



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

3  
4

5 Brian Berkowitz<sup>1</sup>

6

7 <sup>1</sup>Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 7610001,  
8 Israel

9

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

11

12 **Abstract.**

13

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.

30

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



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 and 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 4<sup>th</sup> 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



## 153 2 Fluid flow

154

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

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

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

175 It is thus clear that, in general, there are dynamic aspects of fluid flow, over and above pure  
176 structure: knowledge of pure geometry is not sufficient, and *we must actually solve for the flow*  
177 *field*, at either the pore-scale or a continuum scale, to determine the velocity field and actual flow  
178 paths throughout the domain. Delineation of a flow field and velocity distribution by solution of  
179 the Navier-Stokes equations (or Stokes equation for small Reynolds numbers), or by solution of  
180 the Darcy equation, may be considered “rigorous”, correct and effective. But in the process of  
181 solving for the flow field, two *key* features arise, one more relevant to pore-scale analyses, and the  
182 other more relevant to continuum-scale analysis, as detailed in Sect. 2.1 and Sect. 2.2, respectively.

183

184

### 185 2.1 Pore-scale flow field analysis

186

187 Why is knowledge only of the geometrical “static” structure (spatial distribution of solid phase)  
188 insufficient to know the flow dynamics in a pore-scale domain? Consider the 2d domain shown in  
189 Figure 1, containing sparsely and randomly distributed obstacles (porosity of 0.9). Figure 1 shows  
190 solutions of the Navier-Stokes equations for two Reynolds number ( $Re$ ) values. [Recall:  $Re \equiv$   
191  $\rho v L / \mu$ , where  $\rho$  and  $\mu$  are density and dynamic viscosity of the fluid, respectively,  $v$  is fluid  
192 velocity, and  $L$  is a characteristic linear dimension.]. Andrade et al. (1999) showed clearly that



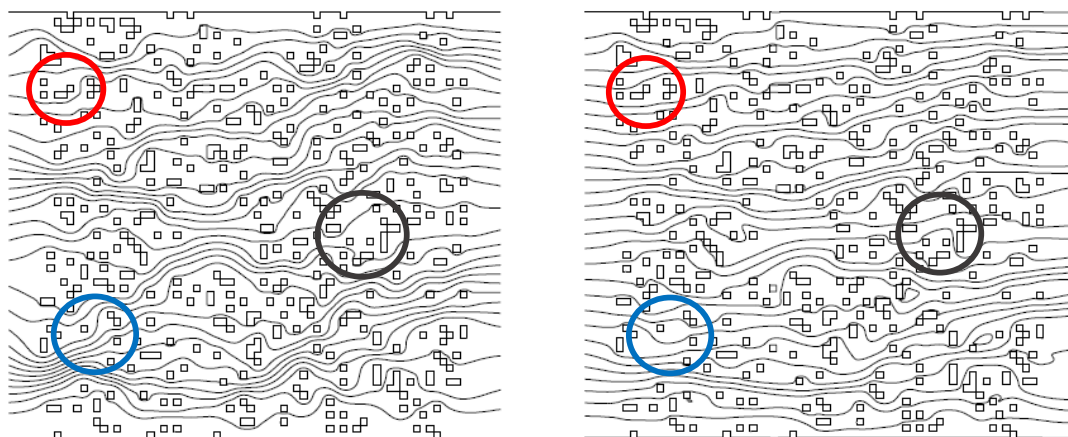
193 well-defined preferential flow channels at lower  $Re$ , while at higher  $Re$ , channeling is less intense  
194 and the streamline distribution is more spatially homogeneous in the direction orthogonal to the  
195 main flow.

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  
211  
212  
213

214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226



227  
228  
229  
230  
231  
232  
233  
234  
235  
236

(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  $Re$ .



## 237 **2.2 Continuum-scale flow field analysis**

238

239 Considering now continuum-scale domains, but in analogy to the example shown in Sect. 2.1, we  
240 illustrate why knowledge only of the geometrical “static” structure (spatial distribution of the  
241 hydraulic conductivity) is insufficient to know the flow dynamics, without solution of the Darcy  
242 equation.

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

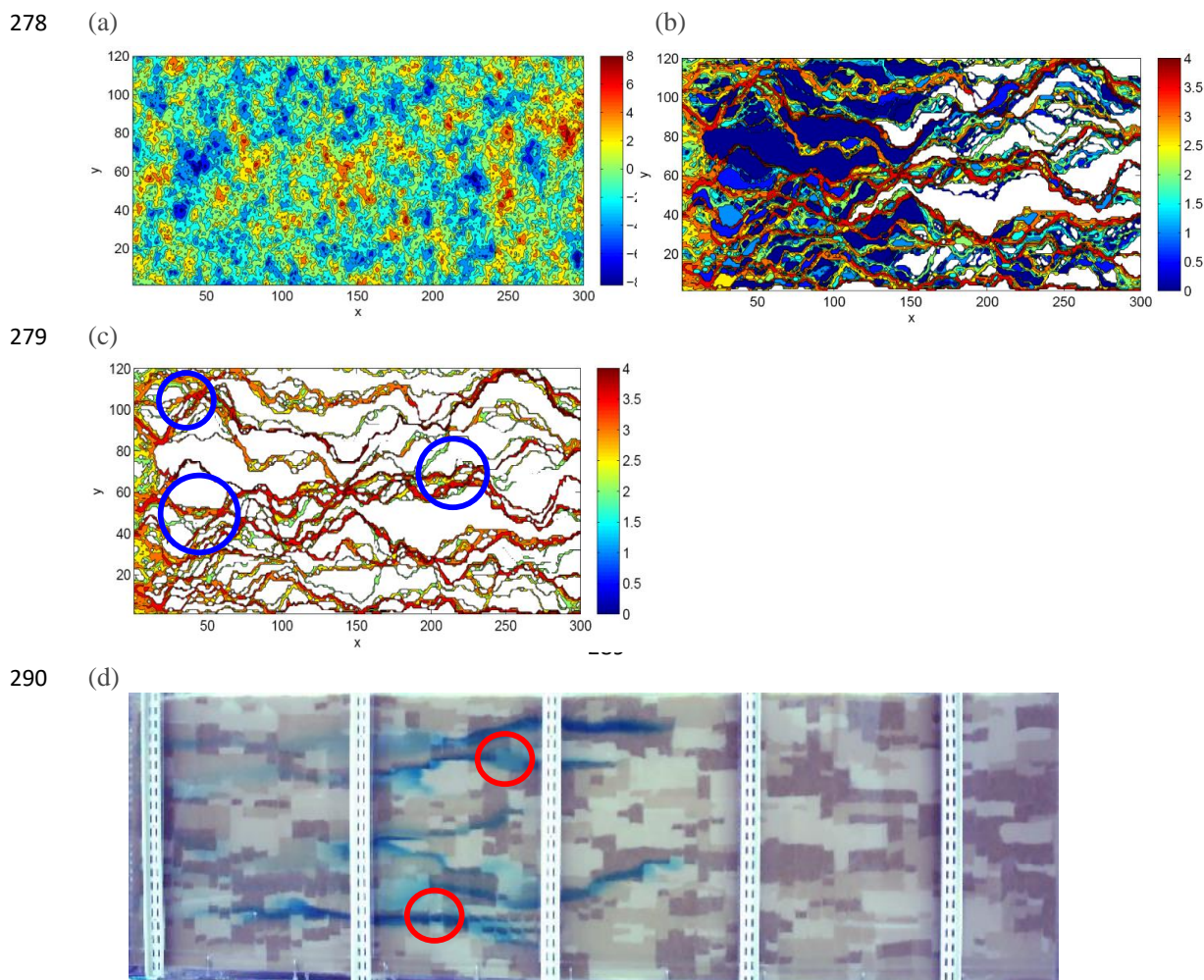
253 Unlike the pore-scale case shown in Sect. 2.1, at the Darcy/continuum scale, streamlines are  
254 not altered with changes in the overall hydraulic gradient, as long as laminar flow conditions are  
255 maintained. And yet, preferential flow paths are (surprisingly) sparse and ramified, sampling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

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

275

276

277



302 **Figure 2.** Maps of (a) hydraulic conductivity,  $K$ , distribution in a domain with  $300 \times 120$  cells, (b)  
303 preferential pathways for fluid flow (and chemical transport), and (c) preferential pathways through cells  
304 that each contain a visitation of at least 0.1% of the total number of chemical species particles injected into  
305 the domain (flux-weighted, along the entire inlet boundary). Flow is from left to right. Note that the color  
306 bars are in  $\ln(K)$  scale for Figure 2a, and  $\log_{10}$  number of particles for Figures 2b,c (modified from Edery  
307 et al., 2014; © with permission from the American Geophysical Union 2014). (d) Laboratory flow cell, 2.13  
308 m length, with an exponentially correlated  $K$  structure, showing preferential pathways for blue dye injected  
309 near the inlet (flow is left to right); dark, medium, and light colored sands represent high, medium and low  
310 conductivity, respectively (modified from Levy and Berkowitz, 2003; © with permission from Elsevier  
311 2003). The circles shown in (c) and (d) highlight two (of many) regions in which the pathways are seen to  
312 contain lower  $K$  “bottlenecks”.

313

314 It is significant, too, that fluid flow (and chemical transport) occurs in preferential pathways  
315 that contain low conductivity sections (indicated by circles in Figs. 2c,d). How do we explain  
316 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 ( $K_{\text{overall}}$ ) of the path is given by the harmonic  
325 mean of the conductivities of the elements comprising the path:  $K_{\text{overall}} = 5 / (\sum_{i=1,5} 1/K_i)$ ;  
326 significantly, in the two cases here, both paths have  $K_{\text{overall}} = 3$ ! So a “bottleneck” ( $K=1$ ) can be  
327 “overcome” and does not 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

### 369 **3.1 Pore-scale chemical transport analysis**

370

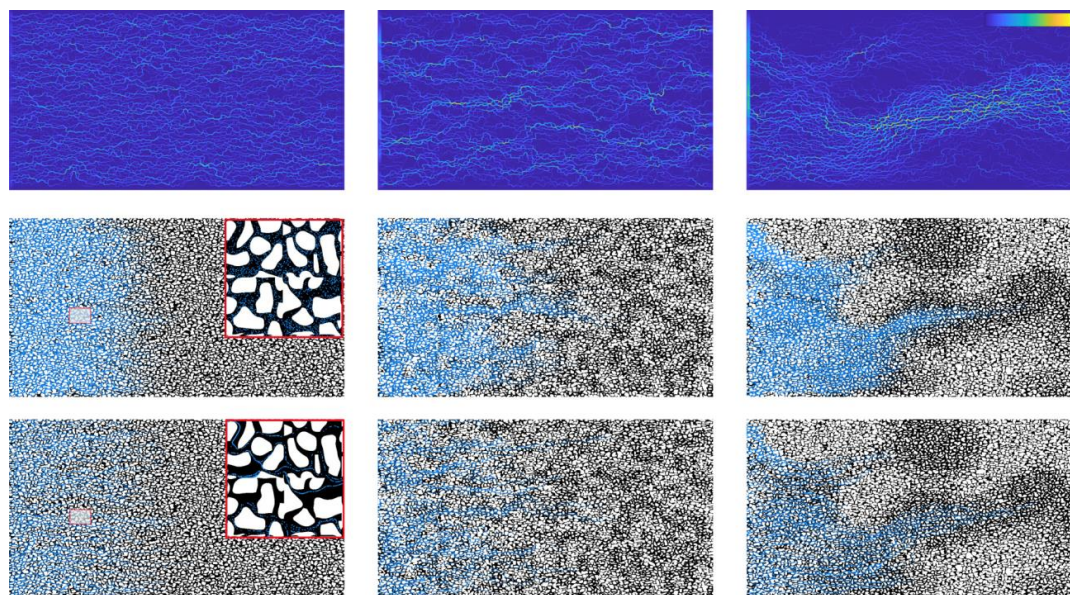
371 To illustrate why knowledge only of only the flow field is insufficient for full quantification of  
372 chemical transport, consider the three porous medium domains shown in Fig. 3. Each domains is  
373 comprised of pore-scale images of a natural rock, modified by enlarging the solid phase grains, 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;  $Pe \equiv vL/D$ , 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

394 The behavior show in Fig. 3 is essentially well-known from extensive simulations and  
395 experiments appearing in the literature. This behavior is described here to stress the importance of  
396 *temporal* effects, and to point out that information only of the advective velocity field – as  
397 discussed in Sect. 2.1 and Sect. 2.2 – is not sufficient to “predict” chemical transport.

397



398

400 **Figure 3.** Fluid velocities and chemical migration in three porous media configurations (from left to right):  
401 homogeneous system, randomly heterogeneous system, and structured heterogeneous system. The upper  
402 row shows the (normalized) velocity field for the three configurations; the color bar represents relative  
403 velocity, with dark blue being lowest. The middle and lower rows show, respectively, numerically-  
404 simulated particle tracking patterns of an inert chemical species (blue dots) at  $Pe = 1$  (middle row) and  $Pe$   
405  $= 100$  (lower row) for the three configurations (white color indicates solid phase; black color indicates  
406 liquid phase). Note: The particles plumes are shown at 10% of the final time of each simulation; absolute  
407 travel times differ among the plots. The insets in the left side plots of the middle and lower rows show the  
408 pore-scale chemical species distributions; note the more diffuse pattern for  $Pe = 1$  (from Nissan and  
409 Berkowitz, 2019, <https://doi.org/10.1103/PhysRevE.99.033108>; © with permission from American  
410 Physical Society 2019).

411

412

### 413 3.2 Continuum-scale chemical transport analysis

414

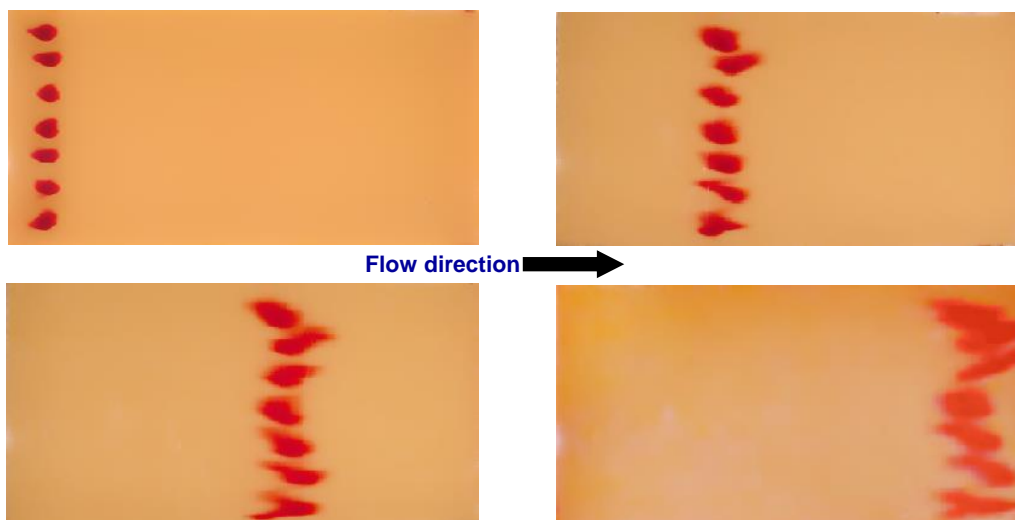
415 The aspects discussed in Sect. 3.1 are relevant, analogous and essentially applicable also to  
416 chemical transport at the continuum scale. Consider the two laboratory experiments shown in Fig.  
417 4 and Fig. 5. Each flow cell was filled with a different clean, sieved sand configuration; see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

425

426

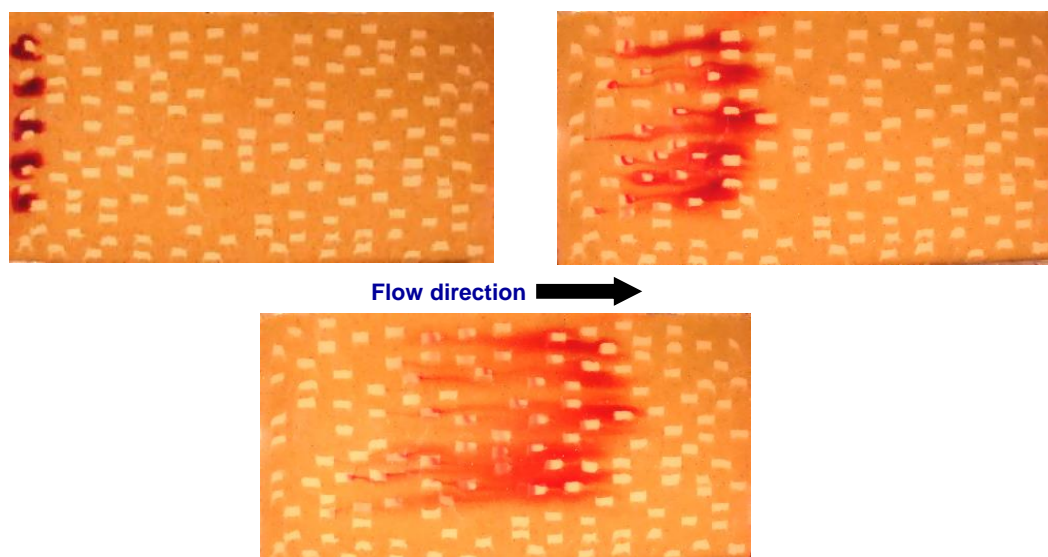


427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444



**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).

448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468



**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  $\sim 0.5\times$  smaller, and hydraulic conductivity  $\sim 3\times$  lower, than the surrounding sand matrix (modified from Levy and Berkowitz, 2003; © with permission from Elsevier 2003).

474



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<sup>-1</sup>, and then traveling  
541 50 km at 99 km h<sup>-1</sup>. 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<sup>-1</sup>. 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:

- 568 1. The desire to work with spatial averaging approaches and equations: The research  
569 community was (and still is) split over the need to recognize and incorporate, *explicitly*,  
570 influences of temporal mechanisms caused largely by spatial heterogeneity (as  
571 characterized by the domain hydraulic conductivity), when formulating “effective” (or  
572 “averaged”) equations. And even when recognized, debate remains as to appropriate  
573 mathematical formulation.
- 574 2. The lack of data: At least part of the difficulty in developing appropriate models is the lack  
575 of availability of high-resolution laboratory data and field measurements against which  
576 chemical transport models can be tested. Indeed, many elaborate theoretical developments  
577 have been advanced over the decades, with accompanying, analytical and numerical  
578 solutions — and yet, remarkably, comparative studies against actual laboratory data remain  
579 limited, and tests with field measurements are even sparser (see also Sect. 4 for further  
580 discussion of this point).
- 581 3. The choice of approach to, and purpose of, chemical transport modeling: Two overarching  
582 approaches to quantifying chemical transport can be defined, focusing on (i) quantification  
583 of “effective”, “overall” chemical transport behavior without requiring high-resolution  
584 discretization and numerical solution of the domain, and, alternatively, (ii) high-resolution  
585 hydrogeological delineation and then intensive numerical simulation on highly discretized  
586 grids. We address approaches (i) and (ii) individually, below, in the context also of points  
587 (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  $10\text{ m}^3$   
607 at the field scale (Eggleston and Rojstaczer, 1998);  $200 \times 200 \times 1\text{ m}^3$  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



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:

$$706 \quad P_{n+1}(\ell) = \sum_{\ell'} p(\ell, \ell') P_n(\ell') \quad (1)$$

707  
708  
709 where  $p(\ell, \ell')$  represents the probability of a random walker (“particle”) advancing from location  
710  $\ell'$  to  $\ell$ ,  $P_n(\ell')$  denotes the probability of a particle being located at  $\ell'$  at (fixed) time step  $n$ , and  
711  $P_{n+1}(\ell)$  denotes the probability of the particle then being located at  $\ell$  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):

$$724 R_{n+1}(\mathbf{s}, t) = \sum_{\mathbf{s}'} \int_0^t \psi(\mathbf{s} - \mathbf{s}', t - t') R_n(\mathbf{s}', t') dt' \quad (2)$$

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

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

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

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



754 differential equation. Thus, the ADE given by

755

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

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

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

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

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

775

776 Equation (4) is essentially an ADE weighted by a temporal memory. When  $\psi(t)$  is an  
777 exponential function (or power law but for  $\beta \geq 2$ ),  $M(t) \rightarrow \delta(t)$  and we recover Fickian transport  
778 described by the ADE; thus, the ADE assumes, implicitly, that particle transition times are  
779 distributed exponentially. But with a power law form  $\psi(t) \sim t^{-1-\beta}$  for  $0 < \beta < 2$ , the transport is  
780 non-Fickian. A wide range of functional forms of  $\psi(t)$  can be chosen, including, e.g., truncated  
781 power law forms that allow evolution to Fickian transport at large times or travel distances (e.g.,  
782 Berkowitz et al., 2006), as well as Pareto (e.g., Hansen and Berkowitz, 2014) and curved (or  
783 inverse gamma; e.g., Nissan and Berkowitz, 2019) temporal distributions. Other, generally  
784 simpler, choices of  $\psi(t)$  or  $M(t)$  lead to mobile-immobile, multirate mass transfer, and time-  
785 fractional derivative formulations. We note, too, that the elegant result derived by Gelhar and  
786 Axness (1983) and others, discussed in Sect. 1.2, is valid only at an asymptotic limit, wherein  
787 transport is Fickian and there is no residual non-Fickian memory in the plume advance.

787

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

### 828 **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



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  $\beta$  exponent *had* to  
849 be included because the mean displacement was not linear with time (i.e., the mean displacement  
850  $\bar{\ell}$  of the electron packet does not advance as  $\bar{\ell} = vt$ , but rather as  $\bar{\ell} \sim t^\beta$ ). 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.



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.*

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)



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  $\beta$  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<sup>3</sup>.

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., Goepfert 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



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 may 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

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



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”!

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.”

1136

1137

1138 *Data availability.* All data have been reported and published previously, as given in the relevant citations.

1139

1140 *Author contributions.* Single author contribution.

1141

1142 *Competing interests.* The author is a member of the editorial board of Hydrology and Earth System  
1143 Sciences. The peer-review process was guided by an independent editor, and the author has  
1144 no other competing interests to declare.

1145

1146 *Acknowledgements.* This contribution has emanated from research and discussions – often animated and  
1147 always thought-provoking – with students, post-doctoral fellows, and more senior colleagues in my group  
1148 and from around the world, over the last two decades. I am deeply grateful to them all! I also appreciate  
1149 critical insights and constructive comments by Alberto Guadagnini and Harvey Scher. B.B. holds the Sam  
1150 Zuckerberg Professorial Chair in Hydrology.

1151

1152

## 1153 **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 Goepfert, 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*



- 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/S0169-7722\(02\)00204-8](https://doi.org/10.1016/S0169-7722(02)00204-8).
- 1213
- 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>.