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

[handwritten: IN CONTEMPORARY PARLANCE HOLY GRAIL IS SOMETIMES USED TO REFER TO AN ATTAINABLE OBJECTIVE OR WISH. NOT AN IDEAL CHOICE OF TERMS.]

5 Brian Berkowitz[1]

7 [1]Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 7610001,
8 Israel

10 *Correspondence to:* Brian Berkowitz (brian.berkowitz@weizmann.ac.il)

12 **Abstract.**

[handwritten: MEANING HERE NOT CLEAR: THEY TO ANTICIPATION]

[handwritten: MANY OF US DID NOT EXPECT MORE THAN WAS FOUND, SO ARE NOT UNSATISFIED, BUT RATHER APPRECIATING NATURE'S COMPLEXITY.]

14 Extensive efforts over decades have focused on quantifying chemical transport in subsurface
15 geological formations, from microfluidic laboratory cells to aquifer field scales. Outcomes of these
16 efforts have remained largely unsatisfactory, however, largely because domain heterogeneity (in
17 terms of, e.g., porosity, hydraulic conductivity, geochemical properties) is present over multiple
18 length scales, and "unresolved", practically unmeasurable heterogeneities and preferential
19 pathways arise at virtually every scale. While *spatial* averaging approaches are effective when
20 considering overall fluid flow – wherein pressure propagation is essentially instantaneous and the
21 system is "well mixed" – purely *spatial* averaging approaches are far less effective for chemical
22 transport, essentially because well-mixed conditions do not prevail. We assert here that an explicit
23 accounting of *temporal* information, under uncertainty, is an additional, but *fundamental*,
24 component in an effective modeling formulation. As an outcome, we further assert that "upscaling"
25 of chemical transport equations – in the sense of attempting to develop and apply chemical
26 transport equations at large (length) scales, based on measurements and model parameter values
27 obtained at significantly smaller length scales – is very much a holy grail. Rather, we maintain that
28 it is necessary to formulate, calibrate and apply models using measurements at similar scales of
29 interest, in both space and time.

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

[handwritten: DOES THIS MEAN A MYTHICAL AND UNATTAINABLE GOAL, OR A VALID OBJECTIVE? I GUESS THE FORMER.]

[handwritten: KEY POINT: IF EVERY MODEL NEEDS TO BE CALIBRATED @ ALL SCALES, IS THE MODELING EXERCISE FUTILE?]

32 **1 Introduction**

33

34 **1.1 Background**

35

36 There have been extensive efforts over the last ~60 years to model and otherwise quantify fluid

37 flow and chemical (contaminant) transport in soil layers and subsurface geological formations,

38 from millimeter-size, laboratory microfluidics cells to aquifer field scales extending to hundreds

39 of meters and even tens of kilometers.

40   Soil layers and subsurface formations can exhibit significant heterogeneity, in terms of domain

41 characteristics such as porosity, hydraulic conductivity, structure, and biogeochemical properties

42 (mineral and organic matter content). However, recognition that effects of heterogeneity over

43 multiple length scales, with "unresolved", practically unmeasurable heterogeneities arising at

44 every length scale (from pore to field) cannot be simply "averaged out", has become broadly

45 accepted only more recently. Indeed, much research on flow and transport in porous media, dating

46 particularly from ~1950-1990, but also essentially to date, has been based on the search for length

47 scales at which one can define a "representative elementary volume", or otherwise-named

48 "averaging volume", above which variability in fluid and chemical properties become constant. In

49 this context, too, many varieties of homogenization, volume averaging, effective medium, and

50 stochastic continuum theories have been developed in an extensive literature. These methods

51 allowed formulation of continuum-scale, generally Eulerian, partial differential equations to

52 quantify ("model") fluid flow and chemical transport, which were then applied in the soil and

53 groundwater literature at length scales ranging from millimeters to full aquifers. While originally

54 deterministic in character, a variety of stochastic formulations, and use of Monte Carlo numerical

55 simulation techniques, introduced from the 1980s, enabled analysis of uncertainties in input

56 parameters such as hydraulic conductivity.

57   However, while analysis of fluid flow using these methods has proven relatively effective,

58 quantification of chemical transport, and an accounting of associated (biogeo)chemical reactions

59 in cases of reactive chemical species and/or host porous media, has remained largely

60 unsatisfactory. We discuss the reasons for this, in detail, in the sections below. Briefly, the

61 overarching reason for these successes and failures is that *spatial* averaging approaches are

62 effective when considering overall fluid flow rates and quantities, wherein pressure propagation is

63 essentially instantaneous and the system is "well mixed" (because mixing of water "parcels" is

64 functionally irrelevant). However, purely *spatial* averaging approaches are far less effective for

65 chemical transport, essentially because well-mixed conditions do not prevail, and spatial averaging

66 is inadequate; here, an explicit, additional accounting of *temporal* effects is required.

67   The focus of the current contribution is on modeling conservative chemical transport in

68 geological media. In terms of modeling, one can delineate two main types of scenarios: (i) *pore-*

69 *scale modeling* in relatively small domains, with a detailed (and specified) pore structure, and (ii)

70 *continuum-scale modeling* in porous media domains, that average pore space and solid phases at

71 scales from laboratory flow cells to field-scale plots and aquifers. Case (i) requires, e.g., Navier-

72   Stokes or Stokes equations solutions for the underlying flow field, coupled with solution of a local
73   (e.g., advection-*diffusion*) equation for transport, while Case (ii) requires Darcy (or related)
74   equation solutions for the underlying flow field, coupled with solution of a governing transport
75   equation for chemical transport. *Note:* here and throughout, we shall use the terms "*continuum*
76   *level*" and "*continuum scale*" in reference to case (ii) scenarios, and "*pore-scale*" to refer to Case
77   (i) scenarios, although we recognize, too, that pore-scale Navier-Stokes and advection-diffusion
78   equations are continuum partial differential equations.
79

80   ***Disclaimer:*** Here and throughout this contribution, the overview comments and references to
81   existing philosophies, methodologies and interpretations are written, largely, in broad terms,
82   without (necessarily limited numbers of) citations selected from the vast literature. This approach
83   is taken with a clear recognition and respect for the body of literature that has driven our field
84   forward over the last decades, but with the express desire to avoid any risk of unintentionally
85   alienating colleagues and/or misrepresenting aspects of relevant studies. *As an Opinion*
86   *contribution, and with length considerations in mind, there is no attempt to provide an exhaustive*
87   *listing and description of relevant literature.*
88

89

90   **1.2 Assertions**

91

92   The pioneering paper of Gelhar and Axness (1983) focused on quantifying conservative chemical
93   transport at the continuum level. They expressed heterogeneity-induced chemical spreading in
94   terms of the (longitudinal) macrodispersion coefficient – as it appears in the classical
95   (macroscopically 1d) advection-dispersion equation – with knowledge of the variance and
96   correlation length of the log-hydraulic conductivity field and the mean, ensemble-averaged fluid
97   velocity. The conceptual approach embodied in Gelhar and Axness (1983) – and by many
98   researchers since then (as well as previously) – was founded on delineation of the *spatial*
99   *distribution* of the hydraulic conductivity and application of an averaging method to determine the
100 governing transport equation with "effective parameters" to describe chemical transport at a given
101 length scale.

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

111   As an outcome of the above assertion and the discussion below, we further assert that
112 "upscaling" of chemical transport equations – development and application of chemical transport

113 equations at large (length) scales, with corresponding parameter values, based on measurements
114 and model parameter values obtained at significantly smaller length scales – is very much a holy
115 grail. Rather, we maintain that it is necessary to formulate, calibrate and apply models using
116 measurements at similar scales of interest, in both space and time. This does not exclude use of
117 similar equation *formulations* at different spatial scales, but it does entail use of different parameter
118 values, at the relevant scale of interest, that cannot be determined a priori or from purely spatial or
119 flow-only measurements.
120
121
122 **1.3 Approach – Outline**
123
124 While our focus is on chemical transport, knowledge of fluid flow and delineation of the velocity
125 field throughout the domain is a prerequisite. We therefore first discuss fluid flow as an intrinsic
126 element aspect of the "information hierarchy". Specifically, we address how:
127 (1) Basic structural information on "conducting elements" in a system representing a
128   geological domain (porous and/or fractured) can provide basic insight regarding overall
129   fluid conduction in the domain, as a function of "conducting element" density. We
130   emphasize that without direct simulation of fluid flow (as well as chemical transport) in
131   such a system, this type of analysis is insufficient in terms of defining the actual flow
132   field and velocity distributions throughout the domain.
133 (2) Spatial information on, in particular, the hydraulic conductivity distribution at a
134   continuum scale, or solid phase distribution at the pore scale, throughout the domain, can
135   be used to *determine the flow field*. We then show that this is insufficient in terms of
136   defining chemical transport.
137 (3) Temporal information on chemical species migration, which quantifies distributions of
138   retention and release times (or rates) of chemicals by advective-dispersive-diffusive
139   and/or chemical mechanisms, can be used to *determine the full spatial <u>and</u> temporal
140   evolution of a migrating chemical plume*, either by solution of a transport equation or use
141   of particle tracking on the velocity field.
142 We comment, parenthetically, that in conceptual-philosophical terms, this hierarchy and the
143 "limitations" of each level are in a sense analogous to representation of geometrical constructs in
144 multiple dimensions; in principle, one can represent, as a *projection*, a d-dimensional object in d–
145 1 dimensions. But of course, by its very nature, a *projection* does not capture all features of the
146 construct in its "full" dimension. To illustrate, an (imaginary) 1d curve can represent a 2d Möbius
147 strip, a 2d perspective drawing can represent a 3d cube, and a 3d construct can represent a 4d object
148 (where the 4th dimension might be considered time) — and yet, none of these d–1 dimensional
149 representations contains all features of the actual d-dimensional objects. Similarly, despite our
150 frequent attempts to the contrary, one cannot properly describe (2) only from (1), or (3) only from
151 (2).
152

2 Fluid flow

Prior to actually solving for fluid flow, to determine the underlying velocity field, efforts are sometimes invested in considering geometrical (structural) information, for example, when examining fracture networks in essentially impermeable host rock.

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

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

It is thus clear that, in general, there are dynamic aspects of fluid flow, over and above pure structure: knowledge of pure geometry is not sufficient, and *we must actually solve for the flow field*, at either the pore-scale or a continuum scale, to determine the velocity field and actual flow paths throughout the domain. Delineation of a flow field and velocity distribution by solution of the Navier-Stokes equations (or Stokes equation for small Reynolds numbers), or by solution of the Darcy equation, may be considered "rigorous", correct and effective. But in the process of solving for the flow field, two *key* features arise, one more relevant to pore-scale analyses, and the other more relevant to continuum-scale analysis, as 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 ≡ $\rho v L/\mu$, where ρ and μ are density and dynamic viscosity of the fluid, respectively, v is fluid velocity, and L is a characteristic linear dimension.]. Andrade et al. (1999) showed clearly that

193 well-defined preferential flow channels at lower Re, while at higher Re, channeling is less intense
194 and the streamline distribution is more spatially homogeneous in the direction orthogonal to the
195 main flow.
196   Figure 1 demonstrates that the streamlines in individual pores change because of the interplay
197 between inertial and viscous forces, given by Re. In other words, with a change in overall fluid
198 velocity (or hydraulic gradient) across the domain, the actual flow paths can be altered, together
199 with a change in overall and (spatially) local residence times of fluid molecules (and chemical
200 species, as addressed below). Of course, the significantly lower porosities and more tortuous pore
201 space configuration in natural, heterogeneous geological porous media may affect the impact of
202 inertial effects, but the principle remains relevant. [We note, too, parenthetically, that the behavior
203 shown in Fig. 1 is relevant also to fluid flow within fracture planes, wherein the obstacles represent
204 contact areas and regions of variable aperture.]
205   Clearly, then, except in highly idealized and simplified geometries, use of a purely analytical
206 solution to identify the full velocity field and streamline patterns is not feasible. Moreover, the
207 extent and changes in streamlines are not intuitively obvious without full numerical solution of the
208 governing flow equations, for any specific set of porous medium structures and boundary
209 conditions.

210 *REALLY UNCONVINCING! IN ALMOST ALL G.W. SYSTEMS flow is*
211 *non-inertial (Re < 1). THIS ARGUMENT DOES NOT CONFORM WITH NATURE,*
212 *AND WILL MISLEAD READERS WHO ARE NOT AWARE OF THESE facts.*
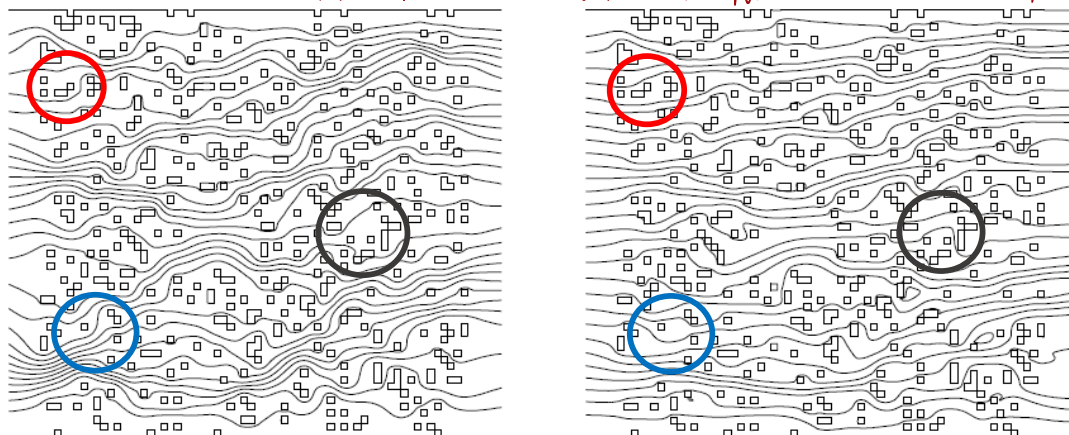
(a) Re = 0.0156   (b) Re = 15.6

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.

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 (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).]

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

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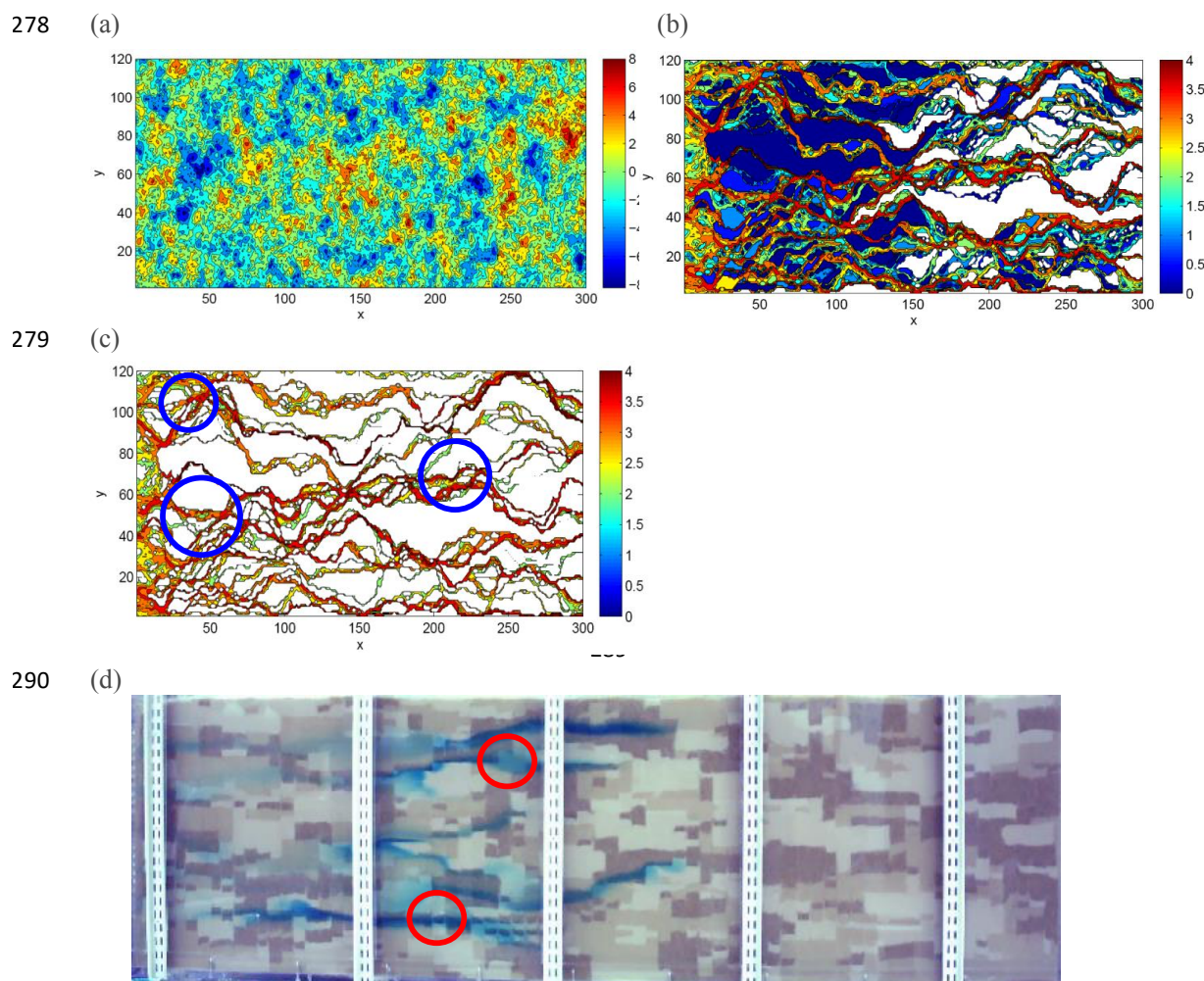Earth System
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278   (a)

279   (c)

290   (d)

301

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

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

317 pathways, and that fluid (and chemicals) do not migrate "only" through the highest conductivity
318 patches?
319   To address this question, we begin by considering what happens in a 1d path. Consider two
320 paths, each containing a series of five porous medium elements (or blocks), with distinct hydraulic
321 conductivity (K_i) values. Consider Path 1, with a series hydraulic conductivity values of 3, 3, 3, 3,
322 3, and Path 2, with values 6, 6, 1, 6, 6 (specific length/time units are irrelevant here). The value of
323 $K = 1$ represents a clear "bottleneck" in an otherwise higher K path than that of Path 1. In a 1d
324 series, however, the overall hydraulic conductivity ($K_{overall}$) of the path is given by the harmonic
325 mean of the conductivities of the elements comprising the path: $K_{overall} = 5 / (\Sigma_{i=1,5} 1/K_i)$;
326 significantly, in the two cases here, both paths have $K_{overall} = 3$! So a "bottleneck" ($K=1$) can be
327 "overcome" and does not cause necessarily cause a potential pathway to be less "desirable" than a
328 pathway without such "bottlenecks". Of course, in 2d and 3d systems, patterns of heterogeneity
329 and pathway "selection" by water/chemicals are significantly more "complicated", but the
330 principle discussed here for 1d systems still holds, in the sense that lower hydraulic conductivity
331 ("bottleneck") elements can (and do) exist in the preferential pathways (Margolin et al., 1998;
332 Bianchi et al., 2011).
333
334
335 **3 Chemical transport**
336
337 We now consider the next level of the "information hierarchy" outlined in Sect. 1.3. To quantify
338 the evolution of a migrating chemical plume, knowledge of the flow field is not generally
339 sufficient, and additional means to characterize and quantify the behavior are needed. Dynamic
340 aspects of chemical transport require us to think (also) in terms of *time*, not just *space* and physical
341 structure. Moreover, it is generally insufficient to determine the transport of the chemical plume
342 center of mass. Rather, in terms of water resource contamination and remediation, for example, it
343 is critical to characterize, respectively, the early and late arrival times at compliance (monitoring)
344 regions downstream of the region (point, areal, volumetric) in which the chemical species entered
345 the system.
346   As we show below, it becomes clear that, in general, there are dynamic aspects of chemical
347 transport, on over and above the role of the flow field, and *we must actually solve for chemical*
348 *transport*, at either the pore-scale or a continuum scale, to determine the spatiotemporal (spatial
349 plume and/or temporal breakthrough curve) evolution of the migrating chemical plume. In *both*
350 pore-scale and continuum-scale domains, the *critical* control that arises is that of time (in addition
351 to space). This is in sharp contrast to fluid flow at pore and continuum scales, as shown in Sect.
352 2.1 and Sect. 2.2: pore-scale fluid flow displays changing streamlines with changes in hydraulic
353 gradient, while continuum-scale fluid flow follows distinct but difficult to identify preferential
354 flow paths essentially independent of the hydraulic gradient.
355   We point out, too, that for both pore-scale and continuum-level scenarios, one can solve,
356 explicitly, a governing equation for transport. Alternatively, though, one can obtain an
357 "equivalent" solution by solving for (Lagrangian framework) "particle tracking" of transport along

358 the calculated streamlines. In other words, particle tracking methods essentially represent an
359 alternative means to solve an ((integro-)partial differential) equation for chemical transport; such
360 methods can be applied, too, when the precise partial differential equation is unknown or the
361 subject of debate. We also note that solution of the relevant equations for fluid flow and chemical
362 transport is sometimes achieved by (semi-)analytical methods, if the flow/transport system can be
363 treated sufficiently simply (e.g., macroscopically, section-averaged 1d flow and transport in a
364 rectangular domain).
365   We first discuss principal features of pore-scale (Sect. 3.1) and continuum-scale (Sect. 3.2)
366 chemical transport, and in Sect. 3.3, we focus on effective model formulations.
367
368

3.1 Pore-scale chemical transport analysis

371 To illustrate why knowledge only of only the flow field is insufficient for full quantification of
372 chemical transport, consider the three porous medium domains shown in Fig. 3. Each domains is
373 comprised of pore-scale images of a natural rock, modified by enlarging the solid phase grains, to
374 yield three different configurations: a statistically homogeneous system domain, a weakly
375 correlated system, and a structured, strongly correlated system (see Nissan and Berkowitz (2019)
376 for details). Fluid flow was determined by solution of the Navier-Stokes equations (Fig. 1a).
377 Transport of a conservative chemical species was then simulated via a (Lagrangian) streamline
378 particle tracking method, for an ensemble of particles that advance according to a Langevin
379 equation. Transport behavior was determined for two values of macroscopic (domain average)
380 Péclet number (Pe). [Recall; Pe ≡ vL/D, where v is fluid velocity, L is a characteristic linear
381 dimension, and D is the coefficient of molecular diffusion.] Here, the macroscopic Pe is based on
382 the mean particle velocity and mean particle displacement distance per transition ("step").
383   Figure 3 shows that regardless of possible (pore-scale) streamline changes as a function of
384 hydraulic gradient (recall Sect. 2.1, considering different values of Re), the choice of *macroscopic*
385 Péclet number in a given domain plays a significant role in the evolution of the migrating chemical
386 plume. In particular, the relative effects of advection and diffusion, which vary locally in space,
387 are critical, as is the overall residence time in the domain. We stress here (and return to this key
388 point in discussion below) that the spatially (and in some case temporally) *local* changes in relative
389 effects of advection and diffusion – characterized by the *local* Pe – dominates determination of the
390 plume evolution. This can be understood from study of Fig. 3, in each of the three heterogeneity
391 configurations, for two choices of macroscopic Pe values; the different patterns of longitudinal
392 and transverse spreading are observed clearly.
393   The behavior show in Fig. 3 is essentially well-known from extensive simulations and
394 experiments appearing in the literature. This behavior is described here to stress the importance of
395 *temporal* effects, and to point out that information only of the advective velocity field – as
396 discussed in Sect. 2.1 and Sect. 2.2 – is not sufficient to "predict" chemical transport.
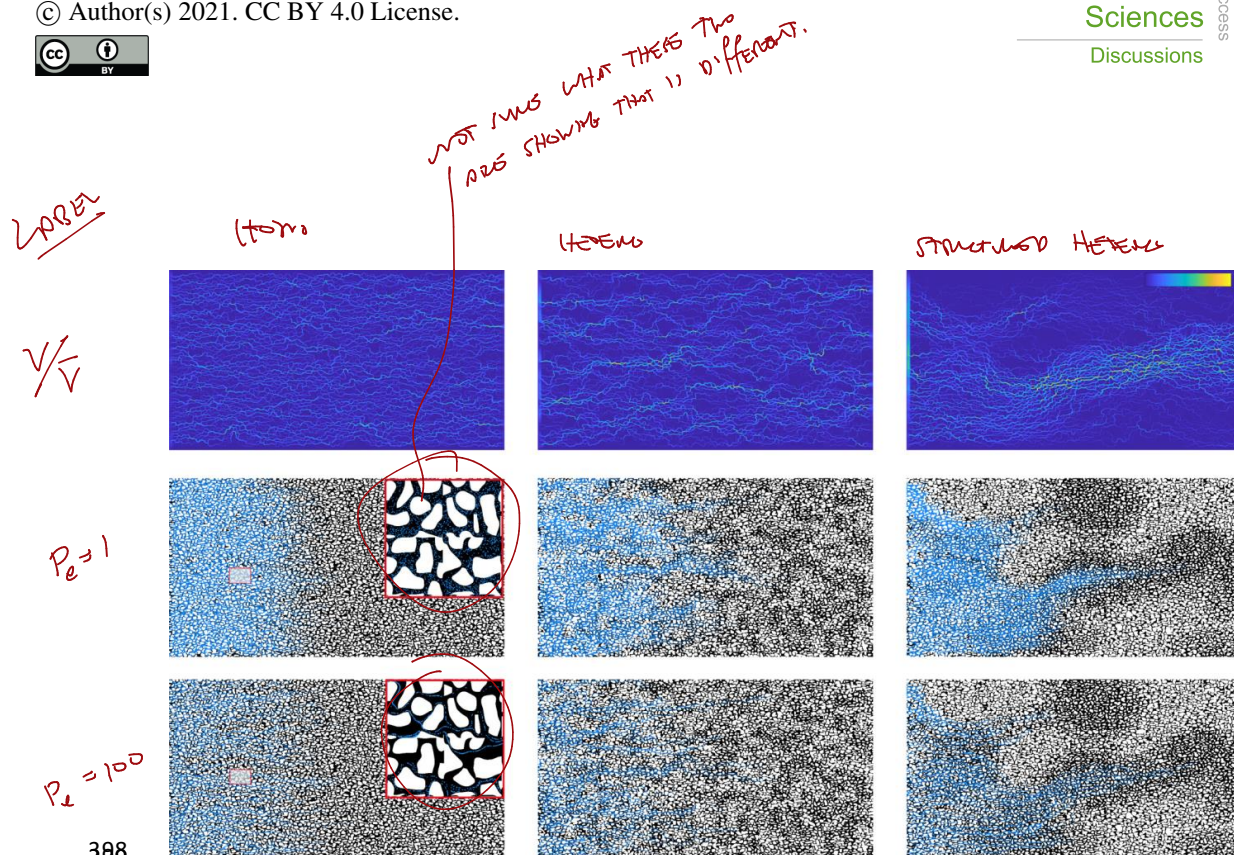397

Figure 3. Fluid velocities and chemical migration in three porous media configurations (from left to right): homogeneous system, randomly heterogeneous system, and structured heterogeneous system. The upper row shows the (normalized) velocity field for the three configurations; the color bar represents relative velocity, with dark blue being lowest. The middle and lower rows show, respectively, numerically-simulated particle tracking patterns of an inert chemical species (blue dots) at Pe = 1 (middle row) and Pe = 100 (lower row) for the three configurations (white color indicates solid phase; black color indicates liquid phase). Note: The particles plumes are shown at 10% of the final time of each simulation; absolute travel times differ among the plots. The insets in the left side plots of the middle and lower rows show the pore-scale chemical species distributions; note the more diffuse pattern for Pe = 1 (from Nissan and Berkowitz, 2019, https://doi.org/10.1103/PhysRevE.99.033108; © with permission from American Physical Society 2019).

3.2 Continuum-scale chemical transport analysis

The aspects discussed in Sect. 3.1 are relevant, analogous and essentially applicable 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.
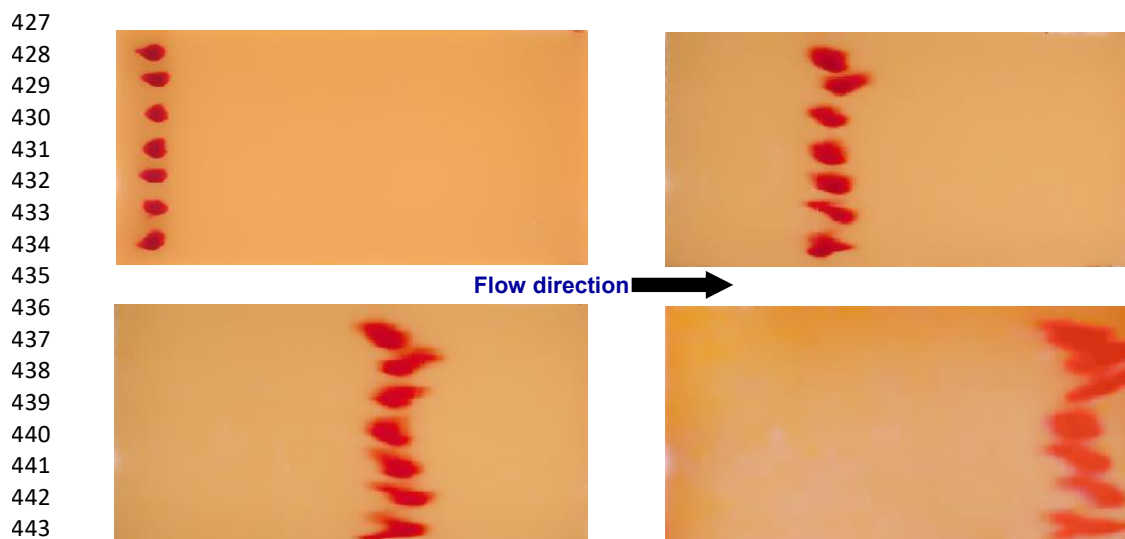
Figure 4. Photographs of dye transport in a flow cell (internal dimensions $0.86 \times 0.45 \times 0.10$ m) containing a uniform packing of quartz sand (average grain diameter 0.532 mm), under a constant flow rate, at four times (modified from Levy and Berkowitz, 2003; © with permission from Elsevier 2003).
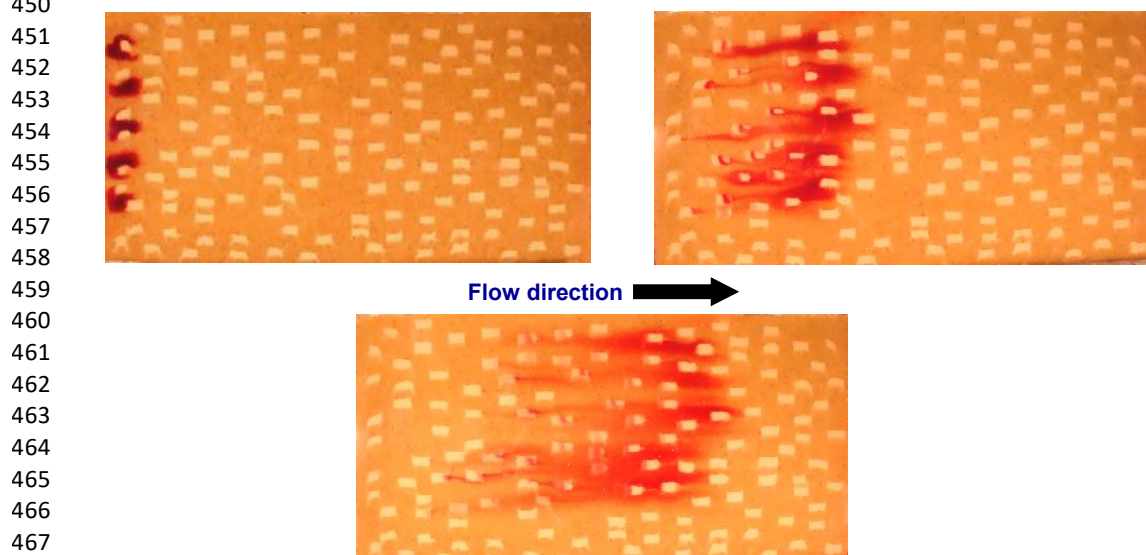
Figure 5. Photographs of dye transport in a flow cell (internal dimensions $0.86 \times 0.45 \times 0.10$ m) containing a randomly heterogeneous packing of quartz sand, under a constant flow rate, at three times. The rectangular inclusions comprise sand with an average grain diameter ~0.5× smaller, and hydraulic conductivity ~3× lower, than the surrounding sand matrix (modified from Levy and Berkowitz, 2003; © with permission from Elsevier 2003).

[handwritten margin notes: "Time scale?", "what if Pe 2.0)?"]

475   Most notably, in both Fig. 4 and Fig. 5: (i) each of the plumes has a different, unique pattern,
476   which continues over the duration of the plume migration; and (ii) none of the plumes is
477   "elliptical", as expected in classical Fickian transport theory and embodied in solutions of the
478   classical advection-dispersion equation (ADE). Indeed, vertical averaging of each plume shown in
479   Fig. 4 and Fig. 5, at each time, does not yield Gaussian (normally distributed) concentration
480   profiles, but rather asymmetrical, "heavy-tailed" profiles.

481   At this juncture, we note that here and below that we use the terms "non-Fickian", or
482   "anomalous" – others sometimes use the terms "pre-asymptotic" or "pre-ergodic" – to denote any
483   chemical transport behavior that differs from that described by the classical ADE or similar type
484   of continuum-scale formulation. Typically, though, non-Fickian transport is characterized by early
485   and or late arrival times of migrating chemical species to some control or measurement plane/point,
486   relative to those resulting from solution of the ADE. The ADE applies to so-called Fickian
487   behavior, in the sense that it accounts for mechanical dispersion as a macroscopic form of Fick's
488   law; mechanical dispersion arises as an "effective" (or "average") quantity that describe local
489   fluctuations around the average (advective) fluid velocity. Thus, in this formulation, a pulse of
490   chemical introduced into a macroscopically 1d, uniform velocity, for example, leads to temporal
491   and spatial concentration distributions that are equivalent to a normal (Gaussian) distribution.

492   It is in this context that the term "homogeneous" packing used above is placed in quotation
493   marks, to indicate that in natural geological media, "homogeneity" does not really exist. Any
494   natural geological sample of porous medium contains multiple scales of heterogeneity; and at each
495   particular scale of measurement, "unresolved" heterogeneities that are essentially unmeasurable
496   are present (even scanning electron microscopy and atomic force microscopy have limits of spatial
497   resolution, for example!). And thus, as seen in Fig. 4 for example, the overall transport pattern
498   even in an "homogeneous" system can be non-Fickian (anomalous). *We therefore emphasize that*
499   *because natural heterogeneity in geological formations occurs over a broad range of scales,*
500   *"normal" (Fickian) transport tends to be the "anomaly", whereas "anomalous" (non-Fickian)*
501   *transport is ubiquitous, and should be considered "normal".*

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

509   Thus, we argue that patterns of chemical transport cannot be fully determined from information
510   only on the velocity field; solution of an appropriate continuum-scale transport equation cannot be
511   avoided. In conclusion, then, and with particular reference to the (conceptually and theoretically
512   beautiful) classical ADE and "conventional" conceptual understanding and quantitative
513   description of chemical transport, we suggest that one must separate mathematical convenience
514   and wishful thinking from the reality of experiments: there is a definitive need for more powerful

515 formulations of transport equations. In this context, one is reminded of the quotation by the
516 biologist Thomas Henry Huxley: "The great tragedy of science—the slaying of a beautiful theory
517 by an ugly fact." (*President's Address to the British Association for the Advancement of Science,*
518 *Liverpool Meeting, 14 Sep 1870*).
519
520

521 **3.3 Modeling chemical transport, and the myth that "fewer parameters is always better"**
522

523 So how *do* we effectively model chemical transport?
524 　As noted at the outset of Sect. 2, solution of the Navier-Stokes or Darcy equations to determine
525 the full *flow* field and velocity distribution in a given porous medium domain has been proven
526 correct and effective in most applications, and is well-accepted in the literature. However,
527 modeling of chemical transport is more contentious, the reasons for which we expand upon below.
528 　We argue here that modeling of chemical species transport requires us to think in terms of *time*,
529 not just *space*. To assist the reader to enter this frame of thinking, and to sharpen our
530 conceptualization, we provide two examples to illustrate aspects of time and space in the context
531 of chemical transport dynamics:
532 (1) The classical example of the brachistochrone (ancient Greek: "shortest time"), or path of
533 　　 fastest descent, is the curve (path) that would carry an idealized point-like body, starting at
534 　　 rest and moving along the curve, without friction, under constant gravity, to a given end
535 　　 point in the shortest time. (Correct solution: Johann Bernoulli, 1697) Somewhat non-
536 　　 intuitively, the path that leads to the shortest travel time is not a straight line, but, rather, a
537 　　 special curve that is longer than a straight line (a cycloid)! (See:
538 　　 http://old.nationalcurvebank.org//brach/brach.htm)
539 (2) What error can be introduced when "averaging" in terms of "space"? Consider the case of
540 　　 driving a total distance of 100 km, by first traveling 50 km at 1 km h^{-1}, and then traveling
541 　　 50 km at 99 km h^{-1}. If we average the speed in terms of space (distance), then we traveled
542 　　 two segments of 50 km at two speeds, so the average speed is $(1 + 99) / 2 = 50$ km h^{-1}. In
543 　　 this framework, the total time to travel the 100 km "should" only have been 2 h. However,
544 　　 in terms of *time*, the travel time is actually 50.5 h.
545 　These simple examples help to emphasize the errors introduced by traditional conceptual
546 thinking, wherein the effects of *spatial* transport and domain heterogeneity are quantified only on
547 the basis of spatial characteristics. It is worth recalling, too, Einstein's quantitative treatment of
548 Brownian motion (Einstein, 1905). Prior to his analysis, researchers applied – with puzzlement –
549 a time-dependent velocity, *v*, to quantify experimental measurements. Einstein (1905) instead
550 examined a recursion relation and expansion that led to a diffusion equation whose solution
551 showed, for the first time, that the root mean squared displacement of particles undergoing
552 Brownian motion is proportional to $\sqrt{t}$, and not to *vt* as had been assumed traditionally. An
553 astounding conceptual breakthrough over a century ago, this nature of diffusive motion is now
554 "common knowledge".

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

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

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

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

588   The debate in the literature between "effective" and high-resolution hydrogeological modeling,
589   as well as various preconceptions and misconceptions discussed below and in Sect. 4, lead
590   naturally to consideration of the (often incorrectly invoked) argument that "fewer model
591   parameters is better".
592   We first discuss briefly aspects of high-resolution hydrogeological modeling in Sect. 3.3.1,
593   and then focus on "effective" transport equation modeling in Sect. 3.3.2. We emphasize that the
594   latter approach is applicable to both small- and large-scale domains. The former approach is

595   generally intended for large- (field-)scale systems (although, in a sense, the same approach is often
596   applied for detailed pore-scale modeling); this approach is ~~not particularly contentious, per se, but~~
597   ~~is~~ hampered by the complexity and cost associated with the demand for highly detailed
598   hydrogeological information. Therefore, research work remains heavily invested in "effective"
599   transport equation modeling.

600
601

602   **3.3.1 High-resolution domain delineation and modeling**

603

604   Efforts to resolve large-scale aquifer systems, to delineate the hydraulic conductivity distribution
605   at increasingly higher resolutions, began in earnest in the 1990s. Analysis of field sites emphasized
606   (relatively) high-resolution discretization of domain structure (e.g., "blocks" of the order of 10 m^3
607   at the field scale (Eggleston and Rojstaczer, 1998); $200 \times 200 \times 1$ m^3 at large regional scales
608   (Maples et al. 2019). These efforts, first focusing on determining the fluid flow field, and
609   subsequently on delineating pathways for chemical transport, began largely because of
610   dissatisfaction with results of application of 1d, 2d, 3d forms of an "effective" (averaged) ADE
611   (see further discussion in Sect. 3.3.2). Acquiring high-resolution measurements of structural (e.g.,
612   mineralogy, porosity) and hydrological properties (e.g., hydraulic conductivity) was made more
613   feasible in recent years by advances in hydrogeophysics, and as well as by advances in
614   computational capabilities that enable incorporation of this information in finely-discretized
615   meshes, and numerical solution for fluid flow and chemical transport.
616   In these highly resolved (high-resolution) gridded domains, the flow field can be determined
617   from solution of Darcy's law. Chemical transport is then simulated either by use of streamline
618   particle tracking methods (accounting for advection and diffusion in a Lagrangian framework) or
619   via solution of a local (mesh element) continuum-scale transport equation. For chemical transport,
620   use of an advection-*diffusion* equation might appear preferable – given that it requires no estimate
621   for the local dispersivity, but some researchers apply an advection-*dispersion* equation, which
622   necessitates use of mesh-scale dispersivity values that are either assumed or estimated from local
623   measurements. The latter case assumes mesh-scale transport to be fully Fickian (recall Sect. 3.2)
624   to quantify overall transport. More recently, we note that alternative formulations of a governing
625   transport equation that incorporate temporal effects more broadly can also be used in this type of
626   modeling approach; see, e.g., Hansen and Berkowitz (2020) for incorporation of a continuous time
627   random walk method (discussed in Sect. 3.3.2) into this modeling framework.
628   [Parenthetically, we note that "analogous", high-resolution measurements are made at the pore-
629   scale – in mm to decimeter rock core samples – as a basis for computationally-intensive modeling
630   of fluid flow and chemical transport at these scales. Similar to the evolution of this approach for
631   field-scale studies, high-resolution measurements advanced from use of 2d rock micrographs to
632   advanced micro-computed tomography protocols (e.g., Thovert and Adler, 2011; Bijeljic et al.,
633   2013; recall Sect. 2.1).]
634   This approach is attractive in terms of the ability to "reproduce" detailed heterogeneous

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

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

651
652

653   **3.3.2 "Effective" characterization and modeling**

654

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

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

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

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

689 To explain this approach, we refer to the continuous time random walk (CTRW) framework,
690 which is particularly broad and general. Significantly, and conveniently, it should be recognized
691 that special (or limit) cases of a general CTRW formulation lead to well-known related "subset"
692 formulations that also quantify various types of non-Fickian transport. These subsets include
693 mobile-immobile, multirate mass transfer, and time-fractional derivative formulations, as
694 explained in, e.g., Dentz and Berkowitz (2003) and Berkowitz et al. (2006). Indeed, in spite of
695 frequent references to these model formulations as being "different", they are closely related, with
696 clear mathematical correspondence. Each formulation has advantages, depending on the domain,
697 problem and objectives of model use; but model selection must first be justified physically, and it
698 is inappropriate, for example, to apply a mobile-immobile (two domain) model to interpret
699 chemical transport in a "uniform, homogeneous" porous medium when it displays non-Fickian
700 transport behavior (recall Fig. 4).

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

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

706

707 $$P_{n+1}(\ell) = \sum_{\ell'} p(\ell, \ell') P_n(\ell') \qquad\qquad (1)$$

708

709 where $p(\ell, \ell')$ represents the probability of a random walker ("particle") advancing from location
710 ℓ' to ℓ, $P_n(\ell')$ denotes the probability of a particle being located at ℓ' at (fixed) time step n, and
711 $P_{n+1}(\ell)$ denotes the probability of the particle then being located at ℓ at step n+1. With this
712 formulation in mind, Einstein (1905) and Smoluchowski (1906a,b) demonstrated that for n
713 sufficiently large and a sufficient number of particles undergoing purely (statistically) random
714 movements *in space,* the spatial evolution of the particle distribution is equivalent to the solution

715 of the (Fickian) diffusion equation. This elegant discovery demonstrated that a partial differential
716 equation and its solution can be represented by following, numerically, the statistical movement
717 of particles (i.e., particle tracking) following a random walk. Generalizing the partial differential
718 equation to include transport by advection, solution of the ADE under various boundary conditions
719 can then be determined by an appropriate random walk method.

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

725
$$R_{n+1}(\mathbf{s}, t) = \sum_{s'} \int_0^t \psi(\mathbf{s} - \mathbf{s}', t - t') R_n(\mathbf{s}', t') dt' \qquad (2)$$

727 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 $n+1$
728 steps and $\psi(\mathbf{s}, t)$ is the probability rate for a displacement from location $\mathbf{s}'$ to time $\mathbf{s}$ with a difference
729 of arrival times of t-t'. It is clear that $\psi(\mathbf{s}, t)$ is the generalization of $p(\ell, \ell')$ in Eq. 1, and that the
730 particle steps can each now take place at different times. Indeed, it is precisely this explicit
731 accounting of a distribution of temporal contributions to particle transport, not just spatial
732 contributions, that offers the ability to effectively quantify transport behaviors as expressed by,
733 e.g., heavy-tailed, non-Fickian particle arrival times.

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

742   In the context of chemical transport in geological formations, the behavior $\overline{\ell} \sim t^\beta$ can be
743 attributed to a wide distribution of transition times in naturally disordered geological media. In the
744 CTRW formulation, the transition time distribution is characterized by a power law of the form
745 $\psi(t) \sim t^{-1-\beta}$ for $t \to \infty$ and $0 < \beta < 2$; significantly, the resulting transport behavior is Fickian for
746 $\beta > 2$. At large times, for this $\psi(t)$ dependence, the mean displacement $\overline{\ell}(t)$ and standard deviation
747 $\overline{\sigma}(t)$ 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 $t \to \infty$, $0 < \beta <$
748 1 (Schlesinger, 1974). Moreover, for $t \to \infty$ with $1 < \beta < 2$, the plume scales as $\overline{\ell}(t) \sim t$ and
749 $\overline{\sigma}(t) \sim t^{(3-\beta)/2}$. These behaviors are notably different than that of Fickian transport models, for
750 which (from the central limit theorem), $\overline{\ell}(t) \sim t$ and $\overline{\sigma}(t) \sim t^{1/2}$.

751   With the concepts described here, and using the generally applicable decoupled form $\psi(\mathbf{s}, t) =$
752 $p(\mathbf{s})\psi(t)$, where $p(\mathbf{s})$ is the probability distribution of the transition lengths and $\psi(t)$ is the
753 probability rate for a transition time t between sites, Eq. 2 can be developed into an (integro-)partial

754   differential equation. Thus, the ADE given by

755

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

757

758   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

759   dispersion tensor, is replaced by the more general CTRW transport equation:

760

761

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

763

764   where $\mathbf{v}_\psi$ and $\mathbf{D}_\psi$ are generalized particle velocity and dispersion, respectively, and $M(t)$ is a

765   temporal memory function based on $\psi(t)$.

766   The strength of this type of formulation is that it effectively quantifies (non-Fickian) early

767   arrivals and late time tailing of migrating chemical species, and the spatial evolution of chemical

768   plumes in heterogeneous media. For example, recalling the scenario in Fig. 2, wherein 99.9% of

769   the inflowing particles traverse the preferential pathways seen in Fig. 2c, detailed numerical

770   simulations indicate that concentration breakthrough curves exhibit significant, non-Fickian, long-

771   time tails (Edery et al., 2014). Choice of an appropriate power-law form of $\psi(t)$ was then shown

772   to capture this behavior; moreover, a functional form defining the value of the power-law exponent

773   β in $\psi(t)$ was identified, based on statistics of the hydraulic conductivity and particle interrogation

774   of the domain (Edery et al., 2014).

775   Equation (4) is essentially an ADE weighted by a temporal memory. When $\psi(t)$ is an

776   exponential function (or power law but for $\beta \geq 2$), $M(t) \rightarrow \delta(t)$ and we recover Fickian transport

777   described by the ADE; thus, the ADE assumes, implicitly, that particle transition times are

778   distributed exponentially. But with a power law form $\psi(t) \sim t^{-1-\beta}$ for $0 < \beta < 2$, the transport is

779   non-Fickian. A wide range of functional forms of $\psi(t)$ can be chosen, including, e.g., truncated

780   power law forms that allow evolution to Fickian transport at large times or travel distances (e.g.,

781   Berkowitz et al., 2006), as well as Pareto (e.g., Hansen and Berkowitz, 2014) and curved (or

782   inverse gamma; e.g., Nissan and Berkowitz, 2019) temporal distributions. Other, generally

783   simpler, choices of $\psi(t)$ or $M(t)$ lead to mobile-immobile, multirate mass transfer, and time-

784   fractional derivative formulations. We note, too, that the elegant result derived by Gelhar and

785   Axness (1983) and others, discussed in Sect. 1.2, is valid only at an asymptotic limit, wherein

786   transport is Fickian and there is no residual non-Fickian memory in the plume advance.

787   Each of these power law forms of course requires one or more parameters – at least β – and in

788   some cases, other parameters that define, e.g., a transition time from non-Fickian to Fickian

789   transport (Berkowitz et al., 2006; Hansen and Berkowitz, 2014; Nissan and Berkowitz, 2017).

790   These parameters have physical meaning, and are not purely empirical; perspectives on "numbers

791   of parameters" associated with all models are discussed in Sect. 3.3.3. The question of how model

792   parameter values are determined is addressed in Sect. 4.1.

793   The efficacy of formulations that incorporate, whether explicitly or implicitly, some type of

794 power-law characterization of temporal aspects of chemical transport, is now generally recognized
795 in the literature. Indeed, applications of mobile-immobile, multirate mass transfer, time-fractional
796 advection-dispersion, and general CTRW formulations have been applied quite extensively and
797 successfully. In particular, solutions of Eq. 4 and related variants have interpreted a wide range of
798 chemical transport scenarios: (i) pore-scale to meter scale laboratory experiments, field studies,
799 and numerical simulations, in (ii) porous, fractured, and fractured porous domains, (iii) accounting
800 for constant and time-dependent velocity fields, and (iv) for both conservative and reactive
801 chemical transport scenarios. Solutions to address some of these scenarios are more easily obtained
802 by use of particle tracking methods that incorporate the same considerations and power-law form
803 of $\psi(t)$, as embedded in Eq. 4.
804   It should be recognized that, like the ADE, Eq. 3, the formulation given in Eq. 4 represents a
805 continuum-level mechanistic model. Discussion in the literature about the need for "mechanistic
806 models" often uses the term rather loosely: "mechanistic" transport model equations are based on
807 fundamental laws of physics, with (constant) parameters that have physical meaning (e.g.,
808 hydraulic conductivity, diffusivity, sorption), and thus offer process understanding. But to quantify
809 the spatiotemporal evolution of a migrating chemical plume, additional parameters are needed. We
810 argue that, because of the nature of geological materials, a transport equation should of course
811 capture the relevant physical (and chemical, if the species is reactive) mechanisms that impact the
812 transport, but to do so, we must *also* capture the uncertain characterization of hydrogeological
813 properties dues to the reality of unresolved (unmeasurable) heterogeneities at any length scale of
814 interest. Thus, we suggest that a *mechanistic-stochastic equation formulation* such as given in Eq.
815 4 (which incorporates a probability density function to account for temporal transitions that cannot
816 be determined only from spatial information) is required, describing known transport mechanisms
817 (and with physically meaningful parameters), and accounting for unknown (and unknowable!)
818 information.
819   We note here, too, that other stochastic continuum averaging methods have been proposed in
820 the literature, in the same context of efforts to formulate a "general", "effective" transport equation
821 at a specific scale of interest (see further discussion on "effective" equations and "upscaling" in
822 Sect. 4). In many cases, though, sophisticated stochastic averaging and homogenization
823 approaches have led to transport formulations that are essentially intractable, in terms of solution,
824 and/or have remained at the level of hypothesis without being tested successfully against actual
825 data.
826
827

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

829
830   The term "modeling" is used in many contexts and with differing intents. However, in the
831 literature dealing with chemical transport in subsurface hydrological systems, there are frequent
832 (often misguided!) "arguments" regarding "which model is better", with a major point of some
833 authors being the claim that "fewer parameters is always best". Not always. Indeed, some models

[handwritten margin note: WOULD THAT THIS LEADS SHOWN ? NO SUCH CONNECTION IS PROVIDED.]

834   involve more parameters than others, but if these parameters have physical meaning and are needed
835   as factors to quantify key mechanisms, then "more parameters" is not a "weakness". We
836   emphasize, too that when weighing use of a specific (any!) model, "better" also depends (at least
837   in part) on what the modeling effort is addressing; clearly – and regardless of the number of
838   parameters – a "back-of-the-envelope" calculation using a simple model is sufficient if, for
839   example, one requires only an order of magnitude estimate of the center-of-mass velocity of a
840   migrating contaminant plume (or in other words, no need for artillery to swat a mosquito!) [In this
841   context, quoting Albert Einstein regarding his simplification of physics into general relativity:
842   "Everything should be made as simple as possible, but not simpler."]
843   Considering chemical transport in subsurface geological formations, and the aim of
844   quantifying (modeling) the evolution of a migrating chemical plume in both space and time, we
845   return to focus on the ADE- and CTRW-based formulations discussed in Sect. 3.3.2. As noted in
846   the preceding sections, CTRW formulations have been demonstrated repeatedly to describe a
847   system effectively, with sufficient parameters to account for the various mechanisms. Most
848   significantly, the seminal work of Scher and Montroll (1975) showed that the β exponent had to
849   be included because the mean displacement was not linear with time (i.e., the mean displacement
850   $\overline{\ell}$ of the electron packet does not advance as $\overline{\ell} = vt$, but rather as $\overline{\ell} \sim t^{\beta}$). Thus, a corresponding
851   parameter, relative to an ADE formulation invoking Fickian transport, is unavoidable in such
852   cases. In a sense, too, one can argue that this parameter is not an "additional" parameter relative
853   to the ADE; rather, a decision to invoke the ADE to quantify a transport problem simply assigns a
854   value to this parameter, implicitly, as $\beta \geq 2$.
855   It should be recognized that – while not (yet?) standard practice in the research community –
856   quantitative model information criteria, or model selection criteria, can be used to assess and
857   compare various model formulations that are applied to diverse scenarios (such as fluid flow,
858   chemical transport) in subsurface geological formations. These information criteria include AIC
859   (Akaike, 1974), AICc (Hurvich and Tsai, 1989), and KIC (Kashyap, 1982) measures, as well as
860   the Bayesian (or Schwarz) BIC (Schwarz, 1978). They are formulated to rank models, or assign
861   (probabilistic) posterior weights to various models in a multimodel comparative framework, and
862   therefore focus on model parameter estimates and the associated estimation uncertainty. As such,
863   these information criteria discriminate among various models according to (i) the ability to
864   reproduce system behavior, and (ii) the structural complexity and number of parameters.
865   Discussion of theoretical and applied features of these criteria is given elsewhere (e.g., Ye et al.,
866   2008).
867   Specifically in the context of the ADE and CTRW formulations, with an accounting also of
868   chemical reactions, for example, it was shown that while solution of an ADE can fit measurements
869   from some locations quite closely, the CTRW formulation offers significantly improved predictive
870   capabilities (in the context of model assessment in the presence of uncertainty) when examined
871   against an entire experimental data set (Ciriello et al., 2015). In addition, focusing on the most
872   sensitive observations associated with the CTRW model provides a stronger basis for model
873   prediction, relative to the most sensitive observations corresponding to the ADE model.

[handwritten margin note: YOU INTRODUCE AIC, BUT DON'T PROVIDE ANY DATA ON HOW THE CTRW MEASURES UP BY THIS METRIC. ALSO, YOU DON'T PRESENT DATA ON PARAMETER INDEPENDENCE, OR STANDARD ERROR.]

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

881

882

883 **4 The holy grail of upscaling, and myths about "a priori" parameter determination**

884

885 We begin by defining the term "upscaling" in the context of the discussion here on chemical
886 transport. As defined in the Introduction, Sect. 1.2, we use the term "upscaling" to describe the
887 effort to develop and apply chemical transport equations at large length scales, and identify
888 corresponding model parameter values, based on measurements and parameter values obtained at
889 significantly smaller length scales.
890   We attempt "upscaling" in the hope of developing governing equations for chemical transport
891 at larger and larger scales, from pore, to core, to plot, and to field length scales. Clearly, then,
892 "upscaling" is relevant to the modeling approach discussed in Sect. 3.3.2 – which focuses on use
893 of "averaged", or "effective" (often 1d, or section-averaged) transport equations – and not to the
894 high-resolution domain delineation and modeling approach of Sect. 3.3.1.
895   However, in light of the discussion in Sect. 2 and Sect. 3, we argue that "upscaling" of chemical
896 transport equations is very much a holy grail. Particularly in light of recognizing temporal effects,
897 in addition to spatial characterization, we maintain that it is necessary to formulate, calibrate and
898 apply models using measurements at similar scales of interest, in both space and time. Of course,
899 similar equation *formulations* can be applied at different spatial scales. But parameter values for
900 transport equations cannot generally be determined a priori or from purely spatial or flow-only
901 measurements; *measurements with a temporal "component", at the relevant length scale of*
902 *interest, are required.*

[handwritten margin note left: YOU MEAN UNATTAINABLE?]

[handwritten margin note right: PROOF?]

903   In Sect. 4.1, we briefly discuss aspects of model calibration. This leads naturally to our
904 discussion of upscaling in Sect. 4.2.

905

906

907 **4.1 Parameter determination and model calibration**

908

909 First, it is prudent to offer some words about the need for parameter estimation, or model
910 calibration. Unless one is dealing with first principles calculations of a physical process (e.g.,
911 molecular diffusion) in a perfectly homogeneous domain, a priori determination of model
912 parameters – for *any* model equation formulation – requires calibration against actual experimental
913 measurements; in some limited cases, detailed numerical simulations can be used at small (pore)

[handwritten margin note right: WHAT ABOUT WITH CT SCAN? WOULD WE NOT BE ABLE, SOME TO ESTIMATE DOY, TO ESTIMATION BASED OR GEOMETRY?]

914   scales (e.g., using an advection-*diffusion* equation with the fluid phase, together with solution of
915   the Navier-Stokes equations to first determine the precise flow field in the pore space). Indeed,
916   then, at any realistic problem or scale of interest, *all* chemical transport models require calibration.
917   This fundamental tenet should be clear and well-recognized, yet the literature contains all-too-
918   frequent – and both misguided and misleading – "criticism" of various model formulations,
919   claiming that "parameters are empirical because they are estimated by calibration (fitting) to
920   experiments"; additional "criticisms" follow, for example, that such as a model is therefore not
921   "universal", and/or "it therefore has no predictive capability". We address these latter "criticisms"
922   in Sect. 4.2. Parameters are *not* "empirical" simply because their values are determined by
923   matching to an experiment! Moreover, it should be recognized that application even of the classical
924   ADE at various column and larger scales requires estimates – obtained by calibration – of
925   dispersivity coefficients (and for high-resolution domain delineation and modeling as discussed in
926   Sect. 3.3.1, "block-scale" dispersivities are needed). [Note: And if dispersivities are not actually
927   determined for a specific experiment, but selected from on the literature for "typical" values of
928   dispersivity, there is still a reliance on calibration from previous "similar" studies.] Moreover, with
929   reference to the desire for model parameters that represent fundamental, *spatial* hydrogeological
930   properties of the domain, note that even the classical ADE dispersivity parameter is not uniquely
931   identified with such properties; rather, it varies even in a given domain as a function of chemical
932   plume travel distance or time.
933   With regard to model "universality", recall that, for example, percolation theory (discussed at
934   the beginning of Sect. 2) offers "universal" exponents in scaling relationships. But even for this
935   type of convenient and useful, statistical model, such scaling relationships, too, can only advance
936   from "scaling" (e.g., $A \sim B$) to a full "equation" (e.g., $A = kB$) by calibration of a coefficient of
937   equality (k) against actual measurements. So even in "simple" models, model calibration cannot
938   be avoided.
939   To address "empiricism" – here enters the question of whether parameters of a particular model
940   (in this case, equations for chemical transport) have a physical meaning. As discussed in Sect.
941   3.3.2, a *mechanistic-stochastic equation formulation* such as given in Eq. 4 incorporates a
942   probability density function to describe known transport mechanisms in a stochastic sense; but
943   stochastic does not mean "unphysical", and the parameters as given in, e.g., particular functional
944   forms of $M(t)$ or $\psi(t)$ are indeed physically meaningful. For example, the key β exponent
945   characterizing the power law behavior can be linked directly to the statistics of the hydraulic
946   conductivity field (Edery et al., 2014), or, in a fracture network, be determined from the velocity
947   distribution in fracture segments (Berkowitz and Scher, 1998), which is related directly to physical
948   properties of the domain. Similarly, corresponding parameters appearing in "subset" formulations
949   to quantify non-Fickian transport – e.g., mobile-immobile, multirate mass transfer, and time-
950   fractional derivative formulations – can be understood to have physical meaning (e.g., Dentz and
951   Berkowitz, 2003; Berkowitz et al., 2006). These parameters, too, of course require determination
952   by model calibration to experimental data (or where appropriate, to results of numerical
953   simulations), just as for any other model, including ADE formulations.

954
955
956 **4.2 Upscaling, the scale of interest, and predictive capabilities**
957
958 ~~Upscaling of *fluid flow* "works" because pressure propagation is essentially instantaneous~~. At
959 the Darcy scale – which is the "practical" scale for most applications – flow paths and streamlines
960 do not change with increasing gradient (as long as a transition to turbulent flow is not reached),
961 the equation formulation remains valid, and the fluid residence time in a domain is irrelevant
962 because self-diffusion of water does not affect overall fluid fluxes. Pore-scale flow analyses are
963 local and more specialized, and "upscaling" is not per se an objective.
964 For chemical transport, though, the situation is totally different. Why? Because "upscaling"
965 entails some kind of "coupled" averaging in both space *and* time, and it is far from clear how, if
966 at all, this can be achieved. Moreover, small-scale concentration fluctuations do not necessarily
967 "average out", but instead propagate from local to larger spatial scales. To illustrate another aspect
968 of the complexity, the Péclet number (Pe) in heterogeneous media, with preferential pathways,
969 varies locally in space (recall Fig. 3 and the discussion in Sect. 3.1). Averaging to obtain a
970 macroscale ("upscaled") Pe must address the relative, locally varying effects of advection and
971 diffusion in space, as well as the overall residence time in the domain; after all, it is these effects
972 that dominate determination of the plume evolution. Thus, upscaling requires spatial averaging,
973 but (at least an) *implicit* temporal averaging must also be included. It can be argued that no single,
974 effective Pe can be defined for the entire domain; whether or not it is possible, and how, it is
975 possible to average local Pe values to achieve a single, meaningful domain-scale Pe remains an
976 open question. And whether we like it or not, even with complete information on the spatial (local)
977 Pe distribution, the impact on the overall transport pattern evolution cannot be determined without
978 actually solving for transport in the domain.
979 For chemically reactive species, the transport situation becomes even more complex, because
980 the local residence time, not just the local Pe, must be taken into consideration. Moreover, when
981 precipitation or dissolution processes are present, the velocity field will change locally, introducing
982 additional local temporal and spatial variability. And when sorption is present but tapers off (when
983 the cation exchange capacity is met, for example), even the diffusion coefficient itself changes.
984 These factors further complicate attempts to upscale. [In this context, too, it should be noted that
985 for chemically-reactive systems, it is well-known (e.g., White and Brantley, 2003) that there is
986 often a significant lack of correspondence between laboratory and field-based estimates of
987 geochemical reaction rates and rates of rock weathering, with field-scale estimates – often based
988 on macroscopically Fickian, ADE-like transport formulations – being generally significantly
989 smaller.]
990 Thus, we suggest that focusing efforts on attempting to develop upscaling methodologies for
991 chemical transport, based on any transport equation formulation, appear to be doomed largely to
992 failure – as evidenced, too, by decades of research publications. Rather, we argue that because of
993 the subtle effects of temporal mechanisms, and their close coupling to spatial mechanisms, use of

994 an "effective", or "averaged" continuum-level equation to describe chemical transport (as opposed,
995 e.g., to intensive numerical simulation using a streamline particle tracking method in a high-
996 resolution hydraulic conductivity field) requires calibration of a suitable model at the appropriate
997 scale of interest, with model parameter values calibrated at essentially the same scale.

998 We emphasize, though, that as stated at the outset of Sect. 4, we do argue that similar
999 (continuum-level) transport equation *formulations* can be applied at different spatial scales, as long
1000 as they are mechanistically correct (with a *temporal* component), and the parameter values are
1001 based on *measurements at the relevant length scale of interest.*

1002 Now, in the context of the above arguments regarding "upscaling" and model application, we
1003 return to the ideas presented in Sect. 3.3.2 and consideration of model formulations that account
1004 for both spatial and temporal effects. We first mention use of the ADE. As pointed out in Sect. 3.2
1005 and extensive literature, the "constant" (as required by the ADE formulation) "intrinsic"
1006 dispersivity parameter changes significantly even over relatively small (e.g., 10's of cm's, Silliman
1007 and Simpson, 1987) increases in length – and therefore also time – scales, so that it makes no real
1008 sense to attempt to define an "upscaled" dispersivity parameter for larger scales. Even in the
1009 framework of high-resolution domain delineation and modeling, discussed in Sect. 3.3.1 – which
1010 is not "upscaling" as defined here – the question remains as to what dispersivity values are relevant
1011 for field-scale aquifer "blocks" of the order of 100 to 1000's of m^3.

1012 In contrast, CTRW and related transport formulations with explicit accounting of time effects,
1013 as outlined in Sect. 3.3.2, can be applied meaningfully to interpret real measurements and transport
1014 behavior at "all" scales. We *can* use the same equation formulation at different scales, with
1015 different but relevant parameters at each scale. We emphasize, too, that we do not argue for "hard"
1016 length scales, so that in principle, e.g., an appropriate (CTRW-based) model calibrated at 20 cm
1017 will be applicable to 100 cm scales, and that a model calibrated on a 100 m scale data set can be
1018 applicable at a kilometer scale. The point, though, is that it makes no sense to calibrate at a
1019 centimeter scale and then expect to somehow "upscale" parameters to apply the same model at a
1020 kilometer scale. [Note: As an aside, over very large field-length and field-time scales, we point out
1021 that homogenization effects of molecular diffusion *may* become more significant, lessening
1022 impacts of some preferential pathways.] Similarly, a CTRW-based approach can be applied over
1023 a range of *time* scales, because the power law accounting for temporal effects can be as broad as
1024 needed. In these cases, temporal effects are critical, because at the continuum (Darcy) scale,
1025 streamlines do not change but residence times do. Specifically, for example, a model formulation
1026 with a fixed set of parameters can interpret transport measurements in the same domain, but
1027 acquired under different hydraulic gradients (fluid velocities), and thus domain residence times
1028 (Berkowitz and Scher, 2009). Indeed, because of the temporal accounting, CTRW has been applied
1029 successfully over scales from pores (e.g., Bijeljic et al., 2013) to kilometers (e.g., Goeppert et al.,
1030 2020), with parameter calibration at the relevant scale of interest. In principle then, too, a calibrated
1031 model shown to be effective/meaningful over one region of a porous medium or geological
1032 formation can offer at least a reasonable estimate of transport behavior elsewhere in the
1033 medium/formation, at a similar length/time scale, and as long as the medium/formation can be

[handwritten marginalia, left: THE AUTHOR is saying that no field data can be approximated to any chosen law of time, not only space/time clouds.]

[handwritten marginalia, right: ON WHAT BASIS DO YOU SAY THIS? ANY PAPER ON SCALING BEHAVIOR OF PARAMETERS?]

1034   expected to have reasonably similar hydrogeological structure and properties.

1035   And finally, another critical aspect must be pointed out with regard to *continuum-scale*
1036   transport models as outlined in Sect. 3.2. The preceding discussion leads to the stated need and
1037   desire – at least in principle – to achieve model "prediction". This term appears often, but it is
1038   often used incorrectly. Fitting a model solution to data is of course not "prediction". On one hand,
1039   using specific experiments and data sets, models can be used to *characterize* transport behavior,
1040   e.g., is transport Fickian or non-Fickian?, or, is a migrating chemical plume compact or elongated
1041   and ramified?, which is of fundamental importance. But if *prediction* is the ultimate goal
1042   (recognizing that addressing *prediction uncertainty* is yet another consideration), then we require
1043   multiple data sets from the same porous medium or geological formation, in the sense that we need
1044   measurements over a range of length scales, and/or over a range of time scales (i.e., same distance,
1045   different flow rates). An intended model can then be calibrated against one part of the data set; the
1046   calibrated model is then applied "as is" and the resulting solution ("prediction") is compared
1047   against other ("previously unknown") measurements. At the laboratory scale, such a protocol is
1048   feasible, but rarely executed. Rather, the literature generally reports fits of transport equation
1049   solutions *at specific scales* (individual data sets at a given length scale), and not over a range of
1050   scales, so that no real testing of "upscaling" or "prediction" is achieved. Thus, even at laboratory
1051   scales, true "predictive capability" of a model is rarely examined or reported. [Note: A similar
1052   approach to "prediction" can be done in a purely numerical/computational study, using "ground
1053   truth simulations" that are *assumed* correct (e.g., Darcy flow calculations and then streamline
1054   particle tracking for chemical transport in a highly-resolved domain; recall Sect. 3.3.1), and then
1055   comparing solutions from a continuum (e.g., partial differential equation) model solution. But it
1056   should be recognized that results from *assumed* simulation methods are often unsatisfactory when
1057   compared against experimental measurements and field observations.]

1058   And at the field scale, the situation is even less satisfying; large-scale field tests for chemical
1059   transport are difficult and expensive to execute, so that systematic data sets that enable testing of
1060   model "prediction" are essentially non-existent. Moreover, at the field scale, there are necessarily
1061   highly limited numbers of measurements, so that oft-used (and non-unique) interpolation of sparse
1062   concentration measurements employed to yield (ideally 3d) contour maps of concentration will
1063   unrealistically smooth and dampen non-uniform, ramified and irregular preferential pathways
1064   (recall Fig. 2). Thus, notwithstanding the extensive research efforts reported in the literature, truly
1065   comparative studies using field measurements – to genuinely test proposed "upscaling"
1066   methodologies – are essentially non-existent (e.g., Berkowitz et al., 2016)! In this context, then,
1067   we note that criticism in the literature that a given continuum model "demonstrates no predictive
1068   capability" is in fact not generally based on its assessment relative to sufficiently resolved,
1069   representative, and real data sets.

1070   Finally, it is important to recognize that models are most commonly tested against 1d, section-
1071   averaged concentration breakthrough curves, which can be (i) measured directly in laboratory
1072   column experiments, (ii) estimated or derived in 2d/3d laboratory flow cells by averaging over
1073   control planes, or (iii) estimated from limited monitoring well measurements (single or multi-level

1074 sampling with depth) at a fixed number of locations. The latter case, in particular, requires
1075 extensive interpolation and/or assumption of a large-scale, essentially 1d and uniform,
1076 macroscopic flow field. Moreover, chemical transport model discrimination often requires
1077 breakthrough curves that extend over the late time tailing, which are particularly difficult to
1078 determine in field conditions, due both to interruptions or lack of practicality in well monitoring
1079 at long times, and to detection limits of measurement methods. While reliance on such 1d (section
1080 averaged, over some control plane) breakthrough curves many not be ideal, it is *reality* in terms of
1081 feasible data acquisition. As a direct consequence, model selection, model parameter fits, and
1082 model calibration results may each (and all) be non-unique and lead to confusing or conflicting
1083 conclusions. It is therefore critical that we at least select from mechanistic-stochastic models based
1084 on fundamental laws of physics, with parameters that have physical meaning, as discussed in Sect.
1085 3.3.2, rather than from models invoking purely statistical distributions or assumptions known to
1086 be incorrect.

1087
1088

1089 **5 Concluding remarks**
1090

his own, not broadly.

1091 The ideas, arguments and perspectives offered here represent an effort to somehow summarize
1092 and synthesize understanding of existing approaches and methods proposed to quantify chemical
1093 transport in subsurface hydrological systems. The literature on this subject is vast, extending over
1094 decades, and measurements and observations of chemical transport range from pore-scale
1095 microfluidic laboratory cells to aquifer field scales. A similarly broad range of model formulations
1096 has been proposed to quantify and interpret these measurements/observations. And yet, outcomes
1097 of these efforts are often largely unsatisfactory.

1098 We contend that modeling obstacles arise largely because domain heterogeneity – in terms of
1099 porosity, hydraulic conductivity, and geochemical properties – is present over multiple length
1100 scales, so that "unresolved", practically unmeasurable heterogeneities and preferential pathways
1101 arise at every length scale. Moreover, while *spatial* averaging approaches are effective when
1102 considering overall fluid flow – wherein pressure propagation is essentially instantaneous and the
1103 system is "well mixed" – purely *spatial* averaging approaches are far less effective for chemical
1104 transport, essentially because well-mixed conditions do not prevail. We assert here that an explicit
1105 accounting of *temporal* information, under uncertainty, is an additional – but *fundamental* –
1106 component in an effective modeling formulation. As a consequence, we argue that for continuum-
1107 scale analysis, mechanistic-stochastic models such as those outlined in Sect. 3.2 must be invoked
1108 to account explicitly for both "additional" temporal effects and unresolved heterogeneity. Clearly,
1109 no single model is "best" for all situations and objectives, but any selected model must be
1110 physically relevant and justified.

1111 We further assert, as an outcome of these arguments, that "upscaling" of chemical transport
1112 equations – in the sense of attempting to develop and apply chemical transport equations at large
1113 (length) scales based on measurements and model parameter values obtained at significantly

[handwritten annotation: AN UNATTAINABLE OBJECTIVE ("Holy Grail")]

1114 smaller length scales – is very much ~~a holy grail~~. Rather, because probabilistic considerations
1115 required to account for small-scale fluctuations do not necessarily "average out" (and can
1116 propagate from local to larger spatial scales), we maintain that it is necessary to formulate, calibrate
1117 and apply models using measurements at similar scales of interest, in both space and time.

1118 In all of our efforts to reasonably model chemical transport in subsurface hydrological systems,
1119 we should recognize and accept the objective of advancing our science by integrating theory,
1120 computational techniques, laboratory experiments and field measurement, with the aim of
1121 extracting broadly applicable insights and establishing practical, functional tools. In this context,
1122 as a close colleague and mentor said to me many, many years ago, "remember, this is hydrology,
1123 with very real problems to address…we're not doing string theory"!

[handwritten annotation: INCLUDE THE FULL BREADTH of MODEL / FORMULATION]

1124 We have included many points for discussion and open thought. The reader may not agree with
1125 all arguments and conclusions raised here, but scholarly debate is critical: it is hoped that this
1126 contribution will stimulate further discussion, assist in ordering classification of the (often
1127 confusing) terminologies and considerations, and identify the most relevant, real questions for
1128 analysis, implementation and future research.

1129 We hope that the above thoughts and illustrations (i) encourage careful consideration prior to
1130 data collection (whether from field measurements, laboratory experiments, and/or numerical
1131 simulations), (ii) assist in experimental design and subsequent analysis, and, even more
1132 significantly, (iii) influence the research agenda for the field by challenging researchers to ask and
1133 address appropriately formulated questions. In terms of "modeling" efforts: recall the statement
1134 by Manfred Eigen (Nobel prize chemistry, 1967): "A theory has only the alternative of being right
1135 or wrong. A model has a third possibility: it may be right, but irrelevant."

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References

1154
1155 Akaike, H.: A new look at statistical model identification, IEEE Trans. Autom. Control, 19, 716–723,
1156   1974, doi:10.1109/TAC.1974.1100705.
1157 Andrade, J. S., Costa, U. M. S., Almeida, M. P., Makse, H. A., and Stanley, H. E.: Inertial effects on fluid
1158   flow through disordered porous media, Phys. Rev. Lett., 82, 5249, 1999,

1159   https://doi.org/10.1103/PhysRevLett.82.5249.

1160   Aronofsky, J. S., and Heller, J. P.: A diffusion model to explain mixing of flowing miscible fluids in
1161   porous media, Trans. Am. Inst. Min. Metall. Pet. Eng., 210, 345–349, 1957.

1162   Berkowitz, B.: Analysis of fracture network connectivity using percolation theory, Math. Geol., 27, 467–
1163   483, 1995, https://doi.org/10.1007/BF02084422.

1164   Berkowitz, B. and Scher, H.: Theory of anomalous chemical transport in fracture networks, Physical
1165   Review E, 57(5), 5858–5869, 1998, https://doi.org/10.1103/PhysRevE.57.5858.

1166   Berkowitz, B. and Scher, H.: Exploring the nature of non-Fickian transport in laboratory experiments,
1167   Advances in Water Resources, 32, 750–755, 2009, doi:10.1016/j.advwatres.2008.05.004.

1168   Berkowitz, B., Cortis, A., Dentz, M., and Scher H.: Modeling non-Fickian transport in geological
1169   formations as a continuous time random walk, Rev. Geophys., 44, RG2003, 2006,
1170   https://doi.org/10.1029/2005RG000178.

1171   Berkowitz, B., Dror, I., Hansen, S. K, and Scher, H.: Measurements and models of reactive transport in
1172   geological media, Rev. Geophys., 54, 930–986, 2016, doi:10.1002/2016RG000524.

1173   Bianchi, M., Zheng, C., Wilson, C., Tick, G. R., Liu, G., and Gorelick, S. M.: Spatial connectivity in a
1174   highly heterogeneous aquifer: From cores to preferential flow paths, Water Resour. Res., 47(5),
1175   W05524, 2011, https://doi.org/10.1029/2009WR008966.

1176   Bijeljic, B., Raeini, A., Mostaghimi, P., and Blunt, M. J.: Predictions of non-Fickian solute transport in
1177   different classes of porous media using direct simulation on pore-scale images, Phys. Rev. E, 87(1),
1178   013011, 2013, https://link.aps.org/doi/10.1103/PhysRevE.87.013011.

1179   Ciriello, V., Edery, Y., Guadagnini, A. and Berkowitz, B.: Multimodel framework for characterization of
1180   transport in porous media, Water Resour. Res., 51, 3384–3402, 2015. doi:10.1002/2015WR017047.

1181   Dai, C., Xue, L., Zhang, D., and Guadagnini, A.: Data-worth analysis through probabilistic collocation-
1182   based ensemble Kalman filter, J. Hydrol., 540, 488-503, 2016,
1183   https://doi.org/10.1016/j.jhydrol.2016.06.037.

1184   Dentz, M. and Berkowitz, B.: Transport behavior of a passive solute in continuous time random walks
1185   and multirate mass transfer, Water Resour. Res., 39(5), 1111, 2003,
1186   https://doi.org/10.1029/2001WR001163.

1187   Edery, Y., Guadagnini, A., Scher, H., and Berkowitz, B.: Origins of anomalous transport in disordered
1188   media: Structural and dynamic controls, Water Resour. Res., 50, 1490–1505,
1189   2014, https://doi.org/10.1002/2013WR015111.

1190   Eggleston, J., and Rojstaczer, S.: Identification of large-scale hydraulic conductivity trends and the
1191   influence of trends on contaminant transport, Water Resour. Res., 34, 2155–2168,
1192   1998, https://doi.org/10.1029/98WR01475.

1193   Einstein, A.: Über die von der molekulartheoretischen Theorie der Wärme geforderte Bewegung von in
1194   ruhenden Flüssigkeiten suspendierten Teilchen, Ann. Phys. Leipzig, 17, 549–560, 1905,
1195   https://doi.org/10.1002/andp.19053220806.

1196   Gelhar, L. W. and Axness, C. L.: Three-dimensional stochastic analysis of macrodispersion in aquifers,
1197   Water Resour. Res., 19(1), 161–180, 1983, https://doi.org/10.1029/WR019i001p00161.

1198   Goeppert, N., Goldscheider N., and Berkowitz, B.: Experimental and modeling evidence of kilometer-
1199   scale anomalous tracer transport in an alpine karst aquifer, Water Res., 178, 115755, 2020,
1200   doi:10.1016/j.watres.2020.115755.

1201   Hansen, S. K. and Berkowitz, B.: Interpretation and nonuniqueness of CTRW transition distributions:
1202   Insights from an alternative solute transport formulation, Adv. Water Resour., 74, 54–63, 2014,
1203   http://dx.doi.org/10.1016/j.advwatres.2014.07.011.

1204   Hansen, S. K. and Berkowitz, B.: Aurora: A non-Fickian (and Fickian) particle tracking package for
1205   modeling groundwater contaminant transport with MODFLOW, Environ. Model. Softw., 134,
1206   104871, 2020, doi:10.1016/j.envsoft.2020.104871.

1207   Hurvich, C. M. and Tsai, C.-L.: Regression and time series model selection in small samples, Biometrika,
1208   76(2), 297–307, 1989. https://doi.org/10.1093/biomet/76.2.297

1209   Kashyap, R. L.: Optimal choice of AR and MA parts in autoregressive moving average models, IEEE

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1210   Trans. Pattern Anal., 4(2), 99–104, 1982, doi:10.1109/tpami.1982.4767213.
1211   Levy, M. and Berkowitz, B.: Measurement and analysis of non-Fickian dispersion in heterogeneous
1212   porous media, J. Contam. Hydrol., 64(3-4), 203–226, 2003, https://doi.org/10.1016/S0169-
1213   7722(02)00204-8.
1214   Margolin, G., Berkowitz, B. and Scher, H.: Structure, flow, and generalized conductivity scaling in
1215   fracture networks, Water Resour. Res., 34(9), 2103–2121, 1998, https://doi.org/10.1029/98WR01648.
1216   Maina, F. H., Ackerer, P., Younes, A., Guadagnini, A., and Berkowitz, B.: Benchmarking numerical
1217   codes for tracer transport with the aid of laboratory-scale experiments in 2D heterogeneous porous
1218   media, J. Contam. Hydrol., 212, 55-64, 2018, https://doi.org/10.1016/j.jconhyd.2017.06.001.
1219   Maples, S. R., Fogg, G. E., and Maxwell, R. M.: Modeling managed aquifer recharge processes in a
1220   highly heterogeneous, semi-confined aquifer system, Hydrogeol. J., 27, 2869–2888, 2019,
1221   https://doi.org/10.1007/s10040-019-02033-9.
1222   Nissan, A. and Berkowitz, B.: Anomalous transport dependence on Péclet number, porous medium
1223   heterogeneity, and a temporally-varying velocity field, Phys. Rev. E, 99, 033108, 2019,
1224   https://doi.org/10.1103/PhysRevE.99.033108.
1225   Nissan, A., Dror, I., and Berkowitz, B.: Time-dependent velocity-field controls on anomalous chemical
1226   transport in porous media, Water Resour. Res., 53, 3760–3769, 2017,
1227   https://doi.org/10.1002/2016WR020143.
1228   Nissan, A. and Berkowitz, B.: Inertial effects on flow and transport in heterogeneous porous media, Phys.
1229   Rev. Lett., 120, 054504, 2018, https://doi.org/10.1103/PhysRevLett.120.054504.
1230   Rizzo, C. B., and de Barros, F. P. J.: Minimum hydraulic resistance and least resistance path in
1231   heterogeneous porous media, Water Resour. Res., 53, 8596–8613, 2017,
1232   https://doi.org/10.1002/2017WR020418.
1233   Scheidegger, A. E.: An evaluation of the accuracy of the diffusivity equation for describing miscible
1234   displacement in porous media, in: Proc. Theory Fluid Flow Porous Media 2nd Conf., 1959, Univ.
1235   Oklahoma, Norman, Oklahoma, USA, 101–116, 1959.
1236   Scher, H., and Lax, M.: Stochastic transport in a disordered solid. I. Theory, Phys. Rev. B, 7, 4491–4502,
1237   1973, https://doi.org/10.1103/PhysRevB.7.4491.
1238   Scher, H., and Montroll, E. W.: Anomalous transit time dispersion in amorphous solids, Phys. Rev. B, 12,
1239   2455–2477, 1975, https://doi.org/10.1103/PhysRevB.12.2455.
1240   Schwarz, G.: Estimating the dimension of a model. Ann. Stat., 6, 461–464, 1978,
1241   https://www.jstor.org/stable/2958889.
1242   Shlesinger, M. F.: Asymptotic solutions of continuous-time random walks, J. Stat. Phys., 10(5), 421–434,
1243   1974, https://doi.org/10.1007/BF01008803.
1244   Silliman, S. E., and Simpson, E. S.: Laboratory evidence of the scale effect in dispersion of solutes in
1245   porous media, Water Resour. Res., 23(8), 1667–1673, 1987,
1246   https://doi.org/10.1029/WR023i008p01667.
1247   Smoluchowski, M. M.: Essai d'une théorie cinétique du mouvement Brownien et des milieux troubles
1248   [Test of a kinetic theory of Brownian motion and turbid media]. Bulletin International de l'Académie
1249   des Sciences de Cracovie (in French): 577, 1906a.
1250   Smoluchowski, M.: Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen.
1251   Annalen der Physik (in German). 326(14), 756–780, 1906b, doi:10.1002/andp.19063261405.
1252   Stauffer, D. and Aharony, A.: Introduction to Percolation Theory, 2nd Ed. Taylor & Francis, London,
1253   1994, 181 pp.
1254   Thovert, J.-F. and Adler, P. M.: Grain reconstruction of porous media: Application to a Bentheim
1255   sandstone, Phys. Rev. E, 83(5), 056116, 2011, https://link.aps.org/doi/10.1103/PhysRevE.83.056116.
1256   White, A. F., and Brantley, S. L.: The effect of time on the weathering of silicate minerals: Why do
1257   weathering rates differ in the laboratory and field?, Chem. Geol., 202(3–4), 479–506, 2003.
1258   https://doi.org/10.1016/j.chemgeo.2003.03.001.
1259   Ye, M., Meyer, P. D., and Neuman, S. P.: On model selection criteria in multimodel analysis, Water
1260   Resour. Res., 44, W03428, 2008, https://doi.org/10.1029/2008WR006803.