~~ 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 ~~in terms of~~to defin~~ing~~e
    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 ~~considered~~ 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

154   (2).

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156

157   **2 Fluid flow**

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159   ~~Prior to actually solving for fluid flow, to determine the underlying velocity field, efforts are~~
160   ~~sometimes invested in considering geometrical (structural) information, for example, when~~
161   ~~examining fracture networks in essentially impermeable host rock.~~ Analysis of the geometry of
162   structural elements in a domain can yield basic insights on fluid flow patterns. This approach is
163   used, for example, when examining fracture networks in essentially impermeable host rock. As
164   discussed below, however, full delineation of the underlying velocity field ultimately requires
165   solution of equations for fluid flow.

166       In this context, percolation theory (Stauffer and Aharony, 1994) is particularly useful in
167   determining, statistically, whether or not a domain with $N$ "conducting elements" (e.g. fractures)
168   ~~is~~ includes sufficient element density to form a connected pathway enabling fluid flow across the
169   domain. One can estimate, for example ~~in this context~~, the critical value, $N_c$, for which the domain
170   is "just" connected, as a function of fracture length distribution, or the critical average fracture
171   length as a function of $N$ needed to reach domain connectivity (Berkowitz, 1995). Similarly,
172   percolation theory shows how the overall hydraulic conductivity of the domain scales as the
173   number of conducting elements, $N$, relative to the $N_c$ critical number of conducting elements
174   required for the system to begin to conduct fluid. Percolation theory also addresses diffusivity
175   scaling behavior of chemical species. But, fundamentally, percolation is a statistical framework
176   suitable for large ("infinite") domains, and provides universal scaling behaviors with no coefficient
177   of equality; see e.g., Sahimi (2021) for detailed discussion.

178       Other approaches have been advanced to analyze domain connectivity, for example using
179   graph theory and concepts of identification of paths of least resistance in porous medium domains
180   (e.g. Rizzo and de Barros, 2017), or topological methods (e.g. Sanderson and Nixon, 2015). Like
181   percolation theory, such approaches provide useful information and "estimates" on the hydraulic
182   connectivity and flow field, and even on first arrival times of chemical species, without solving
183   equations for fluid flow and chemical transport. However, these methods do not provide full
184   delineation of the flow field and velocity distribution throughout a domain.

185       These considerations indicate ~~It is thus clear~~ that, in general, ~~there are~~ dynamic aspects of fluid
186   flow are critical ~~, over and above pure structure~~: knowledge of pure geometry is not sufficient, and
187   *we must actually solve for the flow field*, at either the pore-scale or a continuum scale, to determine
188   the velocity field and actual flow paths throughout the domain. Delineation of a flow field and
189   velocity distribution by solution of the Navier-Stokes equations (or Stokes equation for small
190   Reynolds numbers), or by solution of the Darcy equation, may be considered "rigorous", correct
191   and effective. But in the process of solving for the flow field, two *key* features arise, one more
192   relevant to pore-scale analyses, and the other more relevant to continuum-scale analysis, as
193   detailed in Sect. 2.1 and Sect. 2.2, respectively.

## 2.1 Pore-scale flow field analysis

Why is knowledge only of the geometrical "static" structure (spatial distribution of solid phase) insufficient to know the flow dynamics in a pore-scale domain? Consider the 2d domain shown in Figure 1, containing sparsely and randomly distributed obstacles (porosity of 0.9). Figure 1 shows solutions of the Navier-Stokes equations for two Reynolds number (Re) values. [Recall: Re $\equiv$ $\rho v L / \mu$, where $\rho$ and $\mu$ are density and dynamic viscosity of the fluid, respectively, $v$ is fluid velocity, and $L$ is a characteristic linear dimension. Here and throughout, the fluid is assumed to have constant viscosity.] Andrade et al. (1999) showed clearly that well-defined preferential flow channels at lower Re, while at higher Re, channeling is less intense and the streamline distribution is more spatially homogeneous in the direction orthogonal to the main flow. The domain shown in Fig. 1 is not intended to represent a natural geological domain, but rather to illustrate streamline behavior in even relatively simple pore-scale geometries.

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

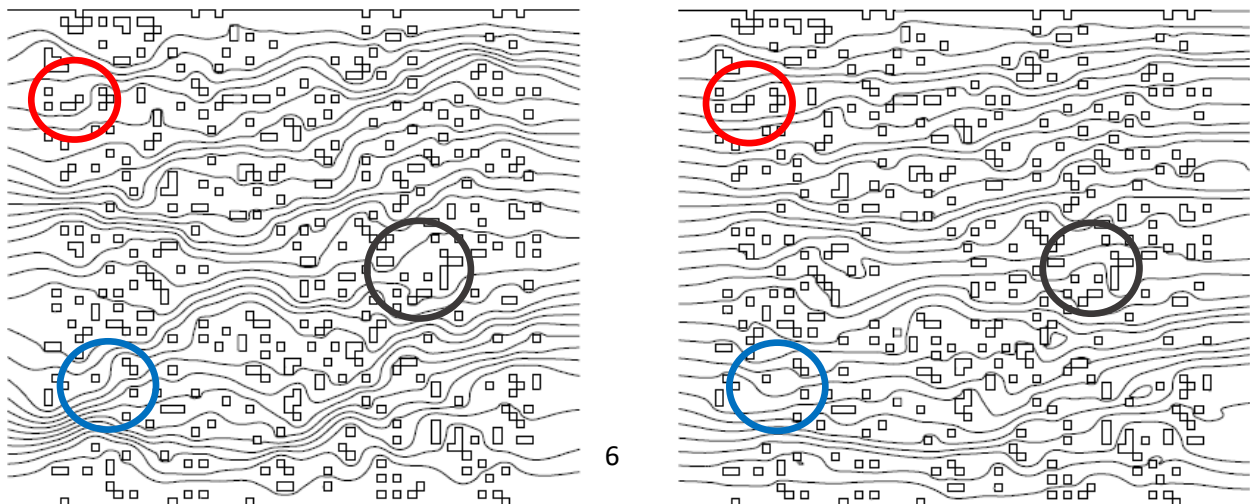
Clearly, then, except in highly idealized and simplified geometries, use of a purely analytical solution to identify the full velocity field and streamline patterns at the pore scale is not feasible. Moreover, the extent and changes in streamlines are not intuitively obvious without full numerical solution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

(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 (modified from Andrade et al., 1999, https://doi.org/10.1103/PhysRevLett.82.5249; 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 ~~(spatial distribution of the hydraulic conductivity)~~ 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, $K$.

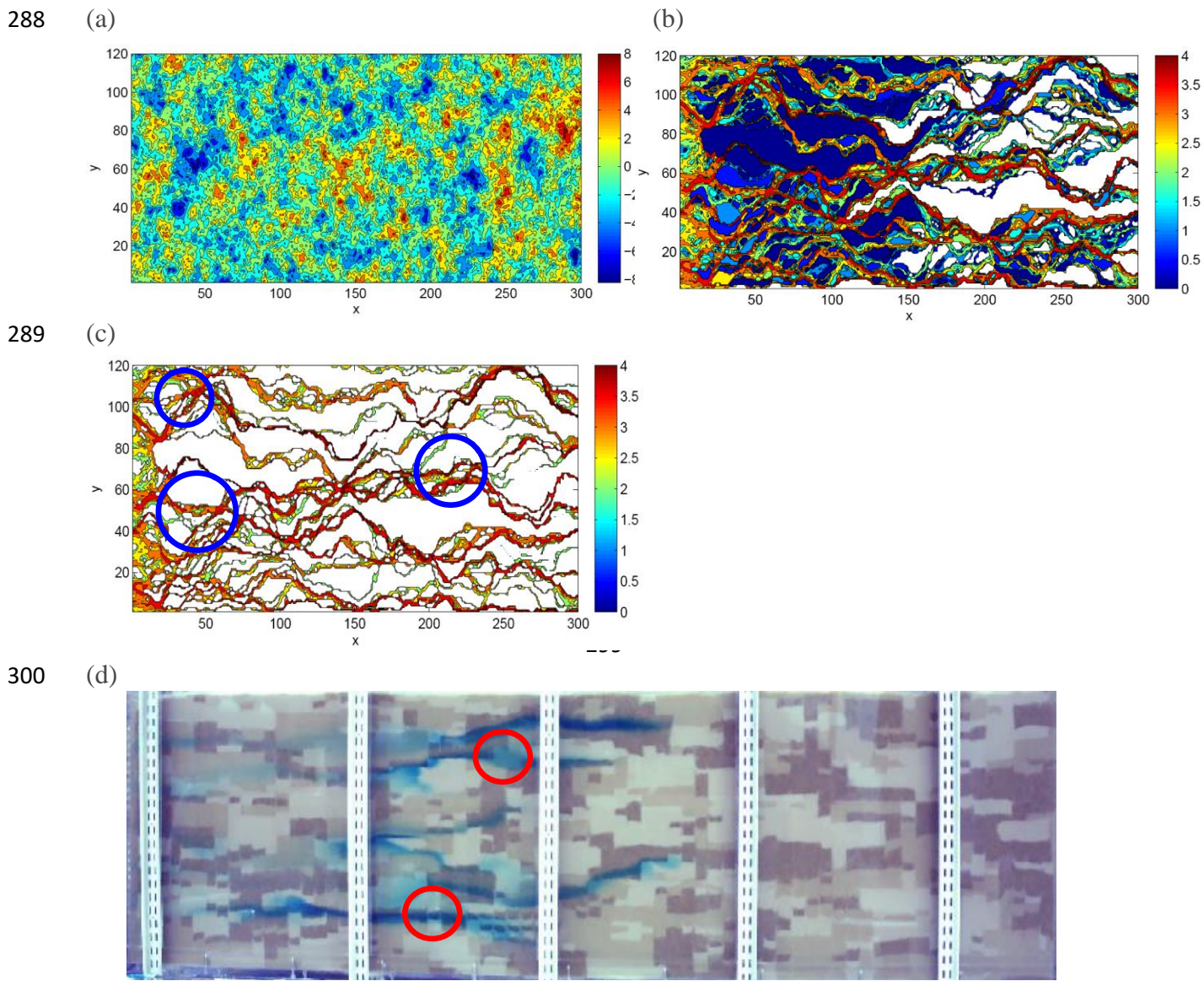
Figure 2 represents a realization of a numerically-generated (statistically homogeneous, isotropic, Gaussian) hydraulic conductivity ~~($K$)~~ 2d domain. The Darcy equation solution for this domain yields values of hydraulic head throughout the domain; these are converted to local velocities, to enable 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 ~~(e.g. homogeneous media),~~ 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).]

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

288    (a)                                                                (b)

289    (c)

300    (d)

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312    **Figure 2.**   Maps of (a) hydraulic conductivity, *K*, distribution in a domain with 300 × 120 cells, (b)
313    preferential pathways for fluid flow (and chemical transport), and (c) preferential pathways through cells
314    that each contain a visitation of at least 0.1% of the total number of chemical species particles injected into

315  the domain (flux-weighted, along the entire inlet boundary). Flow is from left to right. Note that the color
316  bars are in $\ln(K)$ scale for Figure 2a, and $\log_{10}$ number of particles for Figures 2b,c (modified from Edery
317  et al., 2014; © with permission from the American Geophysical Union 2014). (d) Laboratory flow cell, 2.13
318  m length, with an exponentially correlated K structure, showing preferential pathways for blue dye injected
319  near the inlet (flow is left to right); dark, medium, and light colored sands represent high, medium and low
320  conductivity, respectively (modified from Levy and Berkowitz, 2003; © with permission from Elsevier
321  2003). The circles shown in (c) and (d) highlight two (of many) regions in which the pathways are seen to
322  contain lower $K$ "bottlenecks".
323

324  It is significant, too, that fluid flow ~~(and chemical transport)~~ occur~~s~~ in preferential pathways
325  that contain low conductivity sections (indicated by circles in Figs. 2c,d). How do we explain
326  passage through low hydraulic conductivity "bottlenecks" ~~(low hydraulic conductivity patches)~~
327  within the preferential pathways, rather than ~~and that fluid (and chemicals) do not~~
328  ~~migrate~~migration "only" through the highest conductivity patches?
329  To address this question, we ~~begin by~~first consider~~ing~~ what happens in a 1d path. Consider
330  two paths, each containing a series of five porous medium elements ~~(or blocks)~~, with distinct
331  hydraulic conductivity values, ($K_i$~~) values~~. Consider Path 1, with a series hydraulic conductivity
332  values of 3, 3, 3, 3, 3, and Path 2, with values 6, 6, 1, 6, 6 (specific length/time units are irrelevant
333  here). The value of $K = 1$ represents a clear "bottleneck" in an otherwise higher $K$ path than that
334  of Path 1. In a 1d series, however, the overall hydraulic conductivity ($K_{overall}$) of the path is given
335  by the harmonic mean of the conductivities of the elements comprising the path: $K_{overall} = 5 / (\Sigma_{i=1,5}$
336  $1/K_i)$; significantly, in the two cases here, both paths have $K_{overall} = 3$~~!~~. So a "bottleneck" ($K=1$)
337  can be "overcome" and does not cause necessarily ~~cause~~ a potential pathway to be less "desirable"
338  than a pathway without such "bottlenecks". In other words, flow through pathways containing
339  some low $K$ regions should be expected. Of course, in 2d and 3d systems, patterns of heterogeneity
340  and pathway "selection" by water/chemicals are significantly more "complicated", but the
341  principle discussed here for 1d systems still holds, in the sense that lower hydraulic conductivity
342  ("bottleneck") elements can (and do) exist in the preferential pathways (e.g. Margolin et al., 1998;
343  Bianchi et al., 2011).
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346  **3 Chemical transport**
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348  We now consider the next level of the "information hierarchy" outlined in Sect. 1.3. To quantify
349  the evolution of a migrating chemical plume, knowledge of the flow field is not generally
350  sufficient, and additional means to characterize and quantify the behavior are needed. Dynamic
351  aspects of chemical transport require us to think (also) in terms of *time*, not just *space* and physical
352  structure. Moreover, it is generally insufficient to determine the transport of the chemical plume
353  center of mass. Rather, in terms of water resource contamination and remediation, for example, it
354  is critical to characterize, respectively, the early and late arrival times at compliance ~~(or~~
355  monitoring~~)~~ regions downstream of the ~~region~~ (point, areal, or volumetric~~)~~ region in which the
356  chemical species entered the system.

357    As we show below, it becomes clear that, ~~in general,~~ there are dynamic aspects of chemical
358    transport, ~~on~~ over and above the role of the flow field~~:, and~~ *we must actually solve for chemical*
359    *transport*, at either the pore-scale or a continuum scale, to determine the ~~spatiotemporal (~~spatial
360    plume and/or temporal breakthrough curve~~)~~ evolution of the migrating chemical plume. In *both*
361    pore-scale and continuum-scale domains, the *critical* control that arises is that of time, ~~(~~in addition
362    to space~~)~~. This is in sharp contrast to fluid flow at pore and continuum scales, as shown in Sect.
363    2.1 and Sect. 2.2: pore-scale fluid flow displays changing streamlines with changes in hydraulic
364    gradient, while continuum-scale fluid flow follows distinct but difficult to identify preferential
365    flow paths essentially independent of the hydraulic gradient.

366    We point out, too, that for both pore-scale and continuum-level scenarios, one can solve~~,~~
367    explicitly~~,~~ a governing equation for transport. Alternatively, ~~though,~~ one can obtain an
368    "equivalent" solution by solving for ~~(Lagrangian framework)~~ "particle tracking" of transport along
369    the calculated streamlines, in a Lagrangian framework. In other words, particle tracking methods
370    essentially represent an alternative means to solve an ~~((~~integro-~~)~~partial differential~~)~~ equation for
371    chemical transport; such methods can be applied, too, when the precise partial differential equation
372    is unknown or the subject of debate. We also note that solution of the relevant equations for fluid
373    flow and chemical transport is sometimes achieved by (semi-)analytical methods, if the
374    flow/transport system can be treated sufficiently simply (e.g. as macroscopically, section-averaged
375    1d flow and transport in a rectangular domain).

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

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384    **3.1 Pore-scale chemical transport analysis**

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

397     the mean particle velocity and mean particle displacement distance per transition (or "step").

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

409       The behavior shown in Fig. 3 is essentially well-known from extensive simulations and
410     experiments appearing in the literature. This behavior is described here to stress the importance of
411     *temporal* effects, and to point out that information only of the advective velocity field – as
412     discussed in Sect. 2.1 and Sect. 2.2 – is not sufficient to "predict" chemical transport.

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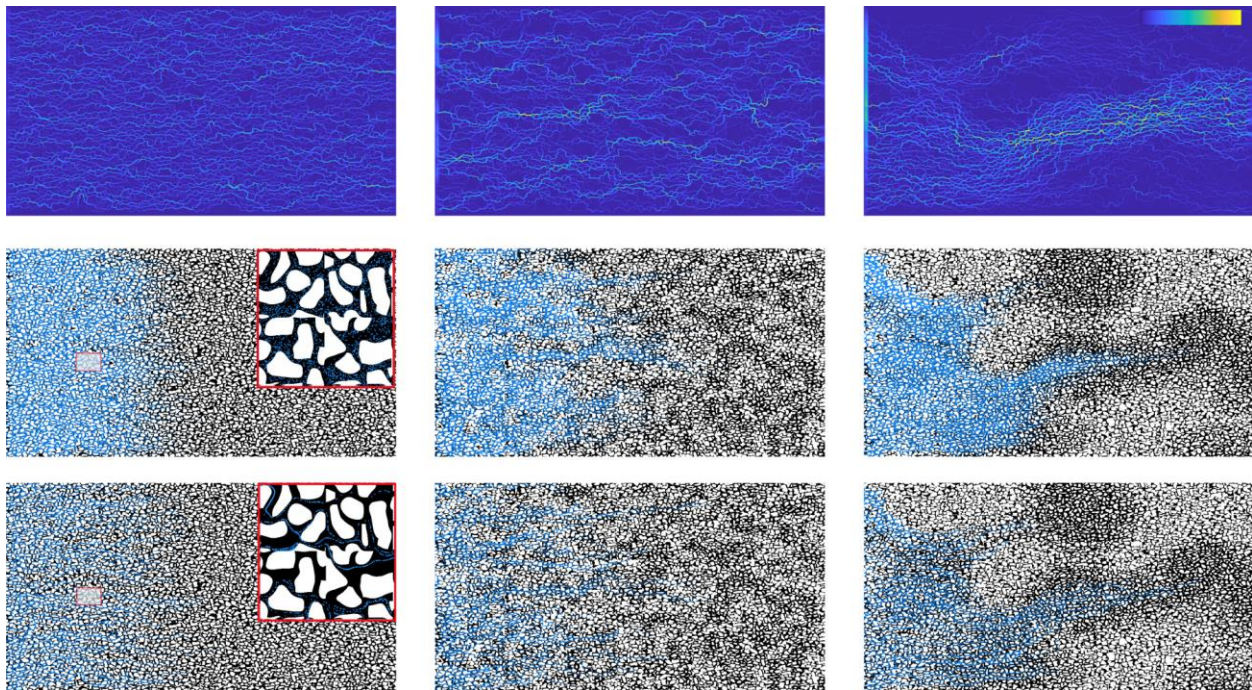
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416 **Figure 3.** Fluid velocities and chemical migration in three porous media configurations (from left to right):
417 homogeneous system, randomly heterogeneous system, and structured heterogeneous system. The upper
418 row shows the (normalized) velocity field for the three configurations; the color bar represents relative
419 velocity, with dark blue being lowest. The middle and lower rows show, respectively, numerically-
420 simulated particle tracking patterns of an inert chemical species (blue dots) at Pe = 1 (middle row) and Pe
421 = 100 (lower row) for the three configurations (white color indicates solid phase; black color indicates
422 liquid phase). Note: The particles plumes are shown at 10% of the final time of each simulation; absolute
423 travel times differ among the plots. The insets in the left side plots of the middle and lower rows show the
424 pore-scale chemical species distributions; note the more diffuse pattern for Pe = 1 (from Nissan and

### 3.2 Continuum-scale chemical transport analysis

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

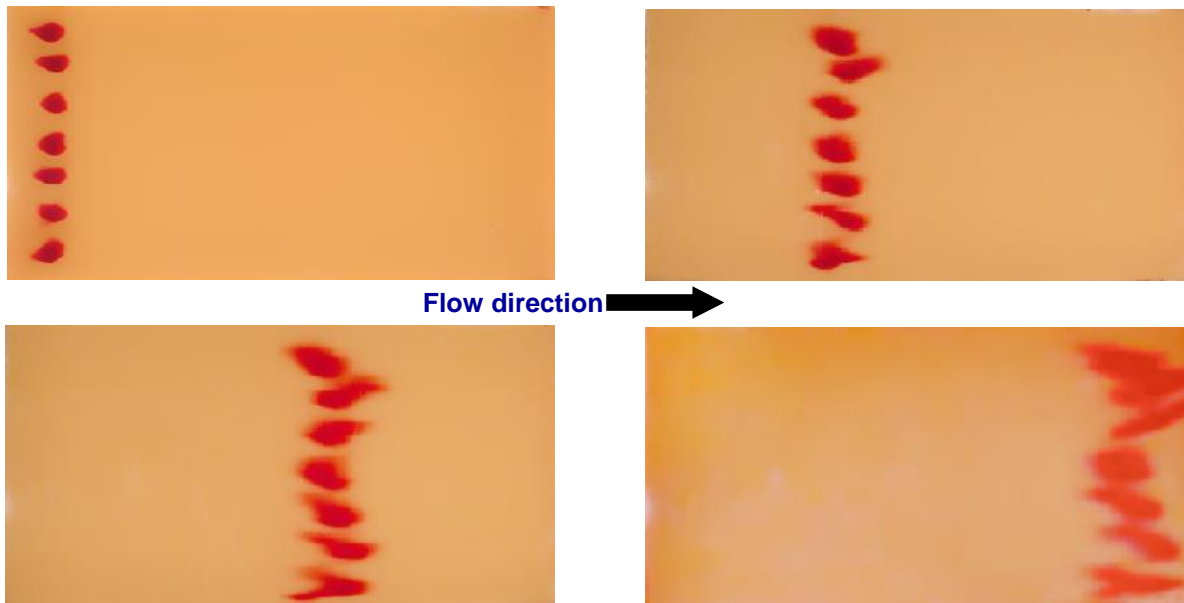
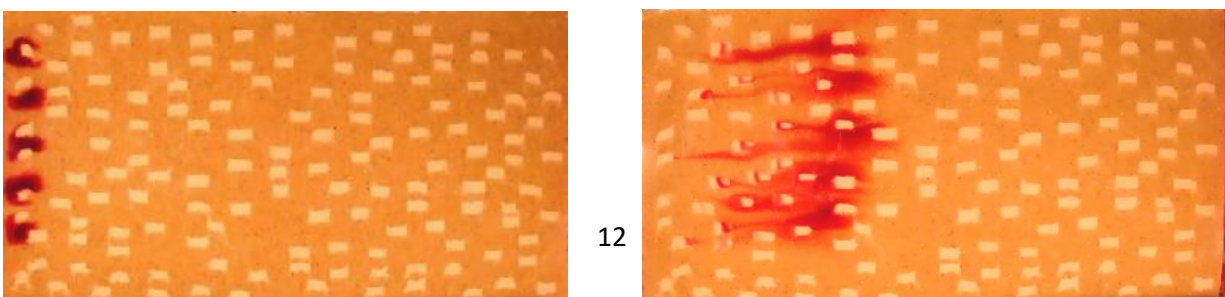



**Figure 4.** Photographs of dye transport in a flow cell (internal dimensions $0.86 \times 0.45 \times 0.10$ m) containing a uniform packing of quartz sand (average grain diameter 0.532 mm), under a constant flow rate with Pe $>1$, at four times (modified from Levy and Berkowitz, 2003; © with permission from Elsevier 2003).

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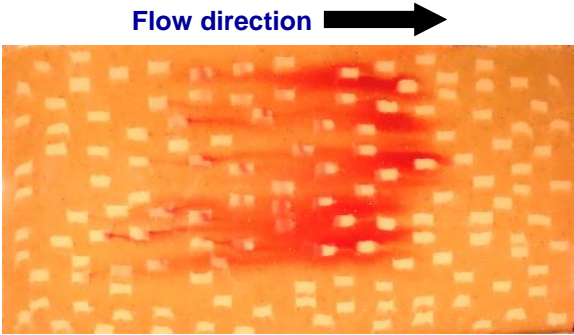
483

**Flow direction**

484 **Figure 5.** Photographs of dye transport in a flow cell (internal dimensions $0.86 \times 0.45 \times 0.10$ m) containing
485 a randomly heterogeneous packing of quartz sand, under a constant flow rate with Pe >1, at three times.
486 The rectangular inclusions comprise sand with an average grain diameter ~0.5× smaller, and hydraulic
487 conductivity ~3× lower, than the surrounding sand matrix (modified from Levy and Berkowitz, 2003; ©
488 with permission from Elsevier 2003).
489

490     Most notably, in both Fig. 4 and Fig. 5: (i) each of the plumes has a different, unique pattern,
491 which continues over the duration of the plume migration; and (ii) none of the plumes is
492 "elliptical", as expected in classical Fickian transport theory and embodied in solutions of the
493 classical advection-dispersion equation (ADE). Indeed, vertical averaging of each plume shown in
494 Fig. 4 and Fig. 5, at each time, does not yield Gaussian (normally distributed) concentration
495 profiles, but rather asymmetrical, "heavy-tailed" profiles.
496     At this juncture, note that here and below we use the terms "non-Fickian", or "anomalous" –
497 others sometimes use the terms "pre-asymptotic" or "pre-ergodic" – to denote any chemical
498 transport behavior that differs from that described by the classical ADE or similar type of
499 continuum-scale formulation. Typically, though, non-Fickian transport is characterized by early
500 and or late arrival times of migrating chemical species to some control or measurement plane/point,
501 relative to those resulting from solution of the ADE. The ADE applies to so-called Fickian
502 behavior, in the sense that it accounts for mechanical dispersion as a macroscopic form of Fick's
503 law; mechanical dispersion arises as an "effective" (or "average") quantity that describes local
504 fluctuations around the average (advective) fluid velocity. Thus, in this formulation, a pulse of
505 chemical introduced into a macroscopically 1d, uniform velocity, for example, leads to temporal
506 and spatial concentration distributions that are equivalent to a normal (Gaussian) distribution.
507     It is in this context that the term "homogeneous" packing used above is placed in quotation
508 marks, to indicate that in natural geological media, "homogeneity" does not really exist. Any
509 natural geological sample of porous medium contains multiple scales of heterogeneity; and at each
510 particular scale of measurement, "unresolved" heterogeneities that are essentially unmeasurable
511 are present (even scanning electron microscopy and atomic force microscopy have limits of spatial
512 resolution, for example!). And thus, as seen in Fig. 4 for example, the overall transport pattern

even in an "homogeneous" system can be non-Fickian (anomalous). *We therefore emphasize that because natural heterogeneity in geological formations occurs over a broad range of scales, "normal" (Fickian) transport tends to be the "anomaly", whereas "anomalous" (non-Fickian) transport is ubiquitous, and should be considered "normal".*

Moreover, as noted in Sect. 2.2, streamlines are not altered with changes in the overall hydraulic gradient, at the continuum (Darcy) scale, as long as laminar flow conditions are maintained, because increasing the hydraulic gradient increases the fluid velocity along the existing, ("predefined") streamlines by the same factor. However, the character of chemical transport can be altered, as the change in residence time in the domain affects the relative effects of advection and diffusion space. And in domains with heterogeneous distributions of hydraulic conductivity, the local Pe (Sect. 3.1) can vary more strongly, too.

Thus, we argue that patterns of chemical transport cannot be fully determined from information only on the velocity field; solution of an appropriate continuum-scale transport equation cannot be avoided. In conclusion, then, and with particular reference to the (conceptually and theoretically beautiful) classical ADE – and to "conventional" conceptual understanding and quantitative description of chemical transport – we suggest that one must separate mathematical convenience and wishful thinking from the reality of experiments: there is a definitive need for more powerful formulations of transport equations. In this context, one is reminded of the quotation by the biologist Thomas Henry Huxley: "The great tragedy of science—the slaying of a beautiful theory by an ugly fact." (*President's Address to the British Association for the Advancement of Science, Liverpool Meeting, 14 Sep 1870*).

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

So how *do* we effectively model chemical transport?

As noted at the outset of Sect. 2, solution of the Navier-Stokes or Darcy equations to determine the full *flow* field and velocity distribution in a given porous medium domain has been proven correct and effective in most applications, and is well-accepted in the literature. However, modeling of chemical transport is more contentious, the reasons for which we expand upon below.

We argue here that modeling of chemical species transport requires us to think in terms of *time*, not just *space*. To assist the reader to enter this frame of thinking, and to sharpen our conceptualization, we provide two examples to illustrate aspects of time and space in the context of chemical transport dynamics:

(1) The classical example of the brachistochrone (ancient Greek: "shortest time"), or path of fastest descent, is the curve (path) 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. (Correct solution: Johann Bernoulli, 1697) 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)[1], as demonstrated by Johann

553    Bernoulli in 1697. (sSee: http://old.nationalcurvebank.org//brach/brach.htm).

554    (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.

560    These simple examples help to emphasize the errors introduced by traditional conceptual thinking, wherein the effects of *spatial* transport and domain heterogeneity are quantified only on the basis of spatial characteristics. It is worth recalling, too, Einstein's quantitative treatment of Brownian motion (Einstein, 1905). Prior to his analysis, researchers applied – with puzzlement – a time-dependent velocity, *v*, to quantify experimental measurements. Einstein (1905) instead examined a recursion relation and expansion that led to a diffusion equation whose solution showed, for the first time, that the root mean squared displacement of particles undergoing 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".

570    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 in (while traveling through, or in/out of) lower velocity regions (pore scale or continuum scale) 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.

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

584    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.

590    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

593    have been advanced over the decades, with accompanying, analytical and numerical
594    solutions — and yet, remarkably, comparative studies against actual laboratory data remain
595    limited, and tests with field measurements are even sparser (see also Sect. 4 for further
596    discussion of this point).

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

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

608 We first discuss briefly aspects of high-resolution hydrogeological modeling in Sect. 3.3.1,
609 and then focus on "effective" transport equation modeling in Sect. 3.3.2. We emphasize that the
610 latter approach is applicable to both small- and large-scale domains. The former approach is
611 generally intended for large- (field-)scale systems, (although, ~~in a sense, the same approach~~it is in
612 some sense often applied for detailed pore-scale modeling~~)~~; this approach is not particularly
613 contentious, per se, but is hampered by the complexity and cost associated with the demand for
614 highly detailed hydrogeological information. Therefore, research work remains heavily invested
615 in "effective" transport equation modeling.

616

617

618 **3.3.1 High-resolution domain delineation and modeling**

619

620 Efforts to resolve large-scale aquifer systems, to delineate the hydraulic conductivity distribution
621 at increasingly higher resolutions, began in earnest in the 1990s. Analysis of field sites emphasized
622 ~~(relatively)~~ high-resolution discretization of domain structure (e.g. "blocks" of the order of 10 m$^3$
623 at the field scale (Eggleston and Rojstaczer, 1998); $200 \times 200 \times 1$ m$^3$ at large regional scales
624 (Maples et al. 2019)~~)~~. These efforts, first focusing on determining the fluid flow field, and
625 subsequently on delineating pathways for chemical transport, began largely because of
626 dissatisfaction with results of application of 1d, 2d, 3d forms of an "effective" (averaged) ADE
627 (see further discussion in Sect. 3.3.2). Acquiring high-resolution measurements of structural (e.g.
628 mineralogy, porosity) and hydrological properties (e.g. hydraulic conductivity) was made more
629 feasible in recent years by advances in hydrogeophysics, and as well as by advances in
630 computational capabilities that enable incorporation of this information in finely-discretized
631 meshes, and numerical solution for fluid flow and chemical transport.

632 In these highly resolved, ~~(high-resolution)~~ gridded domains, the flow field can be determined

from solution of Darcy's law. Chemical transport is then simulated either by use of streamline particle tracking methods, by (accounting for advection and diffusion in a Lagrangian framework,) or via solution of a local, (mesh element) continuum-scale transport equation. For chemical transport, use of an advection-*diffusion* equation might appear preferable – given that it requires no estimate for the local dispersivity –, but some researchers apply an advection-*dispersion* equation, which necessitates use of mesh-scale dispersivity values that are either assumed or estimated from local measurements. The latter case assumes mesh-scale transport to be fully Fickian (recall Sect. 3.2) to quantify overall transport. More recently, we note that alternative formulations of a governing transport equation that incorporates broad temporal effects more broadly can also be used in this type of modeling approach; see, e.g. Hansen and Berkowitz (2020) for incorporation of a continuous time random walk method (discussed in Sect. 3.3.2) into this modeling framework.

[Parenthetically, we note that "analogous", high-resolution measurements are made at the pore-scale – in mm to decimeter rock core samples – as a basis for computationally-intensive modeling of fluid flow and chemical transport at these scales. Similar to the evolution of this approach for field-scale studies, high-resolution measurements advanced from use of 2d rock micrographs to advanced micro-computed tomography protocols (e.g. Thovert and Adler, 2011; Bijeljic et al., 2013; recall Sect. 2.1).]

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

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

**3.3.2 "Effective" characterization and modeling**

At least since the 1960's, the research community has focused enormous efforts on formulation of

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

Solutions of the ADE were compared against conservative tracer experiments in laboratory columns (generally 10-100 cm) to produce breakthrough curves of ~~(~~ concentration vs. time, at a set outlet distance~~),~~; but even from the outset, the applicability of the ADE was questioned by some researchers (e.g. Aronofsky and Heller, 1957; Scheidegger, 1959). Subsequent flow cell experiments demonstrated, for example, that the dispersivity constants are not actually constant, and change with length scale – even over tens of centimeters – to achieve even *approximate* fits to the measurements (e.g. Silliman and Simpson, 1987). Moreover, solutions of the ADE appear inadequate when compared to transport in laboratory flow cells with distinct regions of different 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 m~~M~~ov~~e~~ing 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 ~~of chemical species~~, in addition to the~~a~~ 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 should be recognized that~~it turns out that special, ~~(~~or limit~~)~~, cases of a general CTRW formulation lead to other well-known ~~related "subset"~~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), as explained in, e.g., Dentz and Berkowitz (2003) and Berkowitz et al. (2006). Indeed, in spite of frequent 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 $\ell'$ to $\ell$, $P_n(\ell')$ denotes the probability of a particle being located at $\ell'$ at (fixed) time step $n$, and $P_{n+1}(\ell)$ denotes the probability of the particle then being located at $\ell$ at step $n+1$. With this formulation in mind, Einstein (1905) and Smoluchowski (1906a,b) demonstrated that for $n$ sufficiently large and a sufficient number of particles undergoing purely (statistically) random movements *in space*, the spatial evolution of the particle distribution is equivalent to the solution of the (Fickian) diffusion equation. This elegant discovery demonstrated that a partial differential equation and its solution can be represented by following, numerically, the statistical movement of particles (i.e. particle tracking) following a random walk. Remarkably, random walk formulations are "generic" in the sense that they can be applied in a broad range of phenomena in physics, chemistry, mathematics, and life sciences; here, they describe naturally migration of chemical species (dissolved "particles" or "packets") in water-saturated porous media. Generalizing the partial differential equation to include transport by advection, solution of the ADE under various boundary conditions can then be determined by an appropriate random walk method.

The simple random walk given in Eq. 1 can be generalized by accounting for time, replacing the particle transition (or iteration) counter $n$ by a time distribution. The generalized formalism in Eq. 2, with the joint distribution $\psi(\mathbf{s}, t)$, called "continuous time random walk" and applied to transport, was first introduced by Scher and Lax (1973):

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

where $R_{n+1}(\mathbf{s}, t)$ is the probability per time for a particle to just arrive at site $\mathbf{s}$ at time $t$ after $n+1$ steps and $\psi(\mathbf{s}, t)$ is the probability rate for a displacement from location $\mathbf{s}'$ to time $\mathbf{s}$ with a difference

of arrival times of $t\text{-}t'$. It is clear that $\psi(\mathbf{s}, t)$ is the generalization of $p(\ell, \ell')$ in Eq. 1, and that the particle steps can each now take place at different times. Indeed, it is precisely this explicit accounting of a distribution of temporal contributions to particle transport, not just spatial contributions, that offers the ability to effectively quantify transport behaviors as expressed by, e.g. heavy-tailed, non-Fickian particle arrival times.

To where does the generalization in Eq. 2 lead us? In a mindset similar to that of Brownian motion, and Einstein's 1905 breakthrough mentioned above at the outset of Sect. 3.3, a puzzle arose about seven decades later for researchers attempting to interpret observations of electron transit times in disordered semiconductors. The electron mobility (defined as velocity per unit electric field), which was considered an intrinsic property of the material, was found to depend on variables that changed the duration of the experiment, such as sample length or electric field. Scher and Montroll (1975), considering Eq. 2, discovered that the mean displacement $\overline{\ell}$ of the electron packet does not advance as $\overline{\ell} = vt$, but rather as $\overline{\ell} \sim t^{\beta}$.

In the context of chemical transport in geological formations, the behavior $\overline{\ell} \sim t^{\beta}$ can be attributed to a wide distribution of transition times in naturally disordered geological media. In the CTRW formulation, the transition time distribution is characterized by a power law of the form $\psi(t) \sim t^{-1-\beta}$ for $t \to \infty$ and $0 < \beta < 2$; significantly, the resulting transport behavior is Fickian for $\beta > 2$. 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:

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

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 $\beta$ 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 $\beta \geq 2$), $M(t) \rightarrow \delta(t)$ 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. DentzBerkowitz et al., 20046), 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.

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

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

The efficacy of formulations that incorporate, whether explicitly or implicitly, some type of power-law characterization of temporal aspects of chemical transport, is now generally recognized in the literature. Indeed, applications of mobile-immobile, multirate mass transfer, time-fractional advection-dispersion, and general CTRW formulations have been applied quite extensively and successfully. In particular, solutions of Eq. 4 and related variants have interpreted a wide range of chemical transport scenarios: (i) pore-scale to meter scale laboratory experiments, field studies, and numerical simulations, in (ii) porous, fractured, and fractured porous domains, (iii) accounting for constant and time-dependent velocity fields, and (iv) for both conservative and reactive

832 chemical transport scenarios. Solutions to address some of these scenarios are more easily obtained
833 by use of particle tracking methods that incorporate the same considerations and power-law form
834 of $\psi(t)$, as embedded in Eq. 4.

835 ~~It should be recognized that, l~~Like the ADE, Eq. 3, the formulation given in Eq. 4 represents a
836 continuum-level mechanistic model (as derived in, e.g., Berkowitz et al. 2002), in the sense that
837 both equations contain clear advective and dispersive contributions. The occurrence of a broad
838 distribution of transition times, fundamental to CTRW and related approaches, emanates from a
839 variety of physical controls. Discussion in the literature about the need for "mechanistic models"
840 often uses the term rather loosely: "mechanistic" transport model equations are based on
841 fundamental laws of physics, with ~~(~~constant~~)~~ parameters that have physical meaning (e.g.
842 hydraulic conductivity, diffusivity, sorption), and thus offer process understanding. But to quantify
843 the spatiotemporal evolution of a migrating chemical plume, additional parameters are needed. ~~We~~
844 ~~argue that, b~~Because of the nature of geological materials, a transport equation should of course
845 capture the relevant physical mechanisms that influence the transport, ~~(~~as well as~~and~~ chemical
846 mechanisms, if the species is reactive~~) mechanisms that impact the transport~~,; but to do so, we
847 must *also* capture the uncertain characterization of hydrogeological properties due to the reality of
848 unresolved, ~~(~~unmeasurable~~)~~ heterogeneities at any length scale of interest. Thus, we suggest that a
849 *mechanistic-stochastic equation formulation* such as given in Eq. 4 is required. Such an equation
850 ~~(which~~ (i) incorporates a probability density function to account for temporal transitions that
851 cannot be determined only from spatial information~~) is required~~, (ii) describ~~es~~ing known transport
852 mechanisms ~~(and~~ with physically meaningful parameters~~)~~, and (iii) account~~s~~ing for unknown (and
853 unknowable~~!~~) information.

854 We note here, too, that other stochastic continuum averaging methods have been proposed in
855 the literature, in the same context of efforts to formulate a "general", "effective" transport equation
856 at a specific scale of interest (see further discussion on "effective" equations and "upscaling" in
857 Sect. 4). In many cases, though, sophisticated stochastic averaging and homogenization
858 approaches have led to transport formulations that are essentially intractable, in terms of solution,
859 and/or have remained at the level of hypothesis without being tested successfully against actual
860 data.

861
862

863 **3.3.3 Are fewer parameters always better? (Answer: No!)**

864

865 The term "modeling" is used in many contexts and with differing intents. However, in the
866 literature dealing with chemical transport in subsurface hydrological systems, there are frequent
867 but ~~(~~often misguided~~!)~~ "arguments" regarding "which model is better", with a major point of some
868 authors being the claim that "fewer parameters is always best". Not always. Indeed, some models
869 involve more parameters than others, but if these parameters have physical meaning and are needed
870 as factors to quantify key mechanisms, then "more parameters" is not a "weakness". We
871 emphasize, too, that when weighing use of *any* specific ~~(any!)~~ model, "better" also depends, ~~(~~at

872 least in part~~)~~**,** on what the modeling effort is addressing**.** ~~;~~ **C**~~c~~learly – ~~and~~ regardless of the number

873 of parameters – a "back-of-the-envelope" calculation using a simple model is sufficient if, for

874 example, one requires only an order of magnitude estimate of the center-of-mass velocity of a

875 migrating contaminant plume**,** ~~(~~or in other words, no need for artillery to swat a mosquito~~!)~~**.** [In

876 this context, quoting Albert Einstein regarding his simplification of physics into general relativity:

877 "Everything should be made as simple as possible, but not simpler."]

878    Considering chemical transport in subsurface geological formations, and the aim of

879 quantifying (modeling) the evolution of a migrating chemical plume in both space and time, we

880 return to focus on the ADE- and CTRW-based formulations discussed in Sect. 3.3.2. As noted in

881 the preceding sections, CTRW **and related** formulations ~~have been demonstrated repeatedly to~~**can**

882 describe ~~a~~ **transport**~~system~~ **behaviors** effectively~~, with sufficient parameters to account for the~~

883 ~~various mechanisms~~. Most significantly, the seminal work of Scher and Montroll (1975) showed

884 that the $\beta$ exponent *~~has~~ **must**~~to~~* be included because the mean displacement is not linear with time

885 (i.e. the mean displacement $\overline{\ell}$ of the electron packet does not advance as $\overline{\ell} = vt$, but rather as

886 $\overline{\ell} \sim t^{\beta}$ ). **Similarly**~~Thus~~, a corresponding parameter, relative to an ADE formulation invoking

887 Fickian transport, is unavoidable **when transport is non-Fickian**~~in such cases~~. ~~In a sense, too, one~~

888 ~~can argue that this parameter is not an "additional" parameter relative to the ADE; rather, a~~

889 ~~decision to invoke the ADE to quantify a transport problem simply assigns a value to this~~

890 ~~parameter, implicitly, as $\beta \geq 2$.~~

891    It should be recognized that ~~– while not (yet?) standard practice in the research community –~~

892 quantitative model information criteria, or model selection criteria, can be used to assess and

893 compare various model formulations that are applied to diverse scenarios (such as fluid flow,

894 chemical transport) in subsurface geological formations. These information criteria include AIC

895 (Akaike, 1974), AICc (Hurvich and Tsai, 1989), and KIC (Kashyap, 1982) measures, as well as

896 the Bayesian (or Schwarz) BIC (Schwarz, 1978). They are formulated to rank models, or assign

897 (probabilistic) posterior weights to various models in a multimodel comparative framework, and

898 therefore focus on model parameter estimates and the associated estimation uncertainty. As such,

899 these information criteria discriminate among various models according to (i) the ability to

900 reproduce system behavior, and (ii) the structural complexity and number of parameters.

901 Discussion of theoretical and applied features of these criteria is given elsewhere (e.g. Ye et al.,

902 2008). **Using such measures s**~~S~~pecifically in the context of the ADE and CTRW formulations,

903 with an accounting also of chemical reactions, ~~for example,~~ it was shown that while solution of an

904 ADE can fit measurements from some locations quite closely, the CTRW formulation offers

905 significantly improved predictive capabilities ~~(in the context of model assessment in the presence~~

906 ~~of uncertainty)~~ when examined against an entire experimental data set (Ciriello et al., 2015). In

907 addition, focusing on the most sensitive observations associated with the CTRW model provides

908 a stronger basis for model prediction, relative to the most sensitive observations corresponding to

909 the ADE model.

910    To conclude this section: Notwithstanding the above arguments, some readers might continue

911 to argue that the approach discussed here – viz., the need for time considerations as well as space

912   such (as embodied in the CTRW framework and related formulations) – is "inelegant" because it
913   requires more parameters relative to the classical ADE. In response, the reader is encouraged to
914   recall the words of Albert Einstein following criticism that his theory of gravitation was "far more
915   complex" than Newton's. His response was simply: "If you are out to describe the truth, leave
916   elegance to the tailor".

917

918

919   **4 The holy grail of upscaling, and myths about "a priori" parameter determination**

920

921   We begin by defining the term "upscaling" in the context of the discussion here on chemical
922   transport. As defined in the Introduction, Sect. 1.2, we use the term "upscaling" to describe the
923   effort to develop and apply chemical transport equations at large length scales, and identify
924   corresponding model parameter values, based on measurements and parameter values obtained at
925   significantly smaller length scales.
926        We attempt "upscaling" in the hope of developing governing equations for chemical transport
927   at larger and larger scales, from pore, to core, to plot, and to field length scales. Clearly, then,
928   "upscaling" is relevant to the modeling approach discussed in Sect. 3.3.2 – which focuses on use
929   of "averaged", or "effective" (often 1d, or section-averaged) transport equations – and not to the
930   high-resolution domain delineation and modeling approach of Sect. 3.3.1.
931        However, in light of the discussion in Sect. 2 and Sect. 3, we argue that "upscaling" of chemical
932   transport equations is very much an unattainable holy grail. Particularly in light of recognizing
933   temporal effects, in addition to spatial characterization, we maintain that it is necessary to
934   formulate and, calibrate and apply models, and then apply them, using measurements at similar
935   measurement scales of interest, in both space and time. Of course, similar equation *formulations*
936   can be applied at different spatial scales. But parameter values for transport equations cannot
937   generally be determined a priori or from purely spatial or flow-only measurements; *measurements*
938   *with a temporal "component", at the relevant length scale of interest, are required.*
939        In Sect. 4.1, we briefly discuss aspects of model calibration. This leads naturally to our
940   discussion of upscaling in Sect. 4.2.

941

942

943   **4.1 Parameter determination and model calibration**

944

945   First, it is prudent to offer some words about the need for parameter estimation, or model
946   calibration. Unless one is dealing with first principles calculations of a physical process such as
947   (e.g., molecular diffusion) in a perfectly homogeneous domain, *a priori* determination of model
948   parameters – for *any* model equation formulation – requires calibration against actual experimental
949   measurements.; Iin some limited cases, detailed numerical simulations can be used at small (pore)
950   scales, (e.g. using an advection-*diffusion* equation with the fluid phase, together with solution of
951   the Navier-Stokes equations to first determine the precise flow field in the pore space); but this

952 also necessitates detailed measurements of the pore structure such as obtained by computed
953 tomography measurements (e.g. Bijeljic et al., 2013). Indeed, then, at any realistic problem or scale
954 of interest, *all* chemical transport models require calibration.

955     This fundamental tenet should be clear and well-recognized, yet the literature contains all-too-
956 frequent – and both misguided and misleading – "criticism" of various model formulations,
957 claiming that "parameters are empirical because they are estimated by calibration (fitting) to
958 experiments"; additional "criticisms" follow, for example, that such as a model is therefore not
959 "universal", and/or "it therefore has no predictive capability". We address these latter "criticisms"
960 in Sect. 4.2. Parameters are *not* "empirical" simply because their values are determined by
961 matching to an experiment. Moreover, it should be recognized that application even of the
962 classical ADE at various column and larger scales requires estimates – obtained by calibration –
963 of dispersivity coefficients; and for high-resolution domain delineation and modeling as discussed
964 in Sect. 3.3.1, calibrated "block-scale" dispersivities are needed. [Note: If dispersivities are
965 not actually determined for a specific experiment, but selected from on the literature for "typical"
966 values of dispersivity, there is still a reliance on calibration from previous "similar" studies.]
967 Moreover, with reference to the desire for model parameters that represent fundamental, *spatial*
968 hydrogeological properties of the domain, note that even the classical ADE dispersivity parameter
969 is not uniquely identified with such properties; rather, it varies even in a given domain as a function
970 of chemical plume travel distance or time.

971     With regard to model "universality", recall that, for example, percolation theory (discussed at
972 the beginning of Sect. 2) offers "universal" exponents in scaling relationships. But even for this
973 type of convenient and useful, statistical model, such scaling relationships, too, can only advance
974 from "scaling" (e.g. $A \sim B$) to a full "equation" (e.g. $A = kB$) by calibration of a coefficient of
975 equality ($k$) against actual measurements. So even in "simple" models, model calibration cannot
976 be avoided.

977     To address "empiricism" – here enters the question of whether parameters of a particular model
978 (in this case, equations for chemical transport) have a physical meaning. As discussed in Sect.
979 3.3.2, a *mechanistic-stochastic equation formulation* such as given in Eq. 4 incorporates a
980 probability density function to describe known transport mechanisms in a stochastic sense; but
981 stochastic does not mean "unphysical", and the parameters as given in, e.g., particular functional
982 forms of $M(t)$ or $\psi(t)$ are indeed physically meaningful. For example, the key $\beta$ exponent
983 characterizing the power law behavior can be linked directly to the statistics of the hydraulic
984 conductivity field (Edery et al., 2014), or, in a fracture network, be determined from the velocity
985 distribution in fracture segments (Berkowitz and Scher, 1998), which is related directly to physical
986 properties of the domain. Similarly, corresponding parameters appearing in "subset" formulations
987 to quantify non-Fickian transport – e.g. mobile-immobile, multirate mass transfer, and time-
988 fractional derivative formulations – can be understood to have physical meaning (e.g. Haggerty
989 and Gorelick, 1995; Harvey and Gorelick, 1995; Carrera et al., 1998; Dentz and Berkowitz, 2003;
990 Berkowitz et al., 2006). These parameters, too, of course require determination by model
991 calibration to experimental data, (or where appropriate, to results of numerical simulations), just

992   as for ~~ADE and~~ any other model~~, including ADE~~ formulation~~s~~.

995   **4.2 Upscaling, the scale of interest, and predictive capabilities**

997   Upscaling of *fluid flow* "works" because ~~pressure propagation is essentially instantaneous.~~ ~~a~~At
998   the Darcy scale – which is the "practical" scale for most applications – flow paths and streamlines
999   do not change with increasing gradient (as long as a transition to turbulent flow is not reached)~~.,~~
1000  ~~T~~the equation formulation remains valid, and the fluid residence time in a domain is irrelevant
1001  because self-diffusion of water does not affect overall fluid fluxes. ~~Pore-scale flow analyses are~~
1002  ~~local and more specialized, and "upscaling" is not per se an objective.~~
1003  For chemical transport, though, the situation is totally different. Why? Because "upscaling"
1004  entails some kind of "coupled" averaging or ~~in~~ parameterization in both space *and* time, and it is
1005  far from clear how, if at all, this can be achieved. Moreover, small-scale concentration fluctuations
1006  do not necessarily "average out", but instead propagate from local to larger spatial scales. To
1007  illustrate another aspect of the complexity, the Péclet number (Pe) in heterogeneous media, with
1008  preferential pathways, varies locally in space (recall Fig. 3 and the discussion in Sect. 3.1).
1009  Averaging to obtain a macroscale ("upscaled") Pe must address the relative, locally varying effects
1010  of advection and diffusion in space, as well as the overall residence time in the domain; after all,
1011  it is these effects that dominate determination of the plume evolution. Thus, upscaling requires
1012  spatial averaging, but (at least an) *implicit* temporal averaging must also be included. It can be
1013  argued that no single, effective Pe can be defined for the entire domain; whether or not it is
1014  possible, and how, it is possible to average local Pe values to achieve a single, meaningful domain-
1015  scale Pe remains an open question. And whether we like it or not, even with complete information
1016  on the spatial (local) Pe distribution, the impact on the overall transport pattern evolution cannot
1017  be determined without actually solving for transport in the domain.
1018  For chemically reactive species, the transport situation becomes even more complex, because
1019  the local residence time, not just the local Pe, must be taken into consideration. Moreover, when
1020  precipitation or dissolution processes are present, the velocity field will change locally, introducing
1021  additional local temporal and spatial variability. And when sorption is present but tapers off – ~~(for~~
1022  ~~example,~~ when the cation exchange capacity is met~~, for example),~~ – even the diffusion coefficient
1023  itself changes. These factors further complicate attempts to upscale. [In this context, too, it should
1024  be noted that for chemically-reactive systems, it is well-known ~~(e.g. White and Brantley, 2003)~~
1025  that there is often a significant lack of correspondence between laboratory and field-based
1026  estimates of geochemical reaction rates and rates of rock weathering, with field-scale estimates –
1027  often based on macroscopically Fickian, ADE-like transport formulations – being generally
1028  significantly smaller (e.g. White and Brantley, 2003).]
1029  Thus, we suggest that focusing efforts on attempting to develop upscaling methodologies for
1030  chemical transport, based on any transport equation formulation, appears to be doomed largely to
1031  failure – as evidenced, too, by decades of research publications. Rather, we argue that because of

the subtle effects of temporal mechanisms, and their close coupling to spatial mechanisms, use of an "effective", or "averaged" continuum-level equation to describe chemical transport ~~(as opposed, e.g. to intensive numerical simulation using a streamline particle tracking method in a high-resolution hydraulic conductivity field)~~ requires calibration of a suitable model at the appropriate scale of interest, with model parameter values calibrated at essentially the same scale. The model can then be applied to examine transport behaviors over spatial scales with relatively similar orders of magnitude.

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

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

In contrast, CTRW and related transport formulations with explicit accounting of time effects, as outlined in Sect. 3.3.2, can be applied meaningfully to interpret real measurements and transport behavior at "all" scales. We *can* use the same equation formulation at different scales, with different but relevant parameters at each scale. We emphasize, too, that we do not argue for "hard" length scales~~,~~:~~ so that~~ in principle, e.g., an appropriate ~~(~~CTRW-based~~)~~ model calibrated at 20 cm will be applicable to 100 cm scales, and a model calibrated on a 100 m scale data set can be applicable at a kilometer scale (e.g. Berkowitz and Scher, 1998, 2009; Rhodes et al., 2008; Geiger et al., 2010; Edery, 2021). The point, though, is that it makes no sense to calibrate at a centimeter scale and then expect to somehow "upscale" parameters to apply the same model at a kilometer scale. [Note: As an aside, over very large field-length and field-time scales, we point out that homogenization effects of molecular diffusion *may* become more significant, lessening impacts of some preferential pathways.] Similarly, a CTRW-based approach can be applied over a range of *time* scales, because the power law accounting for temporal effects can be as broad as needed. In these cases, temporal effects are critical, because at the continuum (Darcy) scale, streamlines do not change but residence times do. Specifically, for example, a model formulation with a fixed set of parameters can interpret transport measurements in the same domain, but acquired under different hydraulic gradients or ~~(~~fluid velocities~~)~~, and thus domain residence times (Berkowitz and Scher, 2009). Indeed, because of the temporal accounting, CTRW has been applied successfully

over scales from pores (e.g. Bijeljic et al., 2013) to kilometers (e.g. Goeppert et al., 2020), with parameter calibration at the relevant scale of interest. In principle then, too, a calibrated model shown to be effective/meaningful over one region of a porous medium or geological formation can offer at least a reasonable estimate of transport behavior elsewhere in the medium/formation, at a similar length/time scale, and as long as the medium/formation can be expected to have reasonably similar hydrogeological structure and properties.

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

And at the field scale, the situation is even less satisfying; large-scale field tests for chemical 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 Moreover, at the field scale, there are necessarily highly limited. As a result, numbers of measurements, so that oft-used, (and 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 non-uniform, 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 many 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 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 and apply models, and then apply them, using measurements over spatial scales with at similar orders of magnitude measurement scales of interest, in both space and time.

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, tThe 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."

*Data availability.* All data have been reported and published previously, as given in the relevant citations.

*Author contributions.* Single author contribution.

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